ISBN 978-3-89720-990-9

No.
72

Executive Summaries – 5th International Conference on Oxidation Technologies for Water and Wastewater Treatment

CUTEC-Serial Publication No_72

5th International Conference/
10th IOA-EA$_3$G Berlin Conference
on
Oxidation Technologies for Water and Wastewater Treatment

Executive Summaries

CUTEC INSTITUT·GmbH

Editors:
Michael Sievers,
Sven-Uwe Geissen,
Sven Schäfer,
Britta Kragert and
Michael Niedermeiser

Michael Sievers, Sven-Uwe Geissen, Sven Schäfer, Britta Kragert
and Michael Niedermeiser (ed.):
Oxidation Technologies for Water and Wastewater Treatment
Executive Summaries of the 5th International Conference, 10th IOA-EA$_3$G Berlin Conference,
March 30 – April 2 2009, Berlin 2009

CUTEC-Institut GmbH – 1st Edition – Clausthal-Zellerfeld: Papierflieger, 2009
(CUTEC Serial Publication No 72)
ISBN 978-3-89720-990-9

Bibliographic information published by the Deutsche Bibliothek
The Deutsche Bibliothek lists this publication in the Deutsche Nationalbibliographie:
bibliographic data is available in the internet at:

http://dnb.ddb.de

CUTEC Serial Publication

The Clausthaler Umwelttechnik-Institut GmbH – CUTEC-Institut GmbH –
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Telemannstraße 1· 38678 Clausthal-Zellerfeld
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1st Edition 2009

ISBN 978-3-89720-990-9

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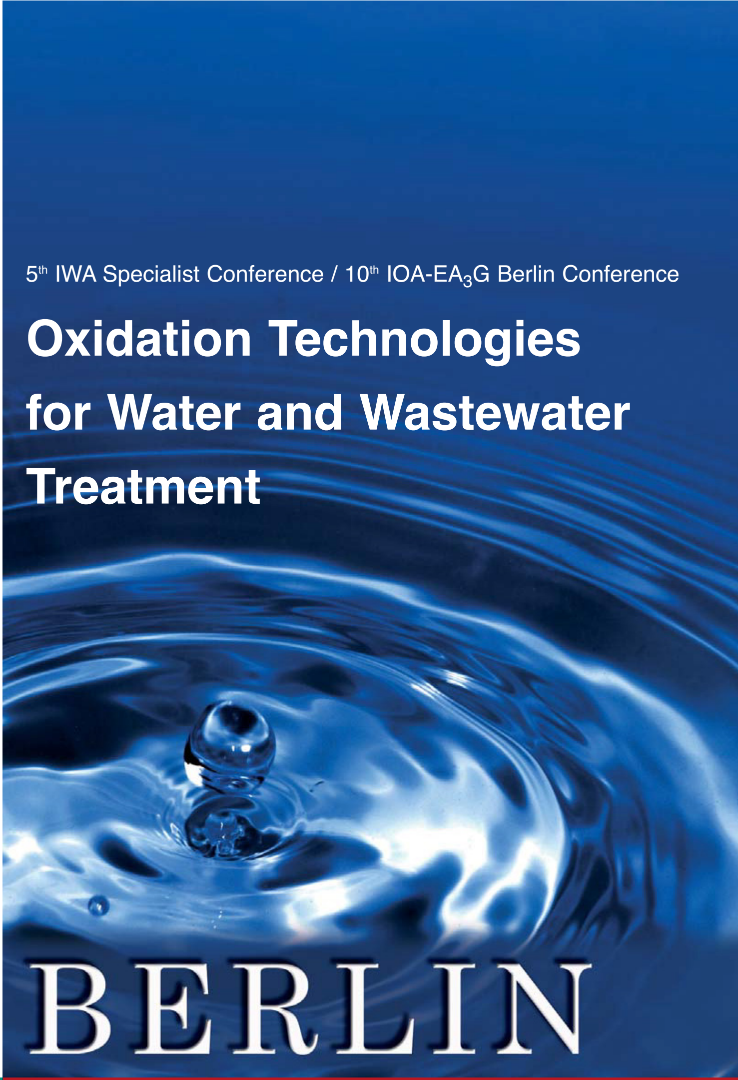
International Ozone Association



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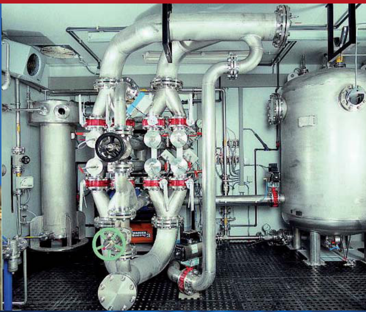

Content

Orals (Sorted by the oral programme)

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Preface

The organisers of the fifth IWA-AOP conference “Oxidation Technologies for Water and Wastewater Treatment“ and the “10th IOA-EAG$_3$ Berlin Conference” welcome you to Germany and particularly Berlin.

This conference is based on the first co-operation of the IWA and IOA and we are very pleased with the quality and quantity of submitted papers, which indicate that Advanced Oxidation Processes and Technologies recently received increasing interest as an important part of water re-use concepts today and for the future.

The conference proceedings contain 174 full papers and eight abstracts summarizing the latest achievements in this field on approx. 1,400 pages. We very much appreciate the contributions of all authors as well as the great abstract review job mastered by the Scientific Committee members.

Following conference tradition that parallel sessions should be avoided to allow more interdisciplinary exchange of knowledge, only 43 oral presentations have been allowed, while many more papers were pre-selected for oral presentation. Extending the conference duration by one additional day was only a drop in the ocean.

Organising this conference involves a lot of work. We are therefore most grateful to all involved persons, especially to Arnd Böhme, Achim Ried and Pierre Liechti and to the staff of CUTEC, TU Berlin, IOA and Wasser Berlin e.V. for their engaged efforts.

We wish all of us a successful and enjoyable AOP5 conference with fruitful discussions.

Clausthal-Zellerfeld/Berlin, March 2009

Prof. Dr. Michael Sievers, CUTEC, Clausthal-Zellerfeld, Germany
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Our projects deal with, e.g.

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The Organising Committee expresses many thanks to all involved parties for their great engagement and support, especially the staff, the members of the Scientific Committee and the sponsors.

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Only your great work, your high competence and the fruitful discussions within our „AOP-family“ enable us to organise this international networking event for the exchange of knowledge.

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Sterilized Water, Free of Bromate

Growing consumer awareness and increasingly stringent regulatory demands have resulted in a renewed emphasis on the quality of water used for human consumption and distributed in PET or glass bottles. For achieving these new quality standards, improved technology must be utilized to provide water free from all bacteria and organics, and to keep water systems free from germs and biofilms.

ANSEROS OZONE WATER STAGE

At the same time, the risk of disinfectants impairing the quality of the product has to be avoided. The technology to achieve these requirements is ozonization, the treatment of water with ozone gas.

The use of ozonized water for finally rinsing recycled or new bottles before filling them ensures that they will be fully sterile. Any residues of cleaning agents, detergents, dust or particles are fully removed to ensure a sterile receptacle that will not impair the taste or quality of the water.

The process is effective not only with bottled water, but also for a wide range of beverage bottling and packaging. Compared to other water disinfectant chemicals, ozone is a more than 50% stronger oxidizer and acts over 3,000 times faster.

When incorporating ozonization, a careful consideration of the water system layout and design will provide significant benefits in maintaining storage tanks, pipework, filters and filling machines free from bacteria with a minimum of maintenance and cleaning.

Ozone is a highly reactive form of oxygen. Produced electrically from ambient air or - as in larger systems - from pure oxygen, ozone rapidly destroys all bacteria, algae and viruses in water or air. With a half life of 10 - 40 minutes, ozone reverts naturally to molecular oxygen, leaving no residual toxins or taints behind. Ozone can be readily measured in air or water using manual test procedures or continuous monitoring instruments.

The ANSEROS PAP system can easily be incorporated in existing bottling, cleaning and filling plants or replace sterilization systems based on chlorine or other chemicals.

ANSEROS, a company specializing in oxidation technologies since 1978, developed a new processing equipment for water disinfection. With still water in bottles becoming more and more popular and taking considerable market shares, sterilization measures to follow up this trend are a key priority for assuring safe drinking water, as regulated by the World Health Organization (WHO).

BOTTLING WATER APPLICATION

To avoid any formation of chemical by-products like bromate, the R&D division of ANSEROS designed a reaction based on hydroxyl radicals to reduce bromide and completely eliminate bromate (TLV < 10µg BRO3-/l). In Europe, the content of bromide in water can be found in a range between 10 and 3000 µg Br-/l.

With the existence of appliances like the ANSEROS PAP system, the questions and discussions about kidney cancer induced by bromate in water can come to an end. Healthy water is now available.

Range of approved applications

- sustainable food and beverages
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- ozone CIP cleaning procedure for pharmaceutical and food processing machinery
- sterile packaging
- animal breeding
- deodorization of air with gas scrubbers
- hygiene control in hospitals
- oxidation of waste water
- surface cleaning of solar wafers
- adhesion improvement of elastomere surfaces
- climate simulation procedures and ageing tests on plants, insulation materials, seals and rubber parts in general

For more information, please contact:
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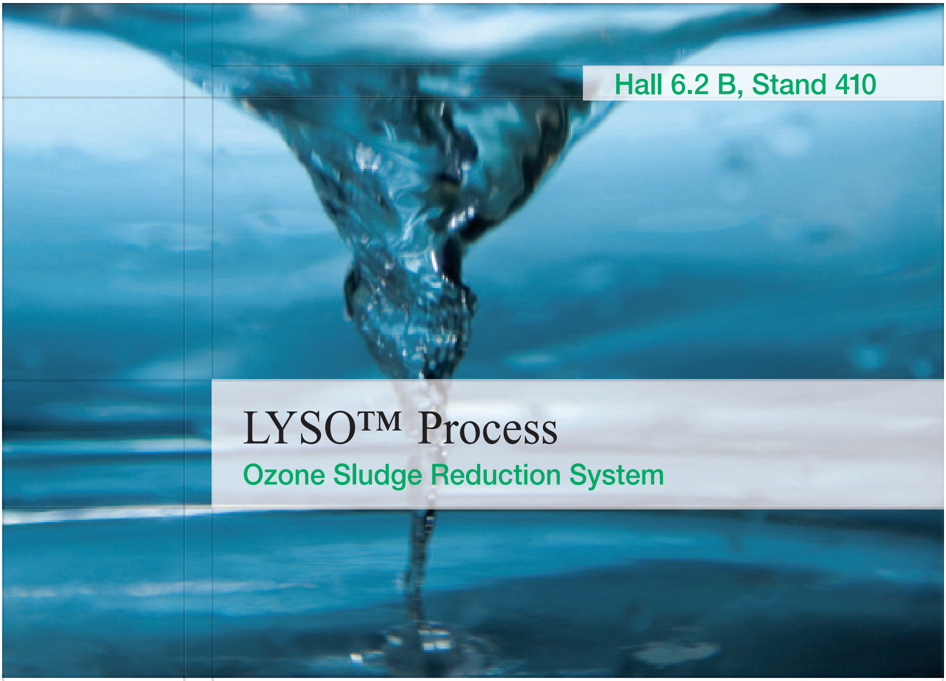
ANSEROS PAP OZONE SYSTEM

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a.c.k. aqua concept GmbH was founded in 1997. The development proofs us to be the world wide market leaders in industrial UV – processing. To the right is shown a turn-key installation for the treatment of hazardous waste (gas and water) of a complete chemical factory.

We utilize the energy of UV-light to remove contamination from process waters, to degrade pollutants in aqueous solutions to disinfect aqueous solutions or to process organics by synthetic photochemistry. For this we construct robust UV reactors and technical systems which are redefining industrial standards.
The picture above shows a 300 kW el. power unit placed at one of the leading European chemical companies.

This picture shows a fully automatic waste water installation for the continuous detoxification at a waste disposal contractor.

Executive Summaries

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Recycling / Reuse
PC 195

Advanced oxidation and artificial recharge: a synergistic hybrid system for removal of organic micropollutants

K. Teunissen, **, J. Krüger***, S.K. Maeng****,**, A. Ried***, J.Q.J.C. Verberk**, A.H. Knol*, G. Amy****,**, J.C. van Dijk***

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Duinwaterbedrijf Zuid-Holland, the drinking water company for The Hague and surroundings, has an objective to produce drinking water of impeccable quality, particularly with respect to organic micropollutants. As organic micropollutants are only a minor part of the total natural organic matter, posing a challenge in targeting removal of a very small, specific part of the DOC, without removing all of the natural organic matter. In addition, organic micropollutans encompass a broad range of physicochemical properties, which make their removal by a single treatment step impossible. Combining AOP with artificial recharge and recovery, two complementary processes are expected to provide a hybrid system for organic micropollutants removal, according to the Dutch multiple barrier approach.

Pilot-scale experiments with O_3 and different advanced oxidation processes (UV/H_2O_2, UV/O_3 and O_3/H_2O_2) were carried out in cooperation between Duinwaterbedrijf Zuid-Holland and ITT Wedeco. The pilot installation had a capacity of about 0.5-2.0 m^3/h, with a varying LP-UV-dose, ozone dose and peroxide dose.

Atrazine, isoproturone, carbamazepine, diclofenac and ibuprofene are well removed by UV/H_2O_2 as well as O_3/H_2O_2. In general, O_3/H_2O_2 is a more energy efficient process compared to UV/H_2O_2. MTBE is best removed by O_3/H_2O_2. Amidotrizoic acid and iohexol are best removed by UV/H_2O_2.

Keywords:
Advanced oxidation; artificial recharge; biodegradation; organic micropollutants

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Oral
Recycling / Reuse
PC 129

Advanced Oxidation for Indirect Potable Reuse – A Practical Application in Australia

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December 2008 marked the completion of Stage 2B of the Western Corridor Recycled Water (WCRW) Project in South East Queensland, Australia. With a maximum combined production capacity of 232 million litres of purified recycled water a day, it is the third largest recycled water scheme in the world and the largest in southern hemisphere. A seven-barrier approach has been used to ensure very highest quality, safe water is produced at all times for the purpose of indirect potable reuse. Three of these barriers occur in the advanced water treatment section of the WCRW Project: micro- or ultra-filtration (MF), reverse osmosis (RO), and H_2O_2/UV advanced oxidation. In addition to providing very efficient disinfection, the advanced oxidation process specifically aims to destroy compounds not fully rejected by RO that are potential health hazards. This includes N-NitrosoDiMethylAmine (NDMA), which is a potential carcinogenic product likely to be formed by chlorination or chloramination of wastewaters. As in many other countries, Australia has adopted a stringent guideline limit for this compound of 10 ng/L in purified recycled water. After 16 months of operations of the WCRW Project's first plant, the AO system has been proven effective in removing NDMA and ensuring 100% compliance with the regulation at a controlled cost.

Keywords:
Advanced oxidation; water recycling; indirect potable reuse; NDMA

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Oral

Recycling / Reuse

PC 236

The use of E. Beam for the removal of recalcitrant compounds : The interesting effect of chemicals introduction

N. Karpel Vel Leitner, B. Roshanil, C. Aubry and S. O. B. Boukari
Laboratory of Water Chemistry and Microbiology, CNRS-University of Poitiers, Poitiers Cedex, France

The active species generated from the irradiation of aqueous solutions by ionizing radiations are the hydroxyl radicals and the solvated electrons. These are expected to make these classes of irradiation processes interesting for water treatment.
The aim of our work was to examine the impact of chemicals introduction during the irradiation by electron beam to convert the solvated electrons into more active radical entities.
The irradiation experiments were performed in a bench scale installation for continuous water treatment. In the system the introduction of persulfate ions was studied. Under these conditions, both OH° and $SO_4^{\circ-}$ radicals are formed:
Phenol (100 μM) and benzotriazol (3 μM) were selected for the study. The improvement brought by the presence of $S_2O_8^{2-}$ during e-beam irradiation was found to depend on the characteristics of waters (organic and inorganic content, pH, …).
Ferrous or ferric ions were also added in order to tentatively catalyze the formation of the sulphate radicals. Under these conditions, the efficiency was highly improved. It follows that the radiation dose necessary to the total removal of phenol could be divided by 3. This could be explained by the additional reaction of ferrous ions with persulfate; Experiments were performed on several other model molecules (nitrophenol, fumaric acid, glycolic and formic acids) and also for the oxidation municipal and industrial wastewaters.
The interest of this combined advanced oxidation process was confirmed by comparison with the treatment without any reactant. The original data obtained in this study show that the production of sulphate radicals complementary to the wellknown OH° radicals could improve the reactivity of AOPs. The use of persulfate ions could offer new prospects for radical oxidation systems in lowering the energy required for a given purpose

Keywords:
electron beam, sulphate radical, wastewater treatment

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Oral

Recycling / Reuse

PC 179

Water-reuse with ozone as an oxidant – a review about technical applications

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** ITT WEDECO, Germany

Regarding the new challenges coming with anthropogenic micropolluntants and future regulations, the ozonation can be an option to solve these tasks especially in combination with biological treatment. Ozone has the ability to oxidise and disinfect simultaneously. Today, 40 technical applications of ozonation in combination with biological treatment already exist but a few are published. The experiences show, that treatment of wastewater with ozone and biology is an economical and promising technology, even in large scale.

Keywords:
Ozone, Water Reuse, Oxidation, Application, Post-Treatment

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Oral
Recycling / Reuse
PC 276

Ultrasound-aided Ozonation of effluents from wastewater treatment plants for disinfection, degradation of endocrine disrupting compounds (EDCs) and enhancement of the aerobic degradation processes in biological reactors

Carmelo Oliveri
Ultrasonic Systems GmbH, Thierhaupten, Germany

By the use of a unique combination of ultrasound and ozone to disinfect the total outlet of a municipal sewage treatment plant over a period of two years the efficacy of such a system has been demonstrated. Despite the frequent usage of ozone for the disinfection and oxidation of organic compounds and the huge number of scientific applications on ultrasound-aided methods, it is still difficult to find such applications on a technical or industrial scale. Furthermore to the disinfection, the degradation of Endocrine Disrupting Compounds (EDCs) and the enhancement of the aerobic degradation processes of biological reactors have also been tested. Besides the disinfection results, which meet the criteria of the limit values of the European and Bavarian bathing water directive, the degradation of Carbamazepine and other substances reached levels far below detection level. Furthermore a reduction of COD and other parameters up to 60% could be attained by feeding back part of the treated effluent stream into the sewage treatment plant. The study also engaged the energy evaluation of the ultrasound and ozone technology in water disinfection. After having examined in all areas, the combination of ultrasound and ozone is very efficient.

Keywords:
disinfection, endocrine disrupting compounds, ozone, ultrasound

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Oral
Drinking Water
PC 261

Bromate Pre-systemic Detoxification Metabolism Research Progress

J. Cotruvo[1], R. Bull[2], B. Cummings[3], J. Fisher[3], O. Quinones[4], S. Snyder[4], C. N. Ong[5], G. Zhongxian[6], J. Keith[7], G. Gordon[7], G. Pacey[7]*

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7. Miami University, Oxford, Ohio, USA.

Bromate is carcinogenic in test animals at high doses and it is a concern in desalination, indirect or direct water recycling, bottled waters and ground waters especially due to ozone’s ability to convert bromide to bromate, which is regulated at 10 ug/l (10 ppb). Bromate is also present in hypochlorite produced from electrolysis of salt that contains small amounts of bromide, and it can also be produced by oxidation of bromide in water by several other disinfectants under the appropriate conditions. We are conducting studies aimed at producing a physiologically based pharmacokinetic (PBPK) model quantifying the metabolism and detoxification that occurs after ingestion and before it would reach a target organ, e.g., kidney. We will then produce a revised risk assessment using that mechanistic information at environmentally relevant doses as opposed to the high doses required in animal bioassay studies. Pre-systemic metabolism can occur to varying degrees at least in the stomach, liver and blood. The liver is not a target organ for bromate carcinogenicity. We have studied the kinetics and conditions of bromate decomposition in simulated stomach acid, rat blood stream and rat hepatocytes. We hope to be able to determine ingestion doses that will be virtually completely detoxified before reaching a target organ where it could cause damage. In that event, bromate might possibly best be considered as a practical threshold carcinogen with essentially no risk below the threshold dose. This report is latest information available on the kinetics of metabolism and disappearance of bromate after ingestion by rats.

Keywords:

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Oral
Drinking Water
PC 77

Elimination of Taste and Odor Compounds and Bromate Formation during Ozonation and the AOP O_3/H_2O_2

Holger Lutze[1,2], Andreas Peter[2] and Prof. Dr. Urs von Gunten[2]

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Institute of Biogeochemistry and Pollutant Dynamics, Zurich, Switzerland

Water utilities worldwide are confronted with consumer complaints related to taste and odor (T&O) compounds accompanied with a loss of trust into the safety of the drinking water. Therefore, it is important for the water suppliers to reduce T&O concentrations in the drinking water to below threshold levels. In this study, conventional ozonation and the Advanced Oxidation Process (AOP) O_3/H_2O_2 were compared with respect to the elimination of T&O compounds as well as bromate formation. Experiments were conducted, with varying ozone doses applied to lake water, which was spiked with T&O compounds and different concentrations of bromide. For a complete removal of ozone-recalcitrant T&O compounds ozone doses between 2 and 5 mg/l are needed. Hereby the reaction time to achieve a certain removal of T&O compounds with intermediate reactivity towards ozone ($k_{ozone} < \sim 500\ M^{-1}s^{-1}$) is substantially shorter in the AOP O_3/H_2O_2 than in conventional ozonation. Even with low bromide concentrations in the lake water (20 µg/l), conventional ozonation with an ozone dose of 5 mg/l leads to a bromate concentration that exceeds US-EPA and EU bromate drinking water standard (10 µg/l) by a factor of two. With the addition of H_2O_2 under the same conditions, bromate formation can effectively be reduced leading to a compliance of the bromate standard.

Keywords:

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PC 262

Full Scale Advanced Oxidation Treatment Plant for Groundwater

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Vienna Waterworks installed a new innovative treatment plant in the Waterworks Moosbrunn to improve the safety and reliability of the water supply system in case of failure or necessary repairs on either of the two spring water supply mains or during times of increased water demand. The abstracted raw water is groundwater, which is contaminated by chlorinated hydrocarbons, such as tetrachloroethene and trichloroethene. Different treatment possibilities were evaluated before the project started. One of the most suitable processes was the combined use of ozone and hydrogen peroxide (advanced oxidation process). This innovative process is installed for the first time on a full-scale basis and with a daily capacity of 64.000 m³/d it also is the biggest treatment plant in Austria. The treatment plant has been running to the complete satisfaction of Vienna Waterworks since start-up.

Keywords:
Advanced Oxidation, Groundwater, Hydrogen Peroxide, Ozone, Tetrachloroethene, Treatment

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Oral
Drinking Water
PC 104

“Ozone” and “GAC Filtration” synergy for emerging micropollutants removal on Drinking Water Treatment Plant?

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Ozonation plays an essential role in water disinfection regarding viruses, bacteria and some parasites (*Giardia*) inactivation. Engineering and process modifications have been implemented to minimize bromate formation. Ozone treatment rates to reach disinfection goals also result in oxidation reactions of emerging pollutants. Pharmaceuticals – except Ciprofloxacin – are very reactive compounds to ozone: they are removed early as the transfer compartment outlet even for an ozone treatment rate lower than 1g/m^3. Glyphosate, AMPA, Amitrole and Diuron – the four major pesticides in the Seine, Marne and Oise rivers – are reactive compounds to ozone. Nevertheless, 21 pesticides are partially reactive to ozone and an additional « GAC filtration » is needed to remove such compounds. Further investigations are ongoing to study Phthalates, Nonylphenols and Hormones removal by the association of « Ozone » and « GAC filtration » process units.

Keywords:
Micropollutants, Pesticides, Pharmaceuticals, Ozone, GAC

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Oral
Drinking Water
PC 150

Evaluation of Pilot-Scale Oxidation of Several PPCPs/ EDCs during Drinking Water Ozonation Treatment

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Several PPCPs/ EDCs are being detected in surface drinking water sources, which is a great concern. The efficacy of ozonation in oxidizing 13 PPCPs/EDCs frequently detected in the Detroit River watershed was examined at pilot scale in the current study. Pilot-scale experiments were conducted at ozone dosages varying between 0.3 – 1.5 mg/L with the 13 PPCPs/ EDCs spiked in raw water obtained from the Detroit River. For 10 of the 13 PPCPs/EDCs with a high reaction rate with ozone (Group A), average oxidation efficiencies exceeded 95% at all ozone doses and contact times of 2 and 8.6 min. For chemicals with low to moderate reaction rate with molecular ozone (Group B), the observed oxidations were variable and ranged between between 2 – 62% for ibuprofen and clorfibric acid and between 28 – 98% for bezafibrate. For the Group B chemicals, the oxidations increased with increasing ozone exposure and was significant influenced by the quality of raw water quality. The oxidation of Group B chemicals was reasonably well predicted by a model based on ozone and hydroxyl exposure.

Keywords:
Drinking Water; Ozone; PPCPs; EDCs; Oxidation; Pilot Plant

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Oral
Drinking Water
PC 249

A Modelling Procedure for On-Site Ozonation Steps in Potable Water Treatment

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This article presents a calibration procedure for a model describing the role of NOM during ozonation. Calibration was conceived as practical tool for engineering purpose. Basing on an experimental plan comprising 64 experiments performed with a monophasic batch protocol, results showed that the calibration procedure enabled the model to predict well changes in ozone dose, temperature and pH. The results were particularly interesting with water with medium/high organic content. Results obtained with water exhibiting lower organic content were more contrasted, but the model was also able to account for most changes in sub listed parameters.

Keywords:
Calibration; Ozonation; SimOx; Modelling; Natural Organic Matter

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Oral
Wastewater
PC 25

Ozonation and AOPs for Oil Shale Industry’s Wastewater Treatment: an Overview

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An overview on the research activities of the Chemical Engineering Department of TUT linked to the environmental problems in oil shale chemical industry since 1990 till the present time has been presented. Four periods (1990-1993; 1994-1996; 2000-2006 and 2006...) in experimental studies have been highlighted. The main results have been presented and illustrated in the form of tables and figures. Further trends in environmental situation and prospective research in oil shale chemical industry is considered.

Keywords:
Bio-oxidation, Fenton treatment, oil shale, ozonation, phenolic effluents, photocatalytic oxidation, thermal treatment

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Oral
Wastewater
PC 54

Integration between chemical oxidation and membrane thermophilic biological process

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Full scale applications of activated sludge thermophilic aerobic process for treatment of liquid wastes are rare. This experimental work was carried out at a facility, where a thermophilic reactor (1 000 m^3 volume) is operated. In order to improve the global performance of the plant, it was decided to upgrade it, by means of two membrane filtration units (ultrafiltration –UF-, in place of the final sedimentation, and nanofiltration –NF-). Subsequently, the integration with chemical oxidation (O_3 and H_2O_2/UV processes) was taken into consideration. Studied solutions dealt with oxidation of both the NF effluents (permeate and concentrate).

Based on experimental results and economic evaluation, an algorithm was proposed for defining limits of convenience of this process.

Keywords:
Economic evaluation, H_2O_2/UV, liquid waste, ozone, termophilic process

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Oral
Wastewater
PC 92

Toxicity and recalcitrant compounds removal of bleaching pulp mill by integrated system: anaerobic packed-bed bioreactor and ozone

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Effluents originated in pulp manufacturing processes are usually toxic and recalcitrant, specially the bleaching effluents, which exhibit high contents of aromatic compounds (e.g. residual lignin derivates). Although biological processes are normally used, their efficiency for the removal of toxic lignin derivates is low. The toxicity and recalcitrance of a bleached Kraft pulp mill were assessed through bioassays and ultraviolet absorption measurements (i.e. acid soluble lignin (ASL), UV_{280}, and specific ultraviolet absorption (SUVA)), using an integrated system comprised of an anaerobic packed-bed bioreactor and oxidation step with ozone. Furthermore, adsorbable organic halides (AOX) were measured. The results demonstrated not only that the toxic recalcitrant compounds can be removed successfully using integrated system, but also the ultraviolet absorption measurements can be an interesting control-parameter in a wastewater treatment.

Keywords:
AOX, acid soluble lignin, Ceriodaphnia dubia, Daphnia similis, SMP, ultraviolet absorption

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Oral
Sludge
PC 97

Wet Air Oxidation of Municipal Sludge: Return Experience of the North Brussels Waste Water Treatment Plant

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For large cities which cannot afford to sustain land disposal of sludge, Wet Air Oxidation appears to be an interesting option, perceived as environmentally friendly to a public opinion some times reluctant toward conventional incineration. However, due to significant investment costs, it is relevant to reduce upstream the amount of sludge by anaerobic digestion. This paper presents the North Brussels WwTP (1.1 M pe), which was started-up in 2006. The sludge treatment consists in thermal hydrolysis of dewatered sludge followed by high load mesophilic anaerobic digestion and Wet Air Oxidation. The Wet Air Oxidation final product is currently dewatered and dried over 90% dryness, prior to be disposed as a cover product for landfill covering.

Keywords:
Sludge, wet air oxidation, Athos™, thermal hydrolysis, mesophilic anaerobic digestion

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Oral
Sludge
PC 145

Full Scale Application of a Novel Sludge Ozonation Process for Achieving up to 80% Excess Sludge Reduction at a 25,000 m^3/day Municipal Wastewater Plant

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Although sludge ozonation in lab scale tests have tended to yield economic dosage rates in the regime of ≤ 0.1 kg O_3/kg SS removed, previous attempts to extend the approach to commercial scale installations have resulted in non-economical ozone dosage levels (Sievers et al, 2004; Yasui et al, 1996; Kobayashi et al, 2001; Sakai et al, 1997), requiring as much as 0.395 kg O_3 per kg SS removed (See Table 2). In this paper, we discuss a novel approach to sludge ozonation and report the results of full scale tests carried out at a 7 MGD wastewater treatment facility which has been in operation since May 2006. A cost effective Ozone consumption value of 0.07 kg O_3/kg SS reduced was attained in the field, demonstrating the successful translation of bench scale type results to field applications using the Praxair approach.

Keywords:
Activated sludge, Ozonation, Lysis, Sludge reduction

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Oral
Sludge
PC 34

Effect of ozone pre-treatment on sludge production of aerobic digestion processes

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The effect of ozone and sequential ozone-biological treatment on sludge was investigated. The combination of aerobic bioreactor with chemical sludge disintegration was tested in bench scale experiments. A significant influence of ozone dose on sludge disintegration was observed. The available ozone in the solution was utilized first to degrade the soluble organic matter and in second stage to destroy the surface of cell and release the cell liquids. For single ozonation step, an optimum ozone dose in the range of 0.008 to 0.013 $gO_3/gTSS$ was found to give the best COD and TSS removal efficiency. Disintegrated sludge was treated in a sequential processes consist of consecutive ozonation and bio-aeration. The tendency of sequential processes was found to be dependent on accumulated O_3, aerobic treatment time, and mode of operation. Accumulated O_3 dose of 0.055 g O_3/g TSS in O_3 + bio_1+ O_3 + bio_2 + O_3 +bio_3 sequential processes was led to COD and TSS removal efficiency by 53 and 46.6 %, respectively. The settling ability of sludge was found to be fast at very low specific ozone dose; higher doses lead to a decreasing in settling ability of sludge. The use of sequential processes improves the settling tendency of sludge by biooxidation of the released portions and eliminates their negative effect of sludge settling.

Keywords:
Degradation, oxidation, ozone, organic matter

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Oral
Fenton
PC 149

Acid Dye Manufacturing Wastewater Treatment with Fenton’s Reagent and Electrocoagulation: Process Modelling, Optimization and Effects on Activated Sludge Inhibition

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In the present study, Fenton oxidation of a chromium complex disazo dye (Acid Blue 193) synthesis wastewater was investigated on compared with experimental results obtained for electrocoagulation of the same effluent. Response Surface Methodology was employed to assess individual and interactive effects of critical process parameters such as Fe^{2+}, H_2O_2 concentrations, initial chemical oxygen demand (COD) and reaction time, on treatment performance in terms of color, COD and total organic carbon (TOC) removal efficiencies. Optimum working conditions in terms of color and organic carbon removals were established as Fe^{2+}=3 mM; H_2O_2=25 mM and reaction time=10 min at pH 3, for a COD content of 245 mg/L. Under these conditions, 96% color, 82% COD and 51% TOC removals were experimentally obtained and fitted the model predictions quite well. Optimized electrocoagulation conditions obtained for the same effluent were established as COD_o=245 mg/L, reaction time=15 min, J_c=50 A/m^2 and pH_o=7. For evaluation of the toxic effect of untreated and Fenton-treated azo dye effluent, relative oxygen uptake rate inhibition of heterotrophic biomass was assessed with respect to synthetic domestic wastewater. Untreated azo dye production wastewater exhibited a slightly inhibitory effect and was still observed for the Fenton-treated effluent, whereas no inhibition was obtained for the azo dye synthesis effluent subjected to electrocoagulation.

Keywords:
Azo dye synthesis wastewater, Fenton process, color and organic carbon removal, process optimization, Response Surface Methodology (RSM)

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Oral
Fenton
PC 200

Application of nanoscaled iron reduction followed by UV/H_2O_2 oxidation for degradation of azo dye in wastewater

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In this study, three di-azo dyes, C.I. Acid Blue 113, C.I. Direct Yellow 4 and C.I. Acid Black 24, synthesized wastewaters were efficiently degraded on both total color and TOC using a combination technology by zero-valent iron (ZVI) reduction followed by UV/H_2O_2 oxidation process. The NZVI reduction in first 30 minutes reduced color successfully up to 98% color removal for Acid Blue 113 and Direct Yellow 4. The supernatant from NZVI process was than pumped through a UV/H_2O_2 process for TOC mineralization. For additional 120 minutes of irradiation time, the residual organic was mineralized to less than 3 mg l^{-1} for all three dyes. In summary, the NZVI reduction followed by UV/H_2O_2 process was demonstrated to be a superior technology for azo dye wastewater treatment.

Keywords:
nanoscale zero-valent iron (NZVI); azo dye; UV/H_2O_2 oxidation; reduction; degradation; mineralization

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Oral
Fenton
PC 257

New insights in the dihydroxybenzenes-Driven Fenton Reaction: Electrochemical study of interaction between dihydroxybenzenes and Fe(III)

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It has been reported that a DHB driven Fenton reaction is more efficient than a simple Fenton reaction on the recalcitrant substrate degradation. The reason for this enhanced reactivity is not clear, but it could be explained by the formation of oxidant species different that those in a classical Fenton reaction or by the redox potential shift of the DHB and Fe(III) in the complex. In order to gain insight into this problem, in this work we studied the Fe(III) reduction and performed cyclic voltammetry study on the system DHBs/Fe(III). The studied DHBs were: 1,2-dihydroxybenzene (catechol, CAT), 2,3-dihydroxybenzoic acid (2,3-DHBA), 3,4-dihydroxybenzoic acid (3,4-DHBA), 1,2-dihydroxy-3,5-benzenedisulfonate (TIRON).
It was determined that the amount of Fe(II) produced by the Fe(III) reduction by the several DHBs is insufficient to explain the enhanced reactivity of this system in the presence of H_2O_2. Also, the cyclic voltammograms of the DHBs/Fe(III) systems show a quasi-reversible or irreversible systems. Moreover, a shifting and splitting of the anodic peak was observed, which correspond to DHBs oxidation by Fe(III). For all the studied systems it was concluded that this effect is caused by independent effect of DHB and Fe(III), but not by a real interaction.

Keywords:
Brow rot fungi, Fenton reaction, dihydroxybenzenes, hydrogen preroxide

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Oral
Fenton
PC 100

Oxidation of cosmetic wastewaters with H_2O_2 using a Fe/γ-Al_2O_3 catalyst

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A catalyst based on Fe supported on γ-Al_2O_3 has been prepared and tested for catalytic wet peroxide oxidation (CWPO) of cosmetic wastewaters. The operating conditions (temperature, as well as catalyst and H_2O_2 doses) have been optimized. Working at 85 ºC, with 5 g/L of the home-made Fe/γ-Al_2O_3 catalyst and a dose of H_2O_2 corresponding to 0.5 times the theoretical stoichiometric H_2O_2/COD ratio, complete consumption of H_2O_2 and a substantial COD reduction (around 80%) has been reached. Thus, the locally allowable limit for COD (1750 mg/L) for industrial wastewaters discharges to the municipal sewer system can be reached. The catalyst showed a high stability in long-term continuous experiments since COD and TOC reductions around 82 and 60%, respectively, were maintained over 100 h. Less than 3% of the initial weight of Fe load was leached at the end of the 100 h time on stream.

Keywords:
AOPs; catalytic wet peroxide oxidation; cosmetic wastewaters; Fe/γ-Al_2O_3 catalysts; heterogeneous Fenton process; hydrogen peroxide

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Oral
Fenton
PC 96

Fe(III)/Photocatalytic removal of Bisphenol A from water

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The photodegradation of the endocrine disrupting chemical Bisphenol A (BPA) under UVA irradiation in the presence of Fe(III) or Fe(III)-polycarboxylate systems was studied. The effect of Fe(III) concentration, aqueous pH and the presence of four carboxylic acids (oxalic, malic, tartaric and citric) were investigated. The Fe(III)/UVA system was able to effectively degrade BPA at pH 3 but failed at pH

>4. At any rate, no mineralization of BPA was achieved with the Fe(III)/UVA system. The presence of carboxylic acids greatly enhanced the BPA removal rate because of the formation of photoactive Fe(III)-polycarboxylate complexes. Aqueous pH in the 3-7 range exerted a negative effect on the BPA removal rate and TOC conversion in the presence of oxalic, malic and tartaric acids. Only slight effect of pH was observed in the presence of citric acid, being the BPA transformation rate significant even at pH 7.

Keywords:
Bisphenol A; Fe(III); photocatalysis; polycarboxylates; UVA radiation

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Oral
Fenton
PC 33

Treatment of Humic Substances by Potassium Ferrate: Oxidation and Coagulation Interactions

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Ferrate (FeO_4^{2-}) is cited as having a dual role in water treatment, both as oxidant and coagulant. Few studies have considered the coagulation effect in detail, mainly because of the difficulty of separating the oxidation and coagulation effects. This paper summarises some preliminary results from laboratory-based experiments that are investigating the coagulation reaction dynamically via a PDA instrument, between ferrate and humic acid (HA) at different doses and pH values, and comparing the observations with the use of ferric chloride. The PDA output gives a comparative measure of the rate of floc growth and the magnitude of floc formation. The results of the tests show some significant differences in the pattern of behaviour between ferrate and ferric chloride. At pH 5 the chemical dose range (as Fe) corresponding to HA coagulation was much broader for ferrate than ferric chloride, and the optimal Fe dose was greater. Ferrate oxidation appears to increase the hydrophilic and electronegative nature of the HA leading to an extended region of charge neutralisation. A consequence of the ferrate oxidation is that the extent of HA removal was slightly lower (~5%) than with ferric chloride. At pH 7, in the sweep flocculation domain, ferrate achieved much greater floc formation than ferric chloride, but a substantially lower degree of HA removal.

Keywords:
Ferrate; ferric chloride; humic acid; oxidation; coagulation; water treatment

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Oral
Electro-chemistry
PC 143

The advanced EctoSys electrolysis as an integral part of a ballast water treatment system

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The advanced EctoSys electrolysis was studied in brackish and river waters as an integral part of a full-scale 500 m³/h ballast water treatment system. The test water quality exceeded by far the minimum requirements for type approval testing. In the whole salinity range from 0.4-15 psu, the disinfectants produced inline by the EctoSys cell were hydroxyl radicals, while in brackish water additionally chlorine and consequently the more stable bromine were formed. Initial residual oxidant concentrations were maximum 2 mg/L as chlorine during treatment of brackish water both at ballast water uptake and discharge, which represents worst-case treatment. In river water, no residual oxidants could be detected due to that the electrochemical process produces solely highly-reactive hydroxyl radicals. Accordingly, disinfection byproduct (DBP) formation was very low and close to the limit of quantification in river water, while in brackish water mostly brominated DBP (especially bromoform and bromate) were detected. Overall considering this worst case test approach, the DBP concentrations of the treated effluents were below or in the range of the WHO Drinking Water Guideline values and therefore evaluated as acceptable for discharge to the environment. The stringent discharge standard by the International Maritime Organization concerning viable numbers of organisms was fully met in river and brackish water, proving the disinfection efficiency of the EctoSys electrolysis against smaller plankton and bacteria.

Keywords:
Ballast water, bromine, chlorine, disinfection, electrolysis, hydroxyl radical

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Oral
Electro-chemistry
PC 192

The Effect of Electrode Material on the Generation of Oxidants for the Electrochemical Disinfection

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This study examined the role of electrode material on the generation of oxidants, and elucidated the different reaction pathways for generating individual oxidants by employing boron-doped diamond (BDD), Ti/RuO$_2$, Ti/IrO$_2$, Ti/Pt-IrO$_2$, and Pt as anode materials. The efficiency of $^{\cdot}$OH production, as determined by *para*-chlorobenzoic acid (*p*CBA) degradation, was in the order of BDD >> Ti/RuO$_2$ ≈ Pt. No significant production of $^{\cdot}$OH was observed at Ti/IrO$_2$ and Ti/Pt-IrO$_2$. The $^{\cdot}$OH was found to play a key role in O$_3$ generation at BDD, but not at the other electrodes. The production of active chlorine was in the order of Ti/IrO$_2$ > Ti/RuO$_2$ > Ti/Pt-IrO$_2$ > BDD > Pt. The large difference in this order from that of ROS was attributed to the difference in the electrocatalytic activity of each electrode material toward the production of active chlorine, as evidenced by linear sweep voltammetry (LSV) measurements.

Keywords:
Electrochemical disinfection; electrode material; hydroxyl radical; active chlorine

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Oral
Electro-chemistry
PC 116

Chlorate and perchlorate – new criterions for environmentally-friendly processes in *Advanced Oxidation*

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Studying electrolysis processes in drinking water disinfection it was found that chlorate and perchlorate can be formed at high extent on several electrode materials. Formation potential differs by orders of magnitude comparing mixed oxide (MIO), Pt and boron doped diamond (BDD) anodes. Highest concentrations were found using the doped diamond electrodes. Extended studies showed that chlorate and perchlorate may be formed also in other processes of so-called *Advanced Oxidation*. Therefore, the authors propose both components as new inorganic assessment criterions in environmentally-oriented water treatment.

Keywords:
Advanced Oxidation; electrolysis; disinfection by-products; chlorate; perchlorate

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Oral
Trace-pollutants (part 1)
PC 191

Ozonation of beta blockers: Kinetic studies and identification of oxidation products

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Oxidation products (OPs) formed during ozonation of metoprolol and propranolol were identified via liquid chromatography (LC) tandem mass spectrometry. Ozonation led to a high number of OPs being formed. Experiments were carried out in MilliQ-water at pH 3 and pH 8 as well as with and without the radical scavenger tertiary butanol (*t*-BuOH). This revealed the influence of pH and the OH radical exposure on OP formation. The major difference of the OP formation of propranolol and metoprolol, was the higher impact of the pH and scavenger concentration on metoprolol, compared to propranolol due to a about 3 orders of magnitude higher reactivity of the protonated propranolol. Impacts of the protonated and non protonated metoprolol species on OH radical formation were determined via a comparison of the measured pCBA attenuation with modeled values obtained by a simplified kinetic model (Acuchem). This indicated a stoichiometric formation of OH radical precursors ($^{\cdot}O_2^-$) during the primary ozone reaction of the deprotonated metoprolol. For reaction of a deprotonated molecule (attack of the aromatic ring) a formation of $^{\cdot}O_2^-$ could be confirmed, but an assumed stoichiometric $^{\cdot}O_2^-$ formation overestimated the formation of OH radicals in the system. For most of the elucidated structures oxidation pathways could be proposed. Analysis of ozonated raw wastewater and municipal WWTP effluent spiked with 10 μM metoprolol exhibited a similar OP formation pattern as detected in the reaction system at pH 8 without adding radical scavenger. This indicated a significant impact of OH radical exposure on the formation of OPs in real wastewater matrices. Although the biological activity of beta blockers will likely be lost after ozonation, the toxicological potential of the OPs is still unknown.

Keywords:

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Oral
Trace-pollutants (part 1)
PC 162

Effects of pH and H_2O_2 on levofloxacin ozonation in water

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A bubble column was used for ozonation of the quinolone antibiotic levofloxacin and the effect of pH and H_2O_2-addition was tested. Degradation at pH 10 decreased levofloxacin half life time to 7.8 min compared to pH 7 (12.8 ± 0.2 min) and pH 3 (15.9 min) whereas H_2O_2-addition (2 – 100 $mmol.m^{-3}$) at pH 7 reduced levofloxacin half life time to 10.6-11.9 min. Degradation product identification revealed strongest degradation at the piperazinyl substituent at pH 10 while degradation at the quinolone moiety seems promising at pH 7. Fastest reduction in antibacterial activity, monitored by agar diffusion tests, was observed at higher pH, in correlation with the levofloxacin degradation rate.

Keywords:
Levofloxacin, agar diffusion tests, degradation products, high resolution mass spectrometry

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Oral
Trace-pollutants (part 1)
PC 170

Efficient degradation of Ketoprofen: UV and VUV photolysis versus ozonization

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After application, most of the pharmaceuticals are partly excreted non-metabolized, reaching the wastewaters and the surface waters, too. Acidic anti-inflammatory drugs are receiving increasing attention because of their high polarity and therefore high mobility in the water media. The advanced oxidation processes (AOPs) are one of the most efficient methods for degradation of such organic pollutants.
Our aim was to compare ultraviolet (UV) and vakuum-ultraviolet (VUV) photolysis as well as ozonisation under the same experimental conditions and using the same reactor parameters. HPLC-MS was used to follow the kinetics of degradation and TOC to determine the level of mineralization.
The UV and VUV photolytic degradations of Ketoprofen have the same efficiency. With both methods complete degradation can be achieved within only one minute. The degree of mineralization with both methods reached 55-60 %. Beside a few simple organic acids, three major metabolites were detected during the degradation.
the ozonisation was less efficient. This notable difference can be probably explained with the formation of radicals having different reactivity.
(2002)

Keywords:
AOPs, degradation, Ketoprofen, pharmaceuticals

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Oral
Trace-pollutants (part 1)
PC 206

Behaviour and transformation of sulfamethoxazole after ozonation in secondary effluent and reverse osmosis concentrate

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After ozonation of sulfamethoxazole in secondary effluent products which are stable against further ozonation have been detected and identified. By the identified products and the formation of sulfate it can be concluded that sulfamethoxazole is attacked by ozone at both the isoxazole ring and the aniline ring. Aerobic degradation tests were conducted and an aerobic soil column was operated with ozonated effluent containing SMX spiked before ozonation (c_{SMX} = 6 mg/L). It could be shown that identified ozonation products resist aerobic biodegradation for four weeks as well as soil infiltration. In further studies secondary effluent from STP Ruhleben (Berlin, Germany) and reverse osmosis concentrate from the Torreele plant (Belgium) were ozonated at different dosages and measured for identified products. At low concentrations of SMX in secondary effluent (200 - 1100 ng/L) and in reverse osmosis concentrates (< 2 μg) none of the identified ozonation products could be detected.

Keywords:
Sulfamethoxazole; ozonation; wastewater treatment; brine

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Oral
Photocatalysis (part 1)
PC 120

Solar aqueous photocatalysis for pharmaceuticals removal in a pilot plant

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In this work, the degradation of a Non-Steroidal Anti Inflammatory Drug (NSAID) Ibuprofen (IBP) was carried out by heterogeneous photocatalysis with solar irradiation. The effect of the TiO_2 was evaluated in two solar installations: one-axis parabolic collector (PC) and CPC photoreactors with 1.5 and 6 L of total volume. The results showed that IBP (200 mg/L) was not totally removed in one-day under any condition tested. Degradation of IBP was 38, 11 and 48% for 0.1, 0.5 and 1 g/L of TiO_2, respectively, in PC-1.5 reactor. In contrast, more than double IBP removal was reached in CPC-6 photoreactor: 70, 50 and 73% by using 0.1, 0.5 and 1 g/L of TiO_2, respectively.

Keywords:
NSAID, IBP, heterogeneous photocatalysis

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Oral
Photocatalysis (part 1)
PC 73

Kinetic modelling of the photocatalytic inactivation of bacteria

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This work analyzes the kinetic modelling of the photocatalytic inactivation of *E. coli* in water using different types of kinetic models; from an empirical equation to an intrinsic kinetic model including explicit radiation absorption effects. Simple empirical equations lead to lower fitting errors, but require a total of 12 parameters to reproduce the results of four inactivation curves when the catalyst concentration was increased. Moreover, these parameters have no physical meaning and cannot be extrapolated to different experimental conditions. The use of a pseudo-mechanistic model based on a simplified reaction mechanism reduces the number of required kinetic parameters to 6, being the kinetic constant the only parameter that depends on the catalyst concentration. Finally, a simple modification of a kinetic model based on the intrinsic mechanism of photocatalytic reactions including explicit radiation absorption effects achieved the fitting of all the experiments with only three parameters. The main advantage of this approach is that the kinetic parameters estimated for the model become independent of the irradiation form, as well as the reactor size and its geometrical configuration, providing the necessary information for scaling-up and design of commercial-scale photoreactors for water disinfection.

Keywords:
Photocatalysis; disinfection; *Escherichia coli*; kinetics

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Oral
Photocatalysis (part 1)
PC 119

Reactor modelling in heterogeneous photocatalysis. Toxicity and biodegradability assessment

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Photocatalysis employing titanium dioxide is a useful method to degrade a wide variety of organic and inorganic pollutants from water and air. However, the application of this advanced oxidation process at industrial scale requires the development of mathematical models to design and scale-up photocatalytic reactors. In the present work, intrinsic kinetic expressions previously obtained in a laboratory reactor are employed to predict the performance of a bench scale reactor of different configuration and operating conditions. 4-Chlorophenol was chosen as the model pollutant. The toxicity and biodegradability of the irradiated mixture in the bench photoreactor was also assessed. Good agreement was found between simulation and experimental data. The root mean square error of the estimations was 9.9 %. The photocatalytic process clearly enhances the biodegradability of the reacting mixture, and the initial toxicity of the pollutant was significantly reduced by the treatment.

Keywords:
Biodegradability; 4-chlorophenol; kinetics; photocatalysis; reactor modelling; toxicity

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Oral
Photocatalysis (part 2)
PC 203

Effect of adsorption on photocatalysis performance of anthraquinone dye

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The adsorption and photocatalytic efficiency of several TiO_2 used as suspensions are compared for the degradation of an organic pollutant: anthraquinone dye Reactive Blue 2 (RB2). Adsorption of RB2 on catalysts follows the Langumuir model and influence of adsorption capacity on degradation performance was established. Correlations between degradation kinetics and maximal capacity of adsorption (qmax) were then determined. Expected correlation between specific surface and qmax, was verified. Addition of sulphate ions in the case of catalysts Degussa P25 and TiO_2-Ishihara ST01 inhibits adsorption of RB2 on TiO_2 surface. The hindrance of adsorption in acidic condition improves photocatalytic degradation efficiency of ST01. No adsorption is observed in alkaline pH and photodegradation kinetic is generally higher in this condition.

Keywords:
adsorption, anthraquinone dye, Langumuir model, photocatalytic degradation

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Oral
Photocatalysis (part 2)
PC 241

Synthesis and photocatalytic activity of boron-doped TiO_2 in aqueous suspensions under UV-A irradiation

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Boron-doped TiO_2 photocatalysts were synthesized employing a sol-gel method. Boric acid was used as the boron source and titanium tetra-isopropoxide as the TiO_2 precursor, both dissolved in isopropanol. Nominal boron to titanium atomic ratios were in the range 0 to 4%. After the hydrolysis step, two different procedures for the recovery of TiO_2 were followed, based on either centrifugation of the resulting reaction mixture or evaporation of the solvent under reduced pressure, both followed by a subsequent calcinations step performed at 400 or 500 ˚C. The photocatalytic efficiency of the synthesized photocatalysts was assessed by measuring the photocatalytic degradation of dichloroacetic acid in aqueous suspensions under UV-A irradiation and it was compared to the corresponding efficiency of the commercial Degussa

P 25 TiO_2. Photocatalytic efficiency of the synthesized catalysts was higher for the boron-doped TiO_2 synthesized at 2% boron to titanium nominal atomic ratio, centrifuged after the hydrolysis step followed by calcinations at 400˚C. However, the synthesized photocatalysts showed lower photocatalytic activity than Degussa P 25 TiO_2, thus highlighting the need of further improvements of the proposed method.

Keywords:
Boron-doped TiO_2, dichloroacetic acid, photocatalysis, sol-gel

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Oral
Photocatalysis (part 2)
PC 242

Degradation of azo dye using a novel TiO_2/Fe^0 composite nanopaticles

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The major obstacle of nanoscale zero-valent iron (nZVI) application is the decline in reduction activity efficiency with time due to the formation of a surface oxide layer. The electrode potential of the photocatalyzed Titanic dioxide ($TiO_{2)}$ could be used to transform ferric to ferrous ion and in turn, improve the efficiency of nZVI. A novel TiO_2/Fe^0 composite (NTFC) nanoparticles was prepared in the lab. The surface characteristics of the NTFC were identified by using TEM, XRD, XPS, EPR and chemical analysis techniques. The results from XPS and XRD analysis indicated that the NTFC was mainly composed of Ti and iron. The degradation of the target compound (azo dye) was conducted in a reactor with suspended NTFC with UV illumination at room temperature and atmospheric pressure. 80% color removals were detected in 5 hours. Although the nZVI produced higher concentration of ferrous ions than NTFC in the initial reaction period, the situation was reversed after long-term reaction. The concentration of ferrous ion decreased significantly in the nZVI suspension while the NTFC suspension maintained high concentration of ferrous ions. The ferrous/ferric ration was about 30 in the NTFC suspension after UV illumination. Therefore, The EPR spectrum results concluded that in NTFC, the electrons generated on the TiO_2 by UV irradiation can be trapped by the half reaction of ferric to ferrous, Which can prevent the electron–hole recombination of TiO_2. The result evidenced the potential of NTFC in the application of photocatalytic reaction. The photocatalytic activity of the heterogeneous catalysts for the mineralization of AB-24 sequence NTFC>nZVI>neutral TiO_2.

Keywords:
nZVI, Ferrous/ferric ions, NTFC, Recombination, TiO_2, Oxide layer

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Oral
Photocatalysis (part 2)
PC 246

Tetracycline oxidation by ZnO photocatalysis assisted by simulated solar light

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The degradation of tetracycline (TC) was performed at optimised conditions for the variables pH and amount of ZnO under simulated solar light irradiation. The higher degradation efficiencies of TC were obtained at pH 11 in parallel with significant photolysis. In the photocatalysed reaction, the TOC was completely removed after 45 min irradiation while the photolysis does not modify in any extent the TOC. For comparison purpose, the reaction was also done at pH 8, where the direct photolysis was less pronounced and the effect of the catalysed reaction was more evident. From these experiments, it is possible to conclude that hydroxyl radicals play a significant role in TC oxidation under alkaline conditions.

Keywords:
Antibiotic, multivariate analysis, photocatalysis, solar light, tetracycline, ZnO

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Oral
Trace-pollutants (part 2)
PC 266

Full scale post-ozonation followed by sand filtration at WWTP Regensdorf (CH) for micropollutant removal and disinfection

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More than 50 biologically active and persistent pharmaceuticals and biocides were selected as suitable indicators for the evaluation of a full-scale ozonation installed in the flocculation reactor (HRT = 3-15 min) between filtration and biological treatment of WWTP Regensdorf (25.000 P.E.). The sand filter acted as polishing step after ozonation. Micropollutants were measured by tandem mass spectrometry after offline or online solid phase extraction. Seven doses in the range 0.2-1.24 gO_3 $gDOC^{-1}$ were tested. The results with 24 and 48 h-volume proportional composite samples show that most of the compounds with aromatic moieties, amine functions or double bonds such as sulfamethoxazole, diclofenac or carbamazepine were eliminated to concentrations below the limit of detection using 0.6 gO_3 $gDOC^{-1}$. Compounds more resistant against oxidation by ozone such as atenolol and benzotriazole were increasingly eliminated with increasing ozone concentration, but a few x-ray contrast media persisted almost completely.
The specific and unspecific toxicity tested was reduced significantly by ozonation indicating that no toxic by-products are formed in higher concentrations. Low concentrations of about 5-10 ng L^{-1} of cancerogenic NDMA, produced as by-product from the oxidative transformation of organic amine precursors, were ca. 50 % removed during sand filtration. As an additional benefit E.coli could be reduced by 2-3 orders of magnitude for > 0.4 gO_3 $gDOC^{-1}$, and no regrowth during sand filtration was observed.
Energy consumption of the ozonation step was optimized during the study and accounts at an ozone dose of 4-5 gO_3 m^{-3} with about 0.06 - 0.08 kWh m^{-3}, which is 20-30% of the total energy consumption of a conventional nutrient removal plant.

Keywords:

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Oral
Trace-pollutants (part 2)
PC 115

Physicochemical and advanced oxidation processes – A comparison of elimination results of antibiotic compounds followed an MBR treatment

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The occurrence of pharmaceuticals in the environment has become a subject of concern in recent years. A vast number of these compounds have been detected in sewage treatment plants (STP) effluents, surface waters and, less frequently, in ground and drinking water all over the world. Adverse effects caused by pharmaceuticals include aquatic toxicity, resistance development in pathogenic bacteria, genotoxicity and endocrine disruption. Nowadays, it is widely accepted that the main source of pharmaceutical pollution in the aquatic environment are STPs effluents. Therefore, the discharge of pharmaceutical residues with the effluents of STPs should be minimized as far as possible. Degradation of persistent organic pollutants such as pharmaceuticals in water and wastewater can be achieved using advanced treatment technologies such as membrane bioreactors (MBRs) in combination with advanced oxidation processes (AOP). This paper evaluates the treatment of three antibiotics of large consumption rates worldwide (roxithromycin, sulfamethoxazole and trimethoprim) by MBR followed by different AOP-steps. The identification and quantification of the precursor compounds and degradation products observable during the different treatment steps applied were performed with liquid chromatography coupled with high resolution mass spectrometry (LC-MS).

Keywords:
Antibiotics, elimination, membrane bioreactor (MBR), pharmaceuticals, wastewater

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Oral
Trace-pollutants (part 2)
PC 205

Advances in Catalyzed Ozonation for Degradation of Organic Pollutants and Full Scale Applications

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This paper reviewed the recent development of heterogeneous catalyzed ozonation for the degradation of refractory organic pollutants. In the first part of this paper, we present a brief summary of the main results obtained by our group in the last fifteen years. The activities of several kinds of catalysts developed in our group were evaluated on the organic pollutants removal compared with ozonation alone. The mechanisms on the degradation of organic pollutants (atrazine, nitrobenzene, oxalic acid, etc.) were discussed, and it is suggested that most of these processes follow hydroxyl radical mechanism. The results of a full scale application of catalyzed ozonation were shown in the second part of this paper. It was observed that the catalyzed ozonation had better performance on both the COD_{Mn} removal and the minimization of bromate formation than ozonation alone during the treatment of raw water with a high concentration of COD_{Mn} and a concentration of 210-220 $\mu g\ L^{-1}$ bromide. Finally, a multi-stage catalyzed ozonation was proposed based on the optimized combination of several catalysts, which could be more effective on COD_{Mn} removal and the minimization of bromate formation than conventional catalyzed ozonation.

Keywords:
Catalyzed ozonation; full scale application; heterogeneous catalyst; metal oxide; organic pollutant

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Oral
Trace-pollutants (part 2)
PC 158

Computer-assisted determination of reaction parameters for the simulation of micropollutant abatement in wastewater ozonation

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The kinetics of the reaction of ozone with wastewater has been determined by stopped-flow and batch quench methods. It can be adequately described by three components and their respective rate constants. Ozone uptake and ozone steady states along a bubble column have been determined. A modelling procedure has been developed that allows us to describe this behaviour and to simulate the degradation of micropollutants. For fast and moderately fast reacting micropollutants this model describes their elimination well. Ozone-refractory micropollutants are also eliminated to some extent due to the presence of $^{\bullet}OH$ radicals (~13% of ozone).

Keywords:
Bubble column, hydroxyl radical, micropollutant, modelling, ozone, wastewater

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Oral
Trace-pollutants (part 2)
PC 68

Removal of analgesic drugs from the aquatic environment using photochemical methods

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The occurrence of analgesics in the environment can be explained by the fact that they are very popular and in common use, for example: to treat the symptoms of colds, aches and pains or for the treatment of painful diseases of rheumatic and non-rheumatic origin. Analgesic drugs are only partly removed from wastewater using the biological wastewater treatment processes. The photochemical methods are mentioned as a useful tool for the removal of analgesic medicines from the aquatic environment. The elimination of three analgesic drugs: diclofenac, naproxen and ibuprofen from the aquatic environment using UV- and UV/H_2O_2-processes was the aim of the study. All experiments were performed in the water with the presence and the absence of the urea as the main urine component. With the presence of urea the values of photo-oxidation rate constants (in the UV/H_2O_2 – process) varied from 0.22 min^{-1} (ibuprofen) to 0.39 min^{-1} (diclofenac). The values of the photodegradation rate constants in the solution without urea (in the UV/H_2O_2 – process) varied from 0.25 min^{-1} (ibuprofen) to 0.45 min^{-1} (diclofenac). The study showed that naproxen, ibuprofen and diclofenac may be effectively removed from the aquatic environment (e.g. from the urine) by means of photochemical methods.

Keywords:
Analgesics, aquatic environment, first order kinetic, UV, UV/H_2O_2, photodegradation

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Oral
Trace-pollutants (part 2)
PC 138

Removal of Carbamazepine upon Sulphate radical oxidation from Urban Wastewater

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In this paper we show that sulphate radicals generated from peroxymonosulfate/Co^{II} was more efficient than with hydroxyl radicals generated from the Fenton's reagent (H_2O_2/Fe^{II}) for the degradation of carbamazepine. The second-order rate constant of $SO_4^{\bullet-}$ with carbamazepine has been determined to be $1.92\cdot10^9$ $M^{-1}\cdot s^{-1}$. Comparatively to $HO^{\bullet}$, $SO_4^{\bullet-}$ yielded a faster degradation of carbamazepine as well as in laboratory grade water as in real urban wastewater. Under strong oxidation conditions, compound mineralization was nearly achieved while in mild oxidizing conditions, several intermediates were identified by LC-MS. These intermediates were similar with those already reported.

Keywords:
Peroxymonosulate, Sulfate radical, Carbamazepine, Advanced Oxidation Technology, kinetic, Rate constant

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Poster
Fundamentals
PC 52

Kinetic study of wet oxidation applied to a real liquid waste

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The aim of this work was to study the mechanisms and kinetics of organic matter degradation by Wet Oxidation (WO). A real liquid waste characterized by high organic matter content (initial concentration of COD: 50,000 mg/L) was submitted to WO, also in presence of homogeneous catalysts (Cu^{2+}, Fe^{2+}, Mn^{2+}). Kinetics of degradation of COD and TOC were studied by developing a conceptual model of the main reaction mechanisms. The effect of temperature on degradation rate constants was also estimated.

Keywords:
Catalysts; kinetic models; liquid waste; reaction mechanism; wet oxidation.

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Poster
Fundamentals
PC 55

Arsenic oxidation by UV radiation combined with hydrogen peroxide

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Arsenic is a widespread contaminant in the environment around the world. In groundwater the most abundant species of arsenic are arsenite [As(III)] and arsenate [As(V)]. Several arsenic removal processes can reach good arsenic removal yields only if arsenic is present as As(V). For this reason it is often necessary to proceed with a preliminary oxidation to As(V) before removal treatment. Several studies are focused on arsenic oxidation with conventional reagents and advanced oxidation processes. In the present study the arsenic oxidation was evaluated by means of hydrogen peroxide, UV radiation and their combination in distilled and in real groundwater. Hydrogen peroxide and UV radiation alone are slightly effective in arsenic oxidation. Good arsenic oxidation yields can be reached in presence of hydrogen peroxide combined with a high UV radiation dose (2,000 mJ/cm^2).

Keywords:
Arsenic oxidation; advanced oxidation process; hydrogen peroxide; UV radiation

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Ozone-activated carbon mineralization of 17-α-ethynyl-estradiol aqueous solutions

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Ozone and activated carbon (AC) have been used on the removal of 17α-ethynylestradiol (ETOL), a pharmaceutical compound, and its oxidation by-products. While single ozonation is not able to remove totally the by-products formed from the degradation of the parent compound (about 65% of TOC removal at pH 7 after 2 hour reaction), the ozone/AC system led not only to lower TOC removal at the same conditions (about 90% in the case of P110 Hydraffin AC) but also to lower ozone consumption. In addition, samples treated with the catalytic process presented ecotoxicity values lower than those resulting from the application of single ozonation.

Keywords:
Ozone, activated carbon, ethynylestradiol, catalytic ozonation

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Mineralization of ranitidine by ozone in water

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Ranitidine has been ozonated under different operating conditions of pH, applied ozone dose, initial ranitidine concentration and presence or absence of free radical inhibitors. Results of ranitidine evolution with time indicate a high reactivity of this compound with molecular ozone. Mineralization levels achieved in the order of 20-25% suggest that the $(CH_3)_2$- N-CH_2- moiety bonded to the furan ring could be separated from the rest of the ranitidine structure and further mineralized. Only alkaline conditions (pH = 11) are capable of increasing TOC conversion up to values close to 70%.

Keywords:
ozone; ranitidine; mineralization; water treatment

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Degradation of a mixture of pollutants in water using UV/H_2O_2 process

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The degradation reaction of a simple mixture of pollutants (Dichloroacetic acid + Formic acid) employing H_2O_2 and UVC radiation (253.7 nm) has been studied in a well-mixed reactor operating inside a recycling system. The final objective of this work is to develop, starting from a rather manageable system, a systematic methodology for treating degradation of mixtures of pollutants, progressing onwards to aggregates that are more complex. In this contribution, the effects of different variables such as hydrogen peroxide/pollutant mixture initial concentration ratio, pH and incident radiation at the reactor wall were studied. The results show that the best degradable conditions are: pH = 3.5 and hydrogen peroxide concentrations of 3.9 to 11.8 mM (134-400 mg/L), for initial concentrations of 1.10 mM and 0.39 mM for Formic acid and Dichoroacetic acid respectively (50 mg/L for both pollutants). The influence of the incident radiation at the reactor wall on the degradation rates of the mixture is markedly significant. In addition, it has been shown that in an aqueous solution no stable reaction intermediates are formed. On this basis, a complete reaction scheme for the mixture is proposed that is apt for a reaction kinetics mathematical modeling of the mixture and ulterior scaling-up.

Keywords:
Degradation; Mixture of pollutants; reaction scheme; UVC/ hydrogen peroxide

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Degradation of Sulfamethoxazole by Photocatalysis and Ozonation

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The quality of surface and drinking water has become an issue of concern due to the presence of new recalcitrant pollutants in aquatic media. Advanced oxidation processes (AOPs) have proved to be highly effective to remove most of the micro-pollutants contained in wastewater. This study deals with the degradation of SMX by means of two different processes: photocatalysis and ozonation. The results state that the degree of SMX mineralization achieved by photocatalysis was higher than that achieved with ozonation (for the same level of SMX degradation), whereas the ozonation process was much faster. In general, the hydroxyl radicals attack takes place primarily either to the aniline or the isoxazole ring, by addition of the functional group –OH to an open carbon position, whereas the reaction with O_3 results in an electrophilic attack, which takes place primarily at the p-sulfoaniline moiety.

Keywords:
Sulfamethoxazole; photocatalysis; ozonation; oxidation products

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PC 134

DECOLORIZATION AND MINERALIZATION OF AZO DYES BY CWAO AND WAO: INFLUENCE OF THE AZO STRUCTURE

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Degradation of several azo dyes, Acid Orange 7 (AO7), Acid Orange 74 (AO74), Direct Blue 71 (DB71), Reactive Black 5 (RB5) and Eriochrome Blue Black B (EBBB), well-known non-biodegradable mono, di and tri azo dyes, has been studied using, wet-air oxidation (WAO) and catalytic wet air oxidation (CWAO), advanced oxidation processes (AOPs). The efficiency of substrate decolorization and mineralization in each process has been comparatively discussed by evolution concentration, chemical oxygen demand, total organic carbon content and toxicity of dyes solutions. The most efficient method on decolorization and mineralization (TOC) was observed to be CWAO process. Mineralization efficiency with AOPs essays was observed in the order of mono-azo > di-azo > tri-azo dye. Final solutions of CWAO applications after 180 min treatment can be disposed safely to environment.

Keywords:
Dyes; catalytic wet air oxidation; heterogeneous catalysts; wet air oxidation

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MnO_2 catalyzed oxidation of aqueous phenol with peracetic acid in the presence of ultrasound

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The combination of peracetic acid as an oxidizing agent with manganese dioxide has been studied in the presence ultrasound for degradation of persistent organics under various experimental conditions. The influence of ultrasound was dual: it catalyzed the oxidation process due to the formation of additional radicals and improved catalyst performance via catalyst fragmentation and mass transfer enhancement. The loss in the catalytic activity was not significant even after four runs. The apparent reaction rate was dominated by the intrinsic reaction rates on the oxide surface rather than the mass transfer rate of the oxidant to the surface. The presence of free radicals in the reaction system has been studied by means of spin trapping technique with electron spin resonance (ESR).

Keywords:
Peracetic acid; phenol; ESR spin trapping; ultrasound

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Degradation of azo dye Reactive Black B using an immobilized iron oxide in a batch photo-fluidized bed reactor

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In this study, a new batch photo-fluidized bed reactor (photo FBR) is designed to degrade azo dye Reactive Black Band (RBB) to avoid the iron species leached from the surface of iron oxide by colliding. In the photo FBR, an immobilized iron oxide, named B1, is employed to be the catalyst of H_2O_2. It has been presented that some of iron oxides are able to activate H_2O_2 for the degradation of organic pollutants. This work also find that B1 catalyst could efficiently adsorb RBB and activate H_2O_2 to degrade RBB in dark. The UV light irradiation (365 nm) systems show that more efficient for the degradation of RBB than dark system. Furthermore, the most attractive potential of B1 catalyst is the nearly total desorption of RBB under alkali condition (pH 12), indicating its high reusable capacity and regeneration ability for industrial applications.

Keywords:
Photo-Fenton process, azo-dye reactive Black B

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Effect of coagulation, electrocoagulation and Fenton treatment processes on organic carbon and phenolics profile of olive mill wastewater

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- No abstract submitted. -
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A Submerged Non-woven Sheet/ Photocatalytic Reactor System for Removal of NP-9 in Water

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In this study, photodegradation of nonylphenol polyethoxylates (NP-9) with continuous mode was carried out in photocatalytic TiO_2 suspension reactor containing submerged non-woven fibrous sheet module. The influence of operational variables,

including light intensity and TiO_2 concentration at fixed feed flow rate on the photodegradation performance and the filtration characteristics of non-woven sheet module were investigated. Treatment effectiveness and feasibility of the non-woven sheet/photocatalytic reactor system for removal of NP-9 was successfully demonstrated. Experimental results showed that photodegradation efficiency increased with increasing light intensity and higher removal efficiency of NP-9 and TOC were found at high light intensity of 288 W for all TiO_2 concentrations. However the highest removal efficiency of NP-9 with 95 % and higher TOC removal efficiency were gained only for 1,000 mg/L of TiO_2 concentration at the light intensity of 144 W and 288 W. In considering filtration behaviour of non-woven fibrous sheet, we found that no significant variation of permeate flux and stable transmembrane pressure (TMP) were obtained for all TiO_2 concentrations at fixed feed flow rate of 100 L/day.

Keywords:
Non-woven fabric sheet; photodegradation; photocatalytic reactor system; nonylphenol polyethoxylates

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Ozonation of ampicillin and toxicological assessment of its oxidation by-products

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This study was performed to investigate the degradation efficiency and potential toxicity of ampicillin at different pH conditions (5, 7.2, and 9). The depletion of AP concentration, kinetic rate constants, chemical oxygen demand (COD), and Total organic carbon (TOC) were investigated. In addition, the enhancement of biodegradability (BOD_5/COD) and the acute toxicity of AP and its oxidation by-products by bioluminescence test (*Vibrio fischeri*) were examined. The second-order rate constants for the direct reaction of AP with ozone were slightly increased with increasing pH of solution and determined to be 2.2 ~5.4×10^5 $M^{-1}s^{-1}$, respectively. The biodegradability at pH 7.2 and 9 constantly increased up to 0.35 and 0.41 after 120 min of ozonation, whereas it was 0.13 at pH 5 under the same condition. The results of acute toxicity test indicated that some oxidation by-products at pH 5 and 7.2 were more toxic than the parent compound and still remained until ozonation time of 100 min. As a consequence, it can be concluded that ozonation is a suitable method to remove AP and improve biodegradability for the treated water; however, for which pH of solution should be carefully adjusted to higher than pH 7.

Keywords:
Ampicillin; biodegradability; Bioluminescence test, Ozonation; pH

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Poster

Fundamentals

PC 177

Integrated Ultrasound/heterogeneous Fenton process for the decolorization of Crystal Violet in aqueous solution

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Ultrasonic irradiation (US) and heterogeneous Fenton process are two promising advanced oxidation processes. The purpose of this study is to assess the decolorization of synthetic organic dyes, Crystal Violet (C.I. Basic Violet 3), in aqueous solutions by means of ultrasonic irradiation coupled with heterogeneous Fenton processes. The results showed that the decolorization efficiency by US/heterogeneous Fenton process can generate synergistic effect together and the decolorization efficiency was affected by pH, H_2O_2 concentration, catalyst dosage, initial dye concentration, and US power density. It is concluded that ultrasonic irradiation combination heterogeneous Fenton process is an effective process for the decolorization of C.I. Basic Violet 3 in wastewater.

Keywords:
Ultrasonic radiation; heterogeneous Fenton process; C.I. Basic Violet 3; decolorization

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An Alternative Approach to Modelling the UV/H_2O_2 Process

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This work focuses on deriving a mathematical model of a UV/H_2O_2 decolouration/mineralisation of industrial coloured textile wastewater. The model comprises four environmental parameters commonly monitored in textile wastewater. These are: Absorbance (A) at three distinctive wavelengths (λ_1= 436 nm, λ_2 = 525 nm, λ_3 = 620 nm), and total organic carbon (TOC). The presented mathematical models can be used to assess the progression of UV/H_2O_2 treatment at fixed operating conditions in cases when the composition of treated wastewater is unknown.

Keywords:
UV/H_2O_2 process; coloured textile wastewaters; mathematical model

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PC 182

Role of Hydrogen Peroxide on Oxidation of Water Treatment Process

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- No abstract submitted. -
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Enhancement in mineralization of a number of natural refractory organic compounds by ultrasonic in conjunction with ozonation: (US/O_3)

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An advanced oxidation process (AOPs) that combines ultrasound and ozone was studied in terms of its potential to oxidize natural organic matter in order to determine whether the approach could extend the application of sonlysis to refractory electrolytes. Sonochemical enhancement of ozone decomposition rates has previously been attributed to ozone pyrolysis in the cavitation bubble or at the bubble interface. In this study, the objective was to explore the decomposition mechanism and the

synergy effect of ultrasonic/ozonation through the extent of mineralization, the reduction in chemical oxygen demand (COD), total organic carbon (TOC) and the colors of humic and tannin acid for biological treated piggery wastewater by ultrasonic (US), ozonation (O_3) and a combination of ultrasonic and ozonation (US/O_3). Under conditions of constant ultrasonic irradiation and continuous ozone gas application, COD and TOC removal rates were enhanced. The ratios of the high molecular humic and tannin acids above 5,000 and 2,000 Dalton, detected by the ultra filtration method, were 90.25 and 89.53% respectively, before being treated by US/O_3. However, after 30 minutes reaction, this ratio rapidly reduced to 3% and 4%, respectively. Low molecular humic and tannin acids below 500 Dalton rapidly increased from 0.8% to 41% and from 0.65% to 39% respectively.
The by-products included formaldehyde, acetone, hydroxylamine, etc.

Keywords:
Piggery wastewater; Tannin acid; Humic acid; Ultrasonic; Ozonation; US/O_3

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Effect of Hydrogen Peroxide on Sonochemical Degradation of Phenol

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The effect of hydrogen peroxide on the sonochemical degradation of phenol was investigated in this study. The concentrations of phenol and hydrogen peroxide were 0.25 mM and 0.018, 0.054 mM, respectively. With the addition of hydrogen peroxide in phenol solution, phenol concentration was almost completely degradable within 30 min. In the case of TOC, the concentration was degraded by 50%. When a high frequency of sonication (1 MHz) was irradiated to a phenol solution, the efficiency of decomposition of phenol was higher than low frequency (35 kHz). At low concentration of hydrogen peroxide was applied many times that was more efficient than high concentration of hydrogen peroxide was applied once. To enhance the degradation of TOC was needed to addition of catalysts, longer sonication time, and high ultrasonic power.

Keywords:
hydrogen peroxide, frequency, phenol, sonochemical, total organic carbon

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Performance of a large-scale sonoreactor for the removal of organic pollutants in aqueous phase

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Liquid height effect on sonochemical reactions was investigated in large-scale cylindrical sonoreactors. Three frequencies of 35, 72, and 110 kHz were applied. Sonochemical and conversion efficiency was enhanced significantly above a certain liquid height. This meant ultrasonic application could be more effective in larger target volume. As liquid height was increased it was revealed that there are two active zones from the images of chemiluminescence: bright zone near the transducer and standing wave field near liquid surface. In addition, as the applied frequency was increased, the intensity of light was decreased for all over the reactor and the intensity of standing wave field was also decreased. Thus larger input power should be applied to use higher frequency in large-scale sonoreactors. In estimation of attenuation coefficient for 35 kHz frequency, however, larger input power resulted in larger attenuation and higher attenuation coefficient. Consequently, it should be important to optimize the applied frequency and input power for effective sonochemical reactions in large-scale sonoreactors.

Keywords:
Sonochemistry; large-scale sonoreactor; sonochemical efficiency; conversion efficiency; chemiluminescence; attenuation

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Degradation of Chlorpyriphos in Water by Advanced Oxidation Processes

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The degradation of chlorpyriphos by different advanced oxidation processes such as photo-Fenton, TiO_2, TiO_2/H_2O_2, O_3 and O_3/H_2O_2 was investigated. The photo-Fenton and TiO_2 processes were optimized using a solar chamber as light source. The optimum dosages of the photo-Fenton treatment were: $[H_2O_2]$=0,01%; $[Fe^{3+}]$ =10 mgl^{-1}; initial pH= 3,5. With these optimum conditions total degradation was observed after 15 minutes of reaction time. The application of sunlight was also efficient as total degradation was achieved after 60 minutes. The optimum dosage using only TiO_2 as catalyst was 1000 mgl^{-1}, obtaining the maximum degradation at 20 minutes of reaction time. On the other hand, the addition of 0,02% of H_2O_2 to a lower dosage of TiO_2 (10 mgl^{-1}) provides the same degradation. The ozonation treatment achieved complete degradation at 30 minutes of reaction time. On the other hand, it was observed that the degradation was faster by adding H_2O_2 (H_2O_2/O_3 molar ratio = 0,5). In this case, total degradation was observed after 20 minutes.

Keywords:
Hydroxyl radical; organophosphorous pesticide; ozone; peroxone; photo-Fenton; titanium dioxide.

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Properties of Hydroperoxyl/Superoxide Anion Radical ($HO_2^{\cdot}/O_2^{-}\cdot$) Formed in the Aqueous TiO_2 Photocatalysis

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The formation of hydroperoxyl radical/superoxide anion radical ($HO_2^{\cdot}/O_2^{\cdot-}$) is very important process to improve the efficiency of TiO_2 photocatalytic reactions due to its involvement on the decrease of electron-hole (e^--h^+) recombination. In this study, the adsorptive and desorptive features of $HO_2^{\cdot}/O_2^{\cdot-}$ formed by TiO_2 photocatalytic reactions were investigated by using the Fenton-like reactions. This study reports that approximately 14 ~ 20% of $HO_2\cdot/O_2^-\cdot$ formed in the irradiation of TiO_2 particles was able to be drift from the surface of irradiated TiO_2, when the sum of fluorescence signal intensity of hydroxybenzoic acid (OHBA) formed through the Fenton-like reaction was assumed to be the sum total of $HO_2\cdot/O_2^-\cdot$ adsorbed on the surface of TiO_2 particles and desorbed in the aqueous sample containing irradiated TiO_2 particles, and $HO_2\cdot/O_2^-\cdot$ formed from the surface of irradiated TiO_2 at alkaline pH was able to be more drift than that at acidic pH. These results indicate that the $HO_2\cdot/O_2^-\cdot$ molecules are desorbed as well as adsorbed on the surface of illuminated TiO_2 particles.

Keywords:
Adsorption; desorption; electron-hole; Fenton-like reaction; fluorescence; hydroxybenzoic acid

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Degradation of Metronidazole by Ozonation Process

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The main objective of this study was to investigate the degradation of Metronidazole (MTZ) using ozonation processes. It was examined the principal parameters of treatment such as concentration, ozone dose, sub-products formation, kinetic parameters (rate constants and half-life times) for the degradation and acute toxicity. Results showed that ozonation was proved to be a resourceful method to degrade metronidazole. Solutions containing $6.0x10^{-5}$ $mol.L^{-1}$ of MTZ was almost completely degraded after applying 35 mg $O_3.L^{-1}$ (60 min ozonation) however the ozonized solutions showed the presence of short chains carboxylic acids and inorganic anions as by-products of degradation. The acute toxicity was followed by Daphnia similis bioassay and results demonstrated the oxidation compounds were more toxic than the original antibiotic. After 60 min ozonation the LC_{50} = 67.95 (%v/v). The discharge of the active form of MTZ into natural waters represents an ecological risk and ozone process permits the degradation of this molecule. However, it could be formed nitro-compounds more toxic and recalcitrant to ozone attack, being necessary a complementary treatment.

Keywords:
Degradation, metronidazole (MTZ), ozone, toxicity

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A complete kinetic model of Ozone decomposition in aqueous solutions as a function of pH under acidic to neutral conditions

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The Ozone decomposition reaction in water, operated under acidic to neutral conditions was studied. Using a proposed 18 steps kinetic scheme existing in the literature, from the reported values compiled in the bibliography, it was not possible to find a consistent set of kinetic constants to represent the experimental data, the reason being that most of the values were obtained under very different operating conditions, particularly the pH. Resulting from a parametric sensitivity analysis, a correction introduced in one kinetic constant (that was made to depend on a simple analytical function of the reacting medium pH) a reliable, 18 steps, kinetic model, valid for the pH range from 2 to 7 was found. The semi-empirical model has shown very good agreement with the experimental results. It was also found that the kinetics has a strong dependence on the concentration of hydrogen peroxide formed at low concentrations, as a stable reaction by-product.

Keywords:
Acidic and neutral pH, homogeneous media, Ozone, semi-empirical kinetic model

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PC 201

OH-Radical Yield in the Peroxone Process (H_2O_2 + O_3)

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The peroxone process is one of the AOPs that generate OH-Radicals (·OH). It is assumed that the ·OH yield is unity with respect to O_3 consumption. To investigate this, experiments were carried out with ·OH generated by the peroxone process, and for comparison, by γ-radiolysis. While the yield of ·OH generated by the peroxone process is an assumption, the ·OH yield generated by γ-radiolysis is calculated using Fricke dosimetry and therefore authentic. The degradation of p-chlorobenzoic acid, p-nitrobenzoic acid and atrazine was determined as a function of the O_3 concentration in a solution containing an excess of H_2O_2 and t-butanol acting as ·OH scavenger to minimize competition reactions of the analytes with their products. The results show, that the ·OH yield in the peroxone reaction is around 50 % of the assumed yield.

To verify these results, more experiments were performed by adding various O_3 concentrations to a t-butanol and H_2O_2 containing solution. The generated ·OH react with t-butanol to aldehydes. These aldehyde yields were compared with these formed from ·OH generated by γ-radiolysis. The comparison of these results also confirms that the ·OH yield is around 50 % of the assumed yield and two mol of O_3 are needed to generate 1 mol of ·OH.

Keywords:
Competition reactions, γ-radiolysis (Gamma-radiolysis), OH-Radicals, peroxone process

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Chloroform degradation by advanced oxidation processes with O_3, H_2O_2, TiO_2 and radiation

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The aim of this research work is to study the chloroform degradation, which is the main trihalomethane detected in natural water, by several advanced oxidation processes (AOPs) with ozone, hydrogen peroxide, titanium dioxide and radiation.

The study of the chloroform degradation provokes to know the AOPs which generate the greater Reactive Oxygen Species (ROS) production since it reacts with ROS generated in these processes by radicalary way.

Among 14 studied treatments, the highest ROS generation is achieved with $O_3/H_2O_2/TiO_2$ and TiO_2/H_2O_2/radiation treatments by which the chloroform degradation is between 50 and 60%.

Keywords:
Chloroform, ozone, hydrogen peroxide, titanium dioxide, radiation

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The hybrid process TiO_2/PAC – performance of membrane filtration

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In investigations concerning the photocatalytic degradation by TiO_2 usually filter discs with a pore size of 0.22 μm and 0.45 μm are used for the removal of photocatalyst particles in aqueous suspensions. In this study the effective rejection of suspended particles by microfiltration in different types of membrane modules and with different mebrane materials was investigated. Furthermore the influence of added Powdered Activated Carbon (PAC), which can be used to gain an increase in photocatalytic degradation rates, on the membrane performance was determined. It is shown that by membrane filtration with a pore size above 0.1 μm, irrespective of the experimental conditions, no complete removal can be achieved. However, UV irradiation was found to improve the removal efficiency for all types of tested membrane materials. The addition of PAC also led to a higher performance of membrane filtration with regard to particle rejection. In long term experiments with a hollow fiber membrane module in attendance of PAC a 5-fold decrease of TiO_2 particles in the permeate could be proven. Besides was shown that added PAC can shield the membrane regarding the abrasivity of TiO_2, which could elsewhise lead to the destruction of the membrane. Therewith PAC exhibits another crucial advantage besides its synergetic effect in photodegradation.

Keywords:
membrane filtration, PAC-TiO_2 synergetic effect, particle rejection, cake layer, abrasion

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Decolourization and modelling of synthetic waste-water by O_3 and H_2O_2/O_3 process

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This research deals with decolourization of synthetic waste-water prepared with acid 1:2 metal complex textile dye C.I. Acid Blue 193 by ozonation (O_3) and H_2O_2/O_3 process was investigated. In order to minimize the number of experiments, experiments were performed using the 2^k factorial design. Five influential parameters were examined: initial dye concentration, ozone flow rate, initial pH value, decolourization time and H_2O_2 addition. The decolourization efficiency was 95% in 20 minutes (pH = 7; O_3 flow rate 2 g/h). According to the variance test analysis, initial dye concentration, ozone flow rate, initial pH value and decolourization time and their first and second order interactions are significant, while the H_2O_2 addition was not important over the discussed range. With the help of significant factors a regression model was constructed and model adequacy checked. The obtained regression polynomial was used to model the relation between absorbance and influential parameters by fitting the response surface. Response surface may be used to predict absorbance resulted from a set of influential parameters, or it can be rearranged in such a way to predict the set of process decolourization parameters necessary to reduce the absorbance of waste water with the given initial dye concentration below the prescribed limit. It is also shown that 2^k factorial design can be suitable to predict ozonation operating expenses.

Keywords:
Decolourization; dye C.I. Acid Blue 193; H_2O_2/O_3 process; ozonation (O_3); synthetic waste-water; 2^k factorial design

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Ozonation of Lignin Aqueous Solutions

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The main objective of the present research was to establish the possibilities of ozonation of lignin aqueous solution. A three-level fractional factorial design was used in the experimental study. The experimental results showed high performance in ozonation of lignin: its removal ranged from 60 to 80% depending on the operating conditions. Also the colour and the chemical oxygen demand (COD) decreased from 19 to 70% and from 56 to 92%, respectively. In all experiments the biodegradability of lignin solutions increased: untreated lignin solution was non-biodegradable (BOD/COD ratio below 0.1), whereas the biodegradability increased 4 to 6 times with the ozone applied, making preliminary ozonation a viable method by means of enhancing subsequent biological treatment. Based on the experimental data, simple empirical models in the form of the regression equations were developed for evaluation of the ozonation process efficiency and for estimation of the influence of the impact factors – initial lignin concentration, ozone delivery rate, ozone inlet gas-phase concentration, pH, and treatment time. The adequacy of the models was tested on experimental data, and the impact of various factors was assessed.

Keywords:
Lignin, ozonation, regression model

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Degradation of chlorinated organic pollutants by a heterogeneous sono-Fenton process

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Abstracttext The aim of this work is related to sono-Fenton processes heterogeneously catalyzed by Fe_2O_3/SBA-15 for the degradation of model phenol and chlorinated derivatives (2-chlorophenol and chlorobenzene). Results demonstrate that hydrogen peroxide concentrations corresponding to the stoichiometric amount for a theoretical complete mineralization of the model pollutant allow obtaining high mineralization grades, as well as complete removal of the pollutant in the first 2 hours of reaction under acidic and natural pHs. Combination of sonolysis with heterogeneous Fenton-like oxidation enhances degradation of model pollutants, even when pyrolytic decomposition is the main degradation pathway. Total 2-chlorophenol degradation after 1 hour of reaction and TOC mineralization of ca. 35% is obtained using a stoichiometric amount of hydrogen peroxide and natural pH Elimination of 2-chlorophenol occurs mainly via hydroxyl radical oxidation whereas chlorobenzene is degraded by pyrolysis inside the cavitation bubbles. In this latter case, the presence of solid catalyst enhances initial mineralization rate, obtaining a TOC conversion of ca. 90% after 60 minutes of sonication.

Keywords:
Chlorophenol, chlorobenzene, sono-Fenton, heterogeneous catalyst, ultrasound, acoustic cavitation

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MnO_2 precipitation on lignite carbon by Mn(II) Ozone oxidation

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MnO_2 can be produced by electrolysis (EMD), chlorine oxidation (CMD) and Mn(II) ozone oxidation (OMD). OMD has a better electric discharge and ion exchange properties than the other two. But the above characteristic depends of temperature and acid concentration conditions. MnO_2 particles produced at high temperatures has high electric discharge properties while when it is produced a low temperatures and high acid concentration the ion exchange properties are improved. Other authors are researched the ozone decomposition by carbon in a slurry. The carbon MnO_2 material and its characterization were the research point in this investigation. Mn(II) solution was prepared and submitted in a glass reactor, where a ozone-oxygen gas flux was injected. Know amount of lignite carbon was introduced before gas mixture was injected. After experimental time was reached the slurry was filtered and carbon was submitted to SEM and adsorption experiments. The SEM images show manganese dioxide particles on carbon surface. MnO_2 is distributed on selective carbon areas. The MnO_2 amount deposited on the carbon surface depends of Ozone concentration, acid concentration, carbon amount and temperature. When intermediacy temperatures were used a high MnO_2 deposition was reaches similar results were got when high amount of carbon was used. The results shows two mechanism when the carbon-MnO_2 material was used as adsorbent, carbon adsorption and MnO_2 ion exchange.

Keywords:
Activated carbon; Adsorption; Ion exchange; Manganese dioxide

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Visible Light Driven Photocatalytic Degradation of Bisphenol A

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The oxidative degradation of a bisphenol A (BPA) was investigated by means of visible light photocatalysis in the presence of carbon doped TiO_2. Several commercial TiO_2 catalysts were screened and an anatase Kronos vlp-7000 sample exhibited considerable activity in terms of BPA degradation and TOC reduction. After 360 min of treatment time BPA degradation increased from 65% to 75% and to 89% for 0.25 g/L, 0.5 g/L and 1 g/L catalyst loadings respectively, while the corresponding values for BPA mineralization were 35%, 45% and 52%. The extent of photocatalytic degradation was found to increase with increasing TiO_2 concentration up to 1 g/L TiO_2, above which degradation remained practically constant, reaching a plateau.

Keywords:
Bisphenol A, Carbon Doped TiO_2, Visible light, Photocatalysis

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Degradation of Naphthalene using a Novel Liquid/Solid-Ozone (LSO) System

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- No abstract submitted. -
"Call for paper-abstract" (more than 200 words) on the stick.

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Carbonate and Chloride Scavenging in $H_2O_2/S_2O_8^{2-}/Fe^{2+}$ Oxidation of PCE

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Contamination of the subsurface by persistent organic contaminants remains a significant problem, even after decades of research on remediation technologies. In the past few years persulfate has shown promising results for in situ and on site oxidation of contaminants. However, scavenger ion is one of the most common factors limiting the oxidation efficiency. Especially chloride and (bi)carbonate have the potential to impact pathway, kinetics, and efficiency of oxidation reactions both as radical scavengers and as metal complexing agents. Furthermore, chloride and (bi)carbonate can also form radicals on their own and high concentrations of chloride have also been reported to result in formation of halogenated by-products. The present work is based on issues from the largest contaminated site in Denmark, Kærgård Plantation, where very high concentrations of chloride (up to 4,600 mg/l) and bicarbonate (up to 6,900 mg/l) have been observed in the groundwater. In order to evaluate the impact of these scavengers during future full scale remediation by chemical oxidation, different batch experiments have been performed. This poster will present the results from the laboratory work and discuss the influence of high concentrations of chloride and (bi)carbonate in oxidations systems with focus on persulfate activated by peroxide and iron.

Keywords:
Remediation; PCE; Persulfate; Hydrogen peroxide; Scavenging

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Modeling of contaminated soil treatment by ozone: simulation and experimental approach

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The present work is compound of two main sections. First section depicts a simple mathematical model describing the ozone mass transfer in solid phase (model soil) into a semi-batch reactor; ordinary differential equation set and the experimental procedure to obtain parameters involved are presented. Numerical solutions compared with experimental data obtained from glass spheres (d=0.5cm), baked sand and real soil ozonation are reported. In second section, the basic model is extended in order to consider the presence of one pollutant and its consequent degradation in the solid phase by ozone. Validation of the extended mathematical model is carry out by the experimental data obtained from an anthracene contaminated soil (baked sand).

Keywords:
Ozone, soil, mathematical modelling, simulation

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Enhanced bio-recalcitrant organics removal by combined adsorption and ozonation

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Removal of bio-recalcitrant and toxic compounds from wastewaters has been a major objective of industrial manufacturers for a few years. Due to the potential risk toward public health, regulations are becoming increasingly strict and classical treatments like biological treatments are not efficient. Other techniques such as incineration, oxidation or adsorption provide higher levels of removal but with a high energy and capital cost. A coupled process involving adsorption and oxidation is studied. Four adsorbents are tested and compared according to two objectives, their adsorption capacity and their capability to decompose ozone into powerful hydroxyl radicals. Two model compounds were chosen: 2,4-dichlorophenol and nitrobenzene. Experimental results allow comparing coupled process with results obtained during ozonation alone. Zeolite (Faujasite Y) gave disappointing results in term of both adsorption kinetics and ozone decomposition. On the contrary, activated carbons showed fast adsorptions and important capabilites to decompose ozone into radicals, almost in nitrobenzene experiments. S-23 activated carbon proved to be the most interesting adsorbent for better mechanical and chemical stabilities over time. Sequential adsorption/ ozonation experiments were conducted, showing a strong loss of adsorption efficiency after the first operation, but the positive point is that the adsorption capacity remains almost constant during further cycles.

Keywords:
Adsorption; activated carbon; bio-recalcitrant; coupled process; ozonation; zeolite

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Inhibition of Triplet-Induced Oxidation Reactions by Different Types of Dissolved Organic Matter

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The excited triplet states of dissolved organic matter (DOM) are important reactive species in sunlit natural waters responsible for the oxidation of a number of organic pollutants. However, DOM can also act as an inhibitor for triplet-induced oxidation of pollutants leading to a significant decrease of transformation rates.

Irradiation experiments with two model triplet-sensitizers, the aromatic ketones 4-carboxybenzophenone (CBBP) and 2-acetonaphthone (2-AN), were performed to investigate the inhibiting effects of different DOM standards and untreated water from lake Greifensee (GSW), a small Swiss lake, on the oxidation of pollutants.

Three main observations were made: (1) Inhibition varied among different pollutants. The strongest decrease in the oxidation rate could be observed with anilines (*N,N*-dimethylaniline, sulfamethoxazole) and a pyrimidine derivative (trimethoprim), whereas the phenylurea diuron showed little and the phenolic compound 4-methylphenol no decreased oxidation. (2) Inhibition increased with increasing DOM concentration and was dependent on the type of DOM. DOM standards generally showed a stronger effect on inhibition than GSW. (3) Although the one-electron reduction potentials of the excited triplet state of CBBP and 2-AN differ by 0.5 V, the inhibition of oxidation was of the same magnitude. This indicates that oxidizing excited triplet states of DOM, whose one-electron reduction potentials were estimated to lie between those of CBBP and 2-AN, should be subject to corresponding inhibition reactions.

Keywords:

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Poster
Fenton/Electro-Fenton
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Complexing agent and heavy metal removals from metal plating effluent by the combined electrocoagulation/Fenton process

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In the present study, the treatment of metal plating wastewater containing complexed metals originating from the nickel and zinc plating process by electrocoagulation (EC) using stainless steel electrodes was explored. In order to improve the organic matter removal efficiency, the effect of H_2O_2 addition to the electrocoagulation (combined EC/Fenton treatments) process was also investigated. A wide range of H_2O_2 concentrations varying between 15 and 230 mM was tested. All EC and EC/Fenton processes performed at an initial pH of 2.6 and at an optimized current density of 22 mA/cm^2 (applied current: 5 A). Although up to 30 mM H_2O_2 addition EC was improved in terms of organic matter removal, the highest COD and TOC removal efficiencies were already obtained for the combined EC/Fenton process in the presence of 20 mM H_2O_2. Nickel and zinc were completely removed for all runs tested in the present study.

Keywords:
Complexed metal and complexing agent removals; electrocoagulation/Fenton; electrocoagulation; metal removal; metal plating effluent; stainless steel electrodes

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A study on the Fenton Treatment Efficacy for the Purification of Different Kind of Wastewater

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The Fenton chemistry comprises both the classical Fenton reagent and its modification, so-called Fenton-like techniques, which have received great attention as a promising technology for wastewater treatment. In the present study real wastewater from different sources (leachate from oil shale semicoke landfill, pharmaceutical effluents from medical ointment production, municipal landfill leachate and wastewater originated from food-processing) were treated by means of Fenton/Fenton-like systems. The effectiveness of wastewater treatment was assessed by COD removal. Additionally, biodegradability improvement (BOD_7/COD) and acute toxicity reduction of investigated wastewater samples were observed. The application of the Fenton chemistry to wastewater samples with different origin resulted generally in 70 % or higher COD removal. Thus, the Fenton could be effectively applied both as a single treatment method and pre-treatment step to improve subsequent biodegradability of wastewater effluents.

Keywords:
The Fenton treatment, Fenton-like process, wastewater, COD removal, toxicity, biodegradability

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Catalytic Degradation of Picric Acid by Heterogeneous Fenton-based Processes

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The efficiency of goethite, magnetite and iron powder (Fe^0) to catalyse Fenton-based oxidation of picric acid (PA) in aqueous solution was studied. The effect of pH, hydrogen peroxide concentration, and catalyst type and dosage on treatment efficacy was investigated. Additionally, the adsorption of PA from aqueous solution by heterogeneous catalysts was examined. The results demonstrated negligible PA removal in H_2O_2/α-FeOOH and H_2O_2/Fe_3O_4 systems independently on process pH and hydrogen peroxide and catalyst dosage. Also, the PA adsorption effects of both iron oxides turned out insignificant for all studied pH values and catalyst dosages. H_2O_2/Fe^0 system proved efficient in PA degradation, but only at acidic conditions (pH=3). The results indicated, that due to rather fast leaching of ferrous ions from the iron powder surface, PA degradation was carried out mainly by the classic Fenton oxidation mechanism in the bulk solution. The adsorption of PA onto the iron powder surface may also contribute to the overall efficiency of PA degradation.

Keywords:
AOPs; chemical oxidation; iron oxides; zero valent iron; 2,4,6-trinitrophenol

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Electrochemically assisted Fenton method using Fe^{2+}/HOCl system

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The feasibility of an electrochemically assisted Fenton treatment using a Fenton-type reaction of ferrous iron and hypochlorous acid (HOCl) was discussed in this research. The reactor used was composed of an undivided single cell with a ruthenium dioxide-coated titanium anode and a stainless steel cathode, in which Fe^{2+} and HOCl were catalytically regenerated from ferric iron at the cathode and from chloride ion at the anode, respectively. Although the reactor functioned well, the degradation rate of 1,4-dioxane as a hydroxyl radical probe decreased at the current density more than 6.92 mA/cm^2. The decrease in degradation rate was inferred to be caused by the vain consumption of hydroxyl radicals by excess HOCl and the deposition of ferric hydroxide on the cathode at relatively high current density. The current efficiency of 1,4-dioxane removal kept more than 90% at the current density less than 6.92 mA/cm^2 and the iron concentration not less than 1.0 mmol/L. Consequently, this technique is thought to be applicable to the treatment of wastewater containing high concentration of chloride ion such as landfill leachate, scrubber wastewater from incineration plants, etc.

Keywords:
Advanced oxidation; electrochemical treatment; electro-Fenton; ferrous iron; hydroxyl radical; hypochlorous acid

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Treatment of TCE/PCE contaminated groundwater using Fenton-like oxidation activated with basic oxygen furnace slag

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The industrial solvents trichloroethylene (TCE) and tetrachloroethylene (PCE) are among the ubiquitous chlorinated-organic compounds found in groundwater contamination. The objective of this study was to evaluate the potential of applying basic oxygen furnace slag (BOF slag) as the catalyst to enhance the Fenton-like oxidation to remediate TCE/PCE contaminated groundwater. Results indicate that TCE/PCE oxidation via the Fenton-like process can be enhanced with the addition of BOF slag. Results from the X-ray powder diffraction analysis reveal that the major iron type of BOF slag/quartz sand media was iron oxides (α-Fe_2O_3). Approximately 81 and 90% of TCE and PCE removal were observed (with initial concentration of approximately 5 mg L^{-1}), respectively, with the addition of 1,000 mg L^{-1} of H_2O_2 and 10 g L^{-1} of BOF slag. Results indicate that the BOF slag can be used to supply catalysts continuously, and it can be installed in a permeable barrier system to enhance the Fenton-like process in situ.

Keywords:
Fenton-like; basic oxygen furnace slag; hydrogen peroxide; groundwater contamination; chlorinated-organic compounds

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Degradation of Organic Dye Using Zero-Valent Iron Prepared from By-product of Pickling Line

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In this study, zero valent iron (ZVI) was produced using iron oxide that is a by-product of a pickling line at a steel work. The reaction activity of the produced ZVI was evaluated through a series of decomposition experiments of Orange II aqueous solution. The size of ZVI particles increased with reduction temperature due to coalescence. Correspondingly, the specific surface area of ZVI decreased with increasing reduction temperature. The decomposition efficiency of synthesized ZVI particles was higher at a lower pH. In particular, no significant decomposition reaction was observed at pH of 4 and higher. The rate of the ZVI-assisted decomposition of Orange II was increased by addition of H_2O_2 at pH of 3, whereas it was reduced by addition of H_2O_2 at a higher pH of 6. Nevertheless, simultaneous use of ZVI, UV and H_2O_2 led to a considerable increase in the decomposition rate even at a high pH condition (pH = 6).

Keywords:
Zero valent iron; azo dye; pH; UV; H_2O_2

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Degradation of ClO_4^- by Zero-Valent Iron in the Combined Reaction with UV/Sonication

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Perchlorate (ClO_4^-), the oxidized form of chloride, is rarely degraded by conventional biological treatments. In this study, the degradation of ClO_4^- by the separate and combined reactions using zero-valent iron (Fe^0), sonication, and UV, respectively. The degradation of ClO_4^- was less than 10% by Fe^0-only, UV-only, and sonication-only reactions even after 20 hr, however, the degradation efficiency in combined reaction of Fe^0 (0.5 g L^{-1}) with sonication, and Fe^0 (0.5 g L^{-1}) with UV-C increased to 21% and 79% at the same time, respectively. In case of the combined reaction with Fe^0 and sonication, ClO_4^- removal was only 21% in Fe^0 (5 g L^{-1})-only condition within 20 h, however, enhanced to 94% by Fe^0 (10 g L^{-1}) with UV-C at the same time. The oxidation of Fe^0 to Fe^{2+} increased to 22% and 16% by the addition of UV and sonication compared to only 0.2 % in the Fe^0-only reaction. From the result, the combined reaction with Fe^0 and UV-C reaction can be the most prominent process to degrade ClO_4^- among the selected reactions; the the mechanism of ClO_4^- degradation is achieved by the reduction with free electron produced by the oxidation of Fe^0. The oxidation efficiency of Fe^0 increased with sonication and especially with UV-C.

Keywords:
Perchlorate; UV-C; Fe^0; Fe^{2+}, sonication

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Oxidation of cyanide by Fenton-like process using magnetite nano particles in the treatment of plating wastewater

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A Fenton-like reaction with a magnetite nano particle (MNP) catalyst is developed for the degradation of cyanide. The goals of this study are (1) to synthesize MNP using co-precipitation method, (2) to evaluate degradation rate of cyanide using Fenton-like reaction, and (3) to test the reusability of MNP. X-ray diffraction (XRD), high resolution transmission electron microscopy (HR-TEM), X-ray photoelectron spectra (XPS), and BET analysis were used to characterize MNP. The results show that the diameter of magnetite nano particle (MNP) was approximately 6 nm and surface area of MNP was much larger than commercial magnetite, approximately twenty-two fold. The removal efficiency of cyanide was demonstrated as free cyanide and total cyanide were degraded nearly 100% (amount of MNP: 0.9 – 3.6g, and $[H_2O_2] = 882$mM) within 2 h. The fastest degradation rate of cyanide, k, was calculated at 3.57×10^{-2} min^{-1} in present study when 0.9 g of MNP and 882 mM of hydrogen peroxide was used. The reusability test of MNP demonstrated the catalytic ability of magnetite nano particle (MNP) to degrade cyanide.

Keywords:
magnetite nano particle (MNP); Fenton-like reaction; cyanide; total cyanide; degradation rate

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The Heterogeneous Photo-Fenton Reaction Using Goethite as Catalyst

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In the present work the degradation of 2-Chlorophenol (2-CP) used as model compound, applying the Heterogeneous Photo-Fenton reaction was studied. Small particles of Goethite or Iron oxyhydroxide were used as a source of iron. The influence of catalyst loading, radiation intensity and the molar ratio between hydrogen peroxide and contaminant were examined. Improvement by illumination is highly significant. During the progress of 2-CP degradation, the reaction shows an unusual acceleration. This autocatalytic comportment, with stronger tendencies at higher temperatures, implies a completely different behaviour than the one typically expected. The autocatalytic performance is successfully explained by the joint action of two factors: (i) the evolution of the available iron in the homogeneous phase during the course of the reaction and (ii) the autocatalytic contribution of some of the reaction intermediates in the iron cycle. The small iron concentration leaching into the solution is produced by two typical liquid medium - solid goethite surface dissolution processes. A reaction mechanism has been proposed and, in a first stage, parameters have been obtained for the dark reaction. In a second step, the complete data for the irradiated operation were obtained.

Keywords:
Fenton; heterogeneous; radiation enhancement; goethite; 2-chlorophenol

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Sulfamethoxazole Pre-Treatment by AOPs: Comparison of Biorecalcitrance in Batch Tests

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This work studies the degradation of a 200 ppm Sulfamethoxazole antibiotic solution using two advanced oxidation processes, ozonation and photo-Fenton, as well as the biodegradation of the resulting compounds in Biological Batch Reactors. In one hand, photo-Fenton reactions using different amounts of H_2O_2 were conducted, while Fe^{2+} concentration, pH and UV irradiation were kept constant. On the other hand, various ozonation reactions were performed using a constant ozone dosage but varying the reaction time. A total of 9 Biological Batch Reactors, five using photo-Fenton pre-treated effluent and other four pre-oxidized with ozonation as the sole carbon source were studied . The information collected from the Batch Reactors studies can be used in order to estimate the biodegradability and biorecalcitrance of the pre-treated effluents, in terms of antibiotic and TOC abatement, which can be very useful as a tool to obtain relevant information at the time to integrate Advanced Oxidation Processes with biological treatments, among other parameters.

Keywords:
Ozone, photo-Fenton, antibiotic, wastewater, biodegradability

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SUPPORT SCREENING FOR HETEROGENEOUS FENTON IN THE DEGRADATION OF MONO AZO DYE CONTAMINATED WASTEWATERS

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In this work, degradation of acid orange II, dye present in textile industry wastewater, by heterogeneous Fenton process (HFP) was performed. In order to select an adequate support heterogeneous Fenton catalysts were prepared using several materials as carbon nanotubes, carbon nanofibers, activated carbon, hidrotalcite, mesoporous silica (MCM-41), silica, silica xerogel, sepiolite and zeolite USY, that were tested in degradation of acid orange II as model compound. Color, total organic carbon, chemical oxygen demand removal and toxicity were studied in the process. The best catalyst was iron (II) supported on sepiolite. In a second stage on the study, the best performing catalyst material was used to investigate the influence of pH, carbonate ions presence and reuse of catalyst on AOII degradation. Also, a real wastewater was successfully treated with this catalyst on the select operation conditions.

Keywords:
Dyes; Fenton’s reagent; heterogeneous catalyst; textile wastewater

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Experimental design applied to photo-Fenton treatment of highly methomyl-concentrated polluted water

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This work is focused on the study of the suitability of photo-Fenton process as an in-situ pretreatment for water highly contaminated with a commercial pesticide coming from a separation stage in Advanced Greenhouses devices. The use of a commercial product will state the possible interferences in the process by the inert ingredients of the pesticide. Initial concentrations of reagents, but also methomyl initial concentration, were evaluated according to a central composite experimental design. The objective prosecuted was to know the incidence of these three variables on the performance of the reaction, and to obtain an optimum range of concentrations to attain highest methomyl depletion rate. Biodegradability assessments were also performed to test the pertinence of a biological treatment afterwards. As a conjunction of the conclusions obtained from pesticide depletion and biodegradability assays, a triad of optimal operation conditions could be determined. $[Met.]_0$=50 mg·L^{-1}, $[H_2O_2]_0$=260 mg·L^{-1} and $[Fe^{2+}]_0$=50 mg·L^{-1} in order to optimize both parameters.

Keywords:
Advanced Oxidation Processes, water treatment, photo-Fenton, pesticide, biodegradability, photocatalytic process, central composite

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Effect of initial Fe oxidation state on Imidacloprid removal using photo-Fenton process

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This paper presents experimental results on the effect of initial Fe oxidation state on Imidacloprid removal by photo Fenton process. Hydroxyl radicals generated by the reaction between ferrous ions and hydrogen peroxide are able to oxidise toxic pesticides, such as Imidacloprid, a widely used and poorly biodegradable insecticide. Experimental results show that the rate of Imidacloprid oxidation depends on the oxidation state of initial iron. Indeed, when Fe(II) was initially present, two distinctive kinetic regimens were observed. The first stage featured a very fast reaction leading to an almost instantaneous decrease in initial Imidacloprid concentration. The abrupt reduction in pesticide concentration was directly proportional to the initial Fe(II) concentration and was attributed to a burst of free hydroxyl radical generated by rapid Fe(II) oxidation to Fe(III). The second phase presented a slower Imidacloprid oxidation process that could be adequately described by a pseudo first order kinetics. Finally, when Fe(III) was initially present, Imidacloprid degradation followed a monotonic pseudo first order decay. The Fe(II) concentration remained fairly constant throughout the process, regardless of the initial Fe oxidation state, and most iron will be as ferric species, since the rate of Fe(II) reaction with hydrogen peroxide is much faster than Fe(III) photo reduction. Using Fe(II) as an initial iron source reduces the time required to attain a final removal target.

Keywords:
Advanced oxidation process, Photo-Fenton, Iron species, Imidacloprid, Kinetics

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Innovative water treatment system coupled with energy production using photo-Fenton reaction

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The treatment of colored effluent coupled with energy production using a modified photo-Fenton process has been examined. Fe and carbon plates were employed as an anode and cathode, respectively. In acidic solution, Fe plates would corrode, which leads to elute ferrous ion from Fe plates into the solution and to yield hydrogen gas at the cathode and to generate an electric energy. The eluted ferrous ion could be used for the photo-Fenton reaction. As a result, decolorization of colored effluent and production of electricity and hydrogen could be carried out simultaneously and effectively. It was found that the Orange II concentration in the colored effluent flow decreased up to 84.2% of inlet concentration at 0.8 of relative position in the liquid flow path of continuous photoreactor. In our proposed system, the energy production, such as an electric power and a hydrogen gas, can be generated at the same time as the decolorization of colored effluent. The produced electric power was 16.5 Wh kg^{-1}-Fe$_{reacted}$. The produced hydrogen gas was estimated 13 g-H_2 kg^{-1}-Fe$_{reacted}$.

Keywords:
colored effluent, decolorization, energy production, hydrogen gas, photo-Fenton reaction

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Study on Absorbance Transformation and Kinetics of Decomposition of H_2O_2 in Fenton-like Process

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The main factors affecting the decomposition of H_2O_2 in Fenton-like process were studied. H_2O_2 decomposition in the Fenton-like system obeys the pesudo-first-order reaction kinetics and the optimum pH was 2.8-3.0. The pseudo-first-order rate constant of H_2O_2 decomposition increased with increasing initial ferric concentration, and affected with the increase of initial H_2O_2 concentration. The equation was acquired for the determination of the pseudo-first-order rate constant of H_2O_2 decomposition in Fenton-like systems.

The absorbance of H_2O_2/Fe^{3+} solution in 340 ~ 400 nm increased with the decrease of initial H_2O_2 concentration, and increased with reaction time, indicating that the change of H_2O_2 concentrations might lead to the change of hydrolyzed Fe(III) species.

Keywords:
Fenton-like process, hydrogen peroxide, ferric ions, absorbance, oxidation

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Oxidative and physical removal of COD from landfill leachate by electro-Fenton method

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The effect of operating conditions such as initial pH, electrical current, the distance between the electrodes and the feeding mode of hydrogen peroxide on the treatment of landfill leachate by process was investigated. COD removal by oxidation as well as by coagulation was quantitatively studied. The results showed that COD removal by oxidation is dominant compared at higher hydrogen peroxide to ferrous mole ratio. COD removal by coagulation increased with initial pH, but changed little at fixed initial pH and ferrous ion dosage. COD removal by oxidation increased with the decrease of initial pH. There existed an optimal electrical current or the distance between the electrodes to reach the highest COD removal by oxidation. The stepwise or continuous addition of hydrogen peroxide was more effective than the addition of hydrogen peroxide in a single step. The curves of overall COD removal at 120 min under various conditions were similar to those of COD removal by oxidation.

Keywords:
Landfill leachate; electro-Fenton; COD removal; oxidation; coagulation

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Fenton Pretreatment in the Catalytic Wet Oxidation of Phenol

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Catalytic Wet Oxidation (CWO) of 1000 mg/L of phenol (PhOH) aqueous solutions has been carried out using a commercial activated carbon as catalyst, placed in a continuous three phase reactor at 16 bar, and temperature was changed in the interval 127-160° C. Pure oxygen was fed as gaseous phase. Pollutant conversion, mineralization, intermediate distribution and toxicity were measured at the reactor exit. Fenton Reagent (FR) has been applied to the same phenolic aqueous samples using different amounts of H_2O_2 (between 10 and 100% of the stoichiometric dose) and 10 mg/L of Fe^{2+}, in a batch way at 50° C. An integrated process has been proposed that combines FR as pretreatment of the CWO process. In the FR step, 10% of H_2O_2, 10 mg/L of Fe^{2+} and reaction times lower than 40 min are used. Efluent from FR step is fed to the CWO reactor at 127° C. High mineralization (80-90%) and total detoxification of the effluent was obtained at the reactor exit using W/Q_L values lower than 10 g.min/mL. Therefore, the FR pretreatment enhances remarkably the efficiency of the CWO at moderate temperature conditions.

Keywords:
Activated Carbon, Catalytic Wet Oxidation, Fenton Reagent, Phenol, Toxicity

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Remediation using *In situ* oxidation: Soil modification by the Fenton Reagent

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The choice of appropriate technologies for soil remediation rarely takes into account the impact on soil quality. The application of hydrogen peroxide as Fenton process oxidant can be a threat to the soil. Therefore, although the pollutant is degraded the risk of hydrogen peroxide could be significant. The application of hydrogen peroxide must be evaluated beforehand taking into account the effects of its application.

The aim of the work is to investigate the effects in soil of hydrogen peroxide reagent. The soil organic matter (SOM) was found to consume and compete for the oxidant. The content and structure of the SOM after hydrogen peroxide oxidation could be changed and it is important to evaluate this aspect.

The influence of the oxidant dosage ($[H_2O_2]_o$ = 20,000 mg L^{-1} and soil weight to liquid phase volume ratio = 0.5 g mL^{-1}) on the change of SOM was investigated using two loamy sand soil samples with different SOM content (S1=14%, S2=8,4%) in a slurry system at 20 °C. Carbon-13 nuclear magnetic resonance spectroscopy (^{13}C-NMR) was used to obtain the SOM composition. The ^{13}C NMR spectra obtained from S1 and S2 showed a relative increase of alkyl C and the relative proportions of O-alkyl C, aromatic C and carboxyl C decreased.

Keywords:
In situ chemical oxidation, Hydrogen peroxide, Organic Matter, Soil

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Modelling and Experimental Verification of a Solar Reactor for the Photo-Fenton Treatment

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In the present work, a novel design of a solar reactor is presented. This pilot plant scale reactor uses the UV-Visible and Near-Infrared solar radiation to promote the photo-Fenton treatment. A theoretical study and experimental verification were performed using formic acid as a model pollutant. The radiative transfer, thermal energy and mass balances equations were solved to compute the formic acid (F) and hydrogen peroxide (P) concentrations as a function of time. The spectral and broadband solar radiation incident on the reactor window was calculated from a computational code: the SMARTS2 program. Statistical estimators have been used to measure the departure of theoretical model from experimental data. A good agreement for formic acid and hydrogen peroxide concentrations, temperature and total and UV broadband solar radiation was obtained. The normalized root mean square errors (NRMSE) of the model for predicted variables were lower than 11%.

Keywords:
Photo-Fenton treatment; pilot plant scale reactor; solar reactor; UV solar radiation

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The role of pressure and temperature in phenol oxidation by Fenton Reagent

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The role of pressure (between 1 and 6 bar) and temperature (between 25-90ºC) in phenol oxidation by Fenton reagent has been evaluated. Working at an initial pH equal to 3, a phenol starting concentration of 100 mg/L, Fe^{2+} concentration of 10 mg/L and a H_2O_2 dose of 500 mg/L (corresponding to the stoichiometric amount to oxidize phenol up to CO_2 and H_2O), TOC conversion increases at increasing temperature, as a consequence of the higher $OH\cdot$ production, whereas pressure did not show any influence upon the evolution of the process. Nevertheless, neither pressure nor temperature affected to the H_2O_2 stability. A kinetic model, where TOC was structured into three types depending on their degradability, describes fairly well the TOC evolution within the range investigated. Values around 40 kJ/mol were obtained for the activation energy.

Keywords:
Fenton oxidation, phenol, kinetics

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PC 231

Use of Fenton for the remediation of petroleum hydrocarbon contaminated site

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- No abstract submitted. -
"Call for paper-abstract" (more than 200 words) on the stick.

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Catalytic in-situ generation of hydrogen peroxide by Pd-supported catalysts and its application in the removal of pollutants by means of Fenton Process

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A catalytic system for the generation of H_2O_2 from formic acid and oxygen at ambient conditions has been developed. Pd-supported catalysts (Pd/C, Pd/TiO_2 and $Pd/\gamma\text{-}Al_2O_3$) have been tested, showing that for bulk purposes (direct H_2O_2 generation) $Pd/\gamma\text{-}Al_2O_3$ is the best option while for in-situ applications Pd/TiO_2 seems to be preferable. However, when these catalysts were tested in the in-situ H_2O_2 generation for the oxidation of phenol by means of the Fenton process (in presence of ferrous ion), Pd/TiO_2 did not demonstrate the expected results, whereas Pd/Al_2O_3 showed to be an efficient catalyst. Therefore, Pd/Al_2O_3 is offered as a good catalyst for Fenton's reactions with in-situ generated H_2O_2. In order to optimize the operating cost of the process, different initial concentrations of formic acid have been tested with $Pd5\%/Al_2O_3$, and it has been seen that lowering the initial amount of formic acid favours the efficiency of the process. This catalytic system has been compared with conventional Fenton process (with commercial H_2O_2), batch- and continuous-wise, showing that the in-situ process is more efficient in the mineralization (60% vs. 45%) and the removal of toxic intermediates, although conventional process is faster. Fully heterogenization of the catalytic system incorporating Fe achieved similar results.

Keywords:
Fenton's Process, formic acid, heterogeneous catalysts, in-situ H_2O_2 generation, phenol degradation

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Using RuO_2 anode for chlorine dioxide production in an un-divided electrochemical cell

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Chlorine dioxide is a well known powerful disinfectant. Although there are several chemical and electrochemical methods developed for on-line chlorine dioxide generation, the details are mostly confined as patents. We studied in this work the electrochemical generation of dissolved chlorine dioxide gas from an un-buffered solution of sodium chlorite and sodium chloride mixture in an *un-divided electrochemical cell* set-up with RuO_2-coated-Ti anode and Pt-coated-Ti cathode under constant current mode. Various process parameters including feed flow rate (10 to 150 ml/min), feed solution pH (2.3 to 9.4), concentration of sodium chloride (0 to 170 mM), concentration of sodium chlorite (0 to 7.7 mM), and the applied current (100 to 1200 mA) were optimized. Experiments were conducted by performing single pass experiments, with no circulation. The current efficiency and the power consumption were calculated for the optimized conditions, and compared with IrO_2 electrode of our previous investigation.

Keywords:
Chlorine dioxide; electrochemical generation; optimization of process parameters; un-buffered solution; un-divided electrochemical cel

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Industrial *E-AOP* application using boron doped diamond electrodes

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In the *E-AOP* treatment using boron doped diamonds, an average COD removal rate of 97% was obtained when treating a large variety of wastewater. The electrical power consumption for treatment was 30kWh/kg-COD. A field test using *E-AOP* pilot facility was conducted during 6 months and COD removal rate comparable with wastewater incineration was obtained with 50% less CO_2 emission.

Keywords:
COD removal, diamond electrodes; wastewater treatment

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Photo-assisted electrochemical degradation of commercial solutions of the herbicide Atrazine

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This paper presents the study of the degradation of the pesticide atrazine employing photo-assisted electrochemical methods at a dimensionally stable anode (DSA$^{\circledR}$) of nominal composition $Ti/Ru_{0.3}Ti_{0.7}O_2$ in a prototype reactor. The effects of current density, electrolyte flow-rate, as well the use of different atrazine concentrations are reported. The results indicate that the energy consumption is substantially reduced for the combined photochemical and electrochemical techniques when compared to the isolated techniques. It is observed that complete atrazine removal is achieved at low current densities when the combined method is employed, thus reducing the energy required to operate the electrochemical system. The results also include the investigation of the phytotoxicity of the treated solutions.

Keywords:
Atrazine, photo-assisted degradation, electrochemical degradation, phytotoxicity

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Photo-assisted electrochemical degradation of real textile wastewater

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In the present study, photo-assisted electrochemical degradation of real textile wastewater was performed. Constant current degradation ($40\ mA\ cm^{-2}$) was carried out in a combined electro/ photochemical flow-cell using a $Ti/Ru_{0.3}Ti_{0.7}O_2$ DSA$^{\circledR}$ type electrode. Additionally, the effect of pH, type, and concentration of supporting electrolyte (Na_2SO_4 and NaCl) was investigated. Chemical oxygen demand (COD) and colour removal were used to follow the degradation, with 72% colour and up to 59% COD removal in 120 min under the optimum operating conditions. Studies of the phytotoxicity of the wastewater before and after photo-assisted degradation assays are also iscussed.

Keywords:
Electrochemical degradation; photo-assisted degradation; phytotoxicity; textile wastewater

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Electro-Oxidation

PC 130

Metoprolol behaviour in drinking water electrolysis using mixed oxide and boron doped diamond anodes

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Metoprolol tartrate was electrolysed at 20°C in aqueous systems using mixed oxide and boron doped diamond anodes. Fast depletion was observed when chloride ions were components of the waters. Additional ions such as sulphate and nitrate decreased the oxidation rate. Higher chloride concentration and current densities up to 200 A m^{-2} accelerated metoprolol destruction.
4-(2-methoxyethyle)-phenol and 3-chloro-4-hydroxyphenyle acidic acid were identified as reaction by-products.

Keywords:
BDD; chlorination; disinfection by-products; drinking water electrolysis; mixed oxide electrode; metoprolol; pharmaceutical residues

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Poster

Electro-Oxidation

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Anodic electrochemical oxidation of azo dye on boron doped diamond electrode

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Electrochemical oxidation of synthetic waste water containing Cibacron brillant yellow on boron doped diamond electrode (BDD) was studied using bulk electrolysis. The effect of different parameters like current density, pH, salts contents like, Cl-, , have been investigated. Their inhibitor effect against the performance of process is so discussed in this paper. It was found that strongly acidic pH improved the degradation rate, a low current density applied is necessary to remove completely colour for concentrated dye solution. Sulphates ions didn't have a significantly inhibition affect but chlorides ions accelerated largely the total discoloration as the thanks of the formation of active chlorine.

Keywords:
azo dye, BDD electrode, electrochemical treatment, electrolysis

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Poster

Electro-Oxidation

PC 214

Electrochemical oxidation of landfill leachates at pilot scale. Evaluation of energy needs

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Conductive diamond electrochemical oxidation (CDEO) of landfill leachate was conducted at a pilot plant with a total anode area of 1.05 m^2. The landfill leachate had an average COD, NH_4^+ and NO_3^- concentration of 860 mgL^{-1}, 780 mgL^{-1} and 1110 mgL^{-1}, respectively. Current densities in the range 300 Am^{-2} to 1200 Am^{-2} were applied and the technical and economic feasibility of the process was evaluated in terms of treatment time and energy costs required to reach the disposal limits to natural watercourses established by legislation. The concentration of COD decreased below the disposal limit (160 mgL^{-1}) for all the applied current densities, but the lowest ammonia concentration reached was 30 mgL^{-1}. Nitrate ions were not eliminated and partial oxidation of N-NH_4^+ to N-NO_3^- occurred. The formation of chlorination by-products appeared to be low as the maximum total THM concentration detected was 432 µg/L. Finally, the specific energy consumption needed to reach the disposal limits for COD and NH_4^+ was estimated at 93 kWh/m^3.

Keywords:
Electrochemical oxidation; landfill leachate; specific energy consumption; trihalomethanes

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Electro-Oxidation

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Treatment of Tannery Effluents by Photoelectrooxidation Process

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The treatment of skins and leathers generates effluents containing inorganic and organic compounds. The conventional treatment of these effluents is not always efficient and encounters great difficulties in attaining the discharge limits established by legislation, which are becoming increasingly restrictive due to the urgency of environmental protection. The search for new technologies for tannery effluent treatment is a great challenge for the sector. In this article, the possibility of tannery effluent treatment through a new concept of technology, also known as advanced oxidation process (AOP), using the process of photoelectrooxidation (PEO) for the degradation of organic matter was investigated. The experiments were carried out in a photolytic reactor, where the anode and cathode were dimensionally stable DSA ($70TiO_2/30RuO_2$ and Ti/TiO_2, respectively). The sources of ultraviolet radiation were medium/high-pressure mercury-vapor lamps of 250 and 400 W power. A current density of 42 $mA.cm^{-2}$ was applied. The industrial effluent for the study was collected after the final stages of conventional treatment. The results show the possibility of using PEO as a polishing treatment. For a 2-hour treatment, a reduction greater than 80% of total organic carbon (TOC) was observed.

Keywords:
advanced oxidation process, dimensionally stable anodes, photoelectrooxidation, tannery effluent

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Poster

Electro-Oxidation

PC 245

Anodic Oxidation of Olive Mill Wastewaters on BDD electrodes

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The electrochemical treatment of olive oil mill wastewaters over boron-doped diamond electrodes was investigated. The effect of operating conditions, such as initial organic loading (1000, 5000 mg/L), treatment time (1, 4 h), current intensity (10, 20 A), initial pH (4, 6) and the use of 500 mg/L H_2O_2 as an additional oxidant, on treatment efficiency was assessed implementing a factorial experimental design. Of the five parameters tested, the first two had a considerable effect on COD removal, while the other three were statistically insignificant. The analysis was repeated at more intense conditions, i.e. initial COD up to 10000 mg/L and reaction time up to 7 h; at this level, the effect of treatment time was far more important than the influent COD concentration. In order to further investigate electrochemical oxidation of OMW, undiluted effluent (COD_0=40000 mg/L) was treated at 20 A for 15 h. This resulted in 19 and 36 % for COD and TPh removal respectively with an energy consumption efficiency of 96 kWh/(kg COD_{rem}).

Keywords:
Boron-doped diamond; electrolysis; factorial design; olive oil mill wastewater

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Electro-Oxidation

PC 247

Photoelectrocatalytic activity of prepared TiO_2/Ti electrodes by anodization

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TiO_2 electrodes are made by anodization of Ti at different applied voltage (Eimp). TiO_2/Ti electrode obtained at 140V, presents high photoelechtrochemical properties. Application of 1 to 2V potential increases the photocurrent which will lead to better methanol (pollutant type) oxidation. Obtained photocurrent increases withmethanol concentration increase and at alkaline pH.

Keywords:
TiO_2, photocatalysis, methanol, electrochemistry

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Electrochemical degradation of PAH compounds in process water: A kinetic study on model solutions and a proof of concept study on process water from harbour sediment purification

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The present study has investigated the possibility to apply electrochemical oxidation in treatment of polycyclic aromatic hydrocarbons (PAHs) in water. The reaction kinetics of naphthalene, fluoranthene, and pyrene oxidation have been studied in a batch recirculation experimental setup applying a commercial one-compartment cell of tubular design with Ti/Pt_{90}-Ir_{10} anode, and the rate has been evaluated upon variations in current density, electrolyte composition and concentration. All three PAHs were degraded by direct anodic oxidation in Na_2SO_4, and the removal rates where significantly enhanced by a factor of two to six in NaCl due to contribution from the indirect hypochlorite oxidation. Second order reaction kinetics was demonstrated for the degradation of naphthalene in all electrolytes whereas fluoranthene and pyrene followed first order kinetics. Decreased current density from 200 to 50 $mAcm^{-2}$ decreased the removal rates, but at the lowest current densities investigated (15 and 25 $mAcm^{-2}$) both the removal rates and the current efficiencies of the PAH oxidation were significantly enhanced. This observation is believed to be due to the suppression of the water oxidation side reaction at the low applied voltages. A proof of concept study demonstrated the applicability of the electrochemical oxidation technique for larger scale use.

Keywords:
Electrochemical oxidation; Polycyclic Aromatic Hydrocarbons (PAHs); Water treatment

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Poster
Catalysts
PC 49

CWPO of 4-CPhOH and industrial wastewater with Al-Fe pillared clays

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Catalysts based on pillared clays with Al-Fe have been synthesized from a commercial bentonite and tested for catalytic wet peroxide oxidation (CWPO) of 4-Chlorophenol (4-CPhOH) and industrial wastewaters. The effect of the synthesis procedure, the iron load and reaction temperature on the catalytic activity was studied using 4-CPhOH as target compound. A lower temperature in the preparation of the pillaring solution, as well as a higher Fe load, gave rise to a higher catalytic activity, but also a higher leaching of the active phase. The best catalyst, in terms of catalytic activity, was also tested for treating cosmetic wastewater by CWPO. Experiments were carried out at 90ºC and atmospheric pressure and the influence of Fe load, catalyst concentration and H_2O_2/COD ratio (between 0.5 and 2 times the stoichiometric ratio) were analyzed. Higher values of these parameters favour COD reduction. The Fe leaching in all cases was lower than 1.2 mg/L, indicating that these catalysts have a high stability under these experimental conditions.

Keywords:
Al-Fe; CWPO; 4-CPhOH; industrial wastewater; pillared clays

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Catalysts

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Preparation of Visible Light Sensitive S-doped TiO_2 Nanotube Site-selectively Loaded With Co-catalysts

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In order to improve photocatalytic activity and visible light sensitivity of the surface of TiO_2 photocatalysts, reduction site and oxidation site on S-doped TiO_2 nanotube should be separated resulting in improving charge separation.

Keywords:
Co-catalysts, Nanotube, S-doped TiO_2, separation of reaction site, site-selectively, Visible light sensitive TiO_2

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Catalysts

PC 75

Enhancement of Detoxification in CWO processes by Using H_2O_2 as Promoter

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The use of hydrogen peroxide to initiate the catalytic wet oxidation of phenolic wastewater over activated carbon catalysts results in a significant decrease in the toxicity of the effluent and in its faster depletion. The detoxification is even higher than that obtained when a co-catalyst like Fe is incorporated on the carbon in a conventional wet oxidation process. Hydrogen peroxide acts as a source of hydroxyl and hydroperoxy radicals which come from its thermal decomposition and its reaction with oxygen, respectively. These radicals initiate the oxidation reaction increasing both phenol and TOC initial rates. Consequently, selectivity of the activated carbon changes and therefore, the oxidation route. With hydrogen peroxide, phenol is only hydroxylated, the carboxylation route is totally inhibited. *p*-Benzoquinone, produced in the hydroxylation route and the only intermediate species responsible of the toxicity, rapidly breaks to yield the low molecular weight acids and CO_2. *p*-Benzoquinone is then present in lower concentrations and is faster oxidized which explains the enhanced detoxification of the treated effluent. Carbon surface properties (textural properties and oxygen surface groups) are additionally modified by the presence of hydrogen peroxide but still the carbon stability is satisfactory.

Keywords:
Activated carbon; hydrogen peroxide; microtox; phenol; wastewater treatment; wet oxidation

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Selectivity of Hydrogen Peroxide Decomposition towards Hydroxyl Radicals in the CWPO over Fe/AC Catalysts

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Two Fe/AC catalysts prepared with different iron precursors (iron nitrate and iron pentacarbonyl) and the same AC support have been tested in H_2O_2 decomposition in presence and absence of methanol, a known strong scavenger of hydroxyl radicals, to investigate the selectivity towards $^{\bullet}$OH formation in this reaction and their behavior in the CWPO of phenol. The catalyst prepared with iron nitrate, with the most oxidized surface and the highest Fe surface content, seems to favor a higher selectivity towards $^{\bullet}$OH formation in CWPO allowing for complete phenol conversion and a significant TOC removal, with the highest mineralization degree at 50º C and atmospheric pressure. The influence of the initial H_2O_2 concentration on phenol oxidation with this catalyst was also studied. A theoretical stoichiometric amount of H_2O_2 for complete oxidation of phenol was chosen as the best starting concentration since auto-scavenging reactions can be minimized and it is sufficient for oxidizing phenol and the aromatic intermediates.

Keywords:
H_2O_2 decomposition; hydroxyl radical; Fe/AC catalysts; CWPO

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PC 154

A novel manganese-catalyst based advanced oxidation process

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Mn-tmtacn (tmtacn: 1,4,7-trimethyl-1,4,7-triazacyclononane) based complexes activate hydrogen peroxide and can thus be used for colour removal in waste water. Similarly, this manganese-based catalyst can be used for COD removal in various waste streams. Moreover, it is shown that the combination of the Mn-tmtacn catalyst in combination with other AOP's (Advanced Oxidation Processes), such as an UV-reactor or boron-doped diamond electrode, affords a large acceleration in rate of degradation of the waste material. Therefore, a much higher throughput can be obtained for these advanced oxidation processes by the addition of this Mn-tmtacn catalyst.

Keywords:
Waste water treatment; advanced oxidation process; hydrogen peroxide; manganese; catalyst

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PC 169

Heterogeneous Catalytic Ozonation of Cationic Dyes using Volcanic Sand

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This work aims to present experimental results on the treatment of methylene blue contaminated waters using heterogeneous catalytic ozonation promoted by volcanic sand. The effect of pH (2-8), and the presence of radical scavengers (acetate ions) in homogeneous and heterogeneous systems are evaluated at laboratory scale. Heterogeneous catalytic ozonation using volcanic sand increases methylene blue removal rate. In the presence of free radical scavengers, only a 37% reduction on methylene blue removal rate is observed in the heterogeneous system, as compared with 70% when homogeneous ozonation is used. The results obtained here indicate the importance of chemical surface properties on methylene blue oxidation reactions, suggesting that acid surface sites of volcanic sand play a key role on the reaction mechanism.

Keywords:
dvanced oxidation processes; cationic dyes; catalytic ozonation; methylene blue; ozone; volcanic sand

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The decomposition of humic substances by ozone and synthetic magnetic catalyst

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This study applies the synthetic magnetic perfluorooctylalumina (MPFOA) as catalyst to decompose humic acids by ozonation and recycle the catalyst MPFOA by magnet. The color removal is above 95 % for all tests after 30 min catalystic oxidation. The humic acids decomposition rate is obtained based upon the first order kinetic equation, while the addition of MPFOA provides 1.6 and 6.3 times improvement under pH 2 and pH 7 cases. After 5 times of recycle catalyst tests, the functional groups of the MPFOA still kept the same.

Keywords:
FTIR, Hydroxyl radical, Humic acids, magnetic perfluorooctylalumina (MPFOA), oxidation

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Catalytic wet hydrogen peroxide oxidation of a petrochemical wastewater

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Continuous Catalytic Wet Hydrogen Peroxide Oxidation (CWHPO) for the treatment of a petrochemical industry wastewater has been studied on a pilot plant scale process. The installation, based on a catalytic fixed bed reactor (FBR) coupled with a stirred tank reactor (STR), shows an interesting alternative for the intensification of a continuous CWHPO treatment. Agglomerated SBA-15 silica-supported iron oxide (Fe_2O_3/SBA-15) was used as Fenton-like catalyst. Several variables such as the temperature and hydrogen peroxide concentration, as well as the capacity of the pilot plant for the treatment of inlet polluted streams with different dilution degrees were studied. Remarkable results in terms of TOC reduction and increased bio-degradability were achieved using 160°C and moderate hydrogen peroxide. Moreover, a good stability of the catalyst was evidence for 8 hours of treatment with low iron leaching (less than 1 mg/L).

Keywords:
Fixed bed reactor, petrochemical wastewater, pilot plant scale, SBA-15, wet peroxide oxidation

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Oxidation and Immobilization of an Iron and Manganese by a Fluidized Bed Reactor

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An iron and manganese species immobilization technology was developed in a fluidized bed reactor (FBR) with a new fluidized media, immobilized iron oxide (namely FeO_x-30). The FeO_x-30 catalyst exhibited excellent performance as a catalyst for the oxidation of Mn^{2+}. About 95% and 30% of the manganese species were immobilized on FeO_x-30 and silica sand in FBR, respectively. The oxidation rates of Fe^{2+} and Mn^{2+} and the immobilization efficiencies of iron and manganese oxides strongly depend on pH value. Usually during oxidization the pH values of the solution containing Fe^{2+} must be above 7, and Mn^{2+} must be above 9. During this study, large amounts of iron species leached from the surface of FeO_x-30 only when manganese was in the system. The surface of the FeO_x-30 became fragile in a single system. However, the removal of iron and manganese species simultaneously was better than only the removal of manganese in an FBR. In the binary system, the optimum pH condition for immobilization of both iron and manganese species was pH_i 9. The higher catalyst loading in the binary system led to a higher removal efficiency of iron and manganese.

Keywords:
Fluidized bed reactor; Oxidation; Iron; Manganese; Immobilization

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Immobilisation of TiO_2 for combined photocatalytic-biological dye degradation

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The biodegradability of Remazol Red RR (100 mg/l) was evaluated using unadapted activated sludge and the experiment confirmed the recalcitrance of the dye. Using a combination of photocatalysis and an aerobic biological step, the biodegradability was improved significantly and complete removal of both colour and COD were achieved. Furthermore, TiO_2 was successfully immobilised on borosilicate glass slides by calcination, which facilitates reuse of the catalyst. The catalytic activity of the immobilised TiO_2 was close to that of suspended TiO_2. A reduced activity was however observed when the TiO_2 slides were used repeatedly. When comparing NaOH, calcination and UV irradiation for regeneration of TiO_2 slides immersion in NaOH was shown to be the most efficient method.

Keywords:
Azo dyes; biodegradation; immobilisation; photocatalysis; regeneration; titanium dioxide

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The Microwave-assisted Photo-catalytic Degradation of Organic Dyes

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In this study, TiO_2 photo-catalyst balls produced by the chemical vapor deposition method were used for degradation of organic dyes in which simultaneous irradiation of microwave and UV was evaluated. An electrodeless UV lamp that emits UV upon the irradiation of microwave was developed to irradiate microwave and UV simultaneously. The degradation reaction rate was shown to be higher with higher microwave intensity, under a stronger acidic or basic condition, and with a larger amount of O_2 gas or H_2O_2 addition. The effect of addition of H_2O_2 was not significant when photo-catalysis was used without additional microwave irradiation or when microwave was irradiated without the use of photo-catalysts.

When H_2O_2 was added under simultaneous use of photo-catalysis and microwave irradiation, however, considerably higher degradation reaction rates were observed.

Keywords:
Photo-catalyst; microwave; UV; Dye; Chemical Vapor Deposition

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Photocatalysis

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Photocatalytic Removal of Geosmin and MIB for Drinking Water Treatment

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Photocatalytic degradation of geosmin and MIB, which are two taste and odour compounds commonly found in drinking water supply sources, was investigated using an immobilised TiO_2 system. It was found that the degradation of geosmin and MIB followed similar pseudo first-order kinetics with reaction rate constants being approximately 0.025 min^{-1} for the two typical geosmin and MIB concentrations investigated (i.e., 250 and 500 ng/L). The effects of dissolved components in the water such as sodium bicarbonate and alcohols on the degradation of geosmin and MIB were also studied to gain a better understanding of the degradation mechanism. It was found that there were slightly increasing negative effects on the degradation of geosmin and MIB as the sodium bicarbonate concentration was raised. At 50 mg/L sodium bicarbonate the reaction rate constants of geosmin and MIB decreased by approximately 5%. Methanol and ethanol with concentrations up to 35 and 50 mg/L, respectively, were found to have slightly stronger negative effects on the degradation of geosmin and MIB. These results provided further indication that the degradation of geosmin and MIB involves attacks by hydroxyl radicals.

Keywords:
Geosmin; MIB; TiO_2; Photocatalysis; Advanced oxidation process; Water treatment

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Photocatalysis

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Preparation for Titania Photocatalyst Film by Oxygen Plasma and Rapid Thermal Annealing

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Titanium was oxidized with oxygen plasma and calcinated with rapid thermal annealing for degradation of humic acid dissolved in water. Titania photocatalytic plate was produced by titanium surface oxidized with oxygen plasma by Plasma treatment system. RF-power and deposition condition is controlled under 100 W, 150 W, 300 W and 500 W. Treatment time was controlled by 5 min and 10 min. The film properties were evaluated by the X-ray Photoelectron Spectroscopy (XPS) and X-Ray Diffraction (XRD). From the experimental results, we found the optimal condition of titania film which exhibited good performance.

Keywords:
Humic acid; oxygen plasma; rapid thermal annealing; titania; titanium

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Atomic layer deposited (ALD) TiO_2 and TiO_{2-x}-N_x thin film photocatalysts in salicylic acid decomposition

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Degradation of salicylic acid (SA) with thin film photocatalyst, titanium dioxide (TiO_2) and nitrogen-doped TiO_2 (TiO_{2-x}-N_x) combined with ultraviolet (UV) radiation was studied. TiO_2 film with thickness of 15 and 65 nm was tested. The TiO_{2-x}-N_x film had thickness of 15 nm on top of TiO_2 (50 nm). Photocatalysts were prepared on glass substrate by atomic layer deposition (ALD) technique. The effect of initial pH (3-10) was studied with SA concentration of 10 mg/l. Decomposition of SA was fastest at pH 6 with both films and the rate was equal at initial pH values 3 and 4.3. However, at higher pH values the non-doped film was more efficient.

Keywords:
Atomic layer deposition; nitrogen-doping; salicylic acid; titanium dioxide; ultraviolet light

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Photocatalysis
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Solar photocatalytic disinfection with immobilised TiO_2 at pilot-plant scale

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The photocatalytic disinfection efficiency has been investigated for two immobilized TiO_2 catalytic systems (wall reactor and fixed-bed reactor) in a solar pilot plant. Their performances have been compared with the use of a slurry reactor and the solar disinfection without catalyst. The use of photocatalytic TiO_2 wall reactors does no show clear benefits over the solar disinfection process in the absence of catalyst. The reason is that the efficiency of the solar disinfection is so high that the presence of titania in the reactor wall reduces the global efficiency due to the competition for the absorption of photons. As expected, the maximum efficiency was shown by the slurry TiO_2 reactor, due to the optimum contact between bacteria and catalyst. However, it is noticeable that the use of the fixed-bed reactor leads to inactivation rate quite close to that of the slurry. Not only the high titania surface area of this configuration is responsible for the bacteria inactivation but the important contribution of the mechanical stress has to be considered. The main advantage of the fixed-bed TiO_2 catalyst is the outstanding stability, without deactivation effects after ten reaction cycles, being readily applicable for continuous water treatment systems.

Keywords:
Photocatalysis; disinfection; solar; immobilized TiO_2; pilot-plant

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Poster
Photocatalysis
PC 78

Shape-controlled anatase TiO_2 particles prepared by hydrothermal treatment in the presence of hydrophilic polymer

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Shape-controlled anatase titanium(IV) oxide(TiO_2) particles were prepared by hydrothermal treatment of peroxo titanic acid (PTA) solution in the presence of hydrophilic polymer as a reagent for shape control. Shape, size and crystal structure of prepared TiO_2 particles were strongly depended on

time of pH of PTA solution, concentration of hydrophilic polymer and hydrothermal treatment. The prepared TiO_2 particle has decahedral shape of anatase TiO_2 which consist of two kinds of exposed crystal-surface, i.e. (101) and (001) surface. The decahedral TiO_2 particles showed higher photocatalytic performance on decomposition of acetaldehyde in gas phase, compared to Degussa P-25 which is known as high performance photocatalyst among commercial TiO_2.

Keywords:
Photocatalyst; titanium(IV) oxide; shape-controlled nano particle; hydrophilic polymer

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Poster
Photocatalysis
PC 110

Response surface methodological approach for the assessment of the photocatalytic degradation of NOM

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- No abstract submitted. -
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Poster
Photocatalysis
PC 111

Reducing potential health risks from drinking water by photocatalysis: Effect of copper ions on NOM removal

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The present study investigated the removal efficiency of aqueous humic acid solutions by TiO_2 photocatalytic process in the presence of Cu(II) species. The pseudo first order kinetics revealed rate constants as $7.19x10^{-3}$, $9.87x10^{-3}$, $3.81x10^{-3}$ min^{-1} for UV$_{254}$, Color$_{436}$ and TOC, respectively. Comparatively, lower rate constants were attained with respect to photocatalytic degradation of humic acid. Considering the source dependent diverse chemical and spectral characteristics of NOM, a particular interaction would be expected for humic acid with Cu(II) species (0.1 mg L^{-1}). The presence of copper ions significantly altered the photocatalytic degradation kinetics of humic acids in relation to the concentration effects of humic acid as expressed by spectroscopic parameters and TOC. Batch equilibrium adsorption experiments revealed a distinct Langmuirian type adsorptive behavior of humic acid onto TiO_2 both in terms of UV$_{254}$ and Color$_{436}$ and a C-type adsorption isotherm was attained for TOC. K_F values displayed an inconsistent effect of Cu(II) species, while adsorption intensity factor 1/n<1 denoted a prevailing favorable type of adsorption for UV$_{254}$ and Color$_{436}$. Due to role of intra- and intermolecular interactions between copper ions and humic molecular size fractions, fluorescence spectroscopic techniques were also employed for the assessment of the adsorption as well as photocatalytic degradation efficiencies.

Keywords:
Humic acid, copper, molecular size fractionation, photocatalysis

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Poster
Photocatalysis
PC 148

Photocatalytic degradation of Methylene Blue by TiO_2- coated polypropylene granules irradiated by sunlight

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Titanium dioxide was coated onto buoyant polypropylene granules. Titanium dioxide coated polypropylene granules (TCPG) had high mechanical and attritional stability as well as appreciable photocatalytic activity under solar irradiation. Chosen model pollutant, Methylene Blue (MB) could be totally decolorized and partially mineralized within 3 h of treatment. TCPG might successfully be applied as suspended in the column flow-through system. Degradation rates depended strongly on pH, initial dye concentration, and optimal media dosage, following pseudo-first-order kinetic model.

Keywords:
Photocatalytic; photooxidation; Titanium oxide; polypropylene granule

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Poster

Photocatalysis

PC 172

Nanocrystalline TiO_2 film on fibrous substrates as an efficient photocatalytic material for organics removal in water

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The photocatalytic efficiency of supported TiO_2 nanoparticles, immobilized onto supporting materials, namely silica and alumina fibers, was compared versus the performance of conventional TiO_2 Degussa P25 catalyst. For this purpose the degradation of Methyl Red dye was used as evaluation test. The obtained results showed that the nanostructured supported catalyst has a similar performance of TiO_2 Degussa P25 being the Methyl Red completely removed within 45 and 20 min, respectively. The kinetics of the investigated processes were monitored and a study on the reaction products and intermediates was carried out in order to evaluate possible difference in the reaction courses in presence of immobilized nanoparticles vs suspended catalyst. The results demonstrate that the mechanisms of parent dye degradation in presence of supported TiO_2 nanoparticles are the same as those occurring in presence of TiO_2 Degussa P25 catalyst.

Keywords:
TiO_2 colloidal nanocrystals; TiO_2 Degussa P25; organic pollutant; by-products; photocatalysis

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Poster

Photocatalysis

PC 181

Photocatalytic activity of sol-gel derived TiO_2 co-doped with Nb and various transition metals

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- No abstract submitted. -
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Keywords:

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Poster
Disinfection
PC 28

Influences of inorganic catalyst on the kinetics of water disinfection by gaseous oxidant

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Obtained that at disinfections of drinking water by chloride total content of organic admixture decreases to about 50% and presence in water Cu, Mn, Zn, Al and Fe increase the content of trighalogentmethans in 2-3 times; and Pb in 5.6 times. As a result, during chlorination there are formed trichlormetan, chloride vinegar acid, chloracetone, polychlorinated phenols and chlorates.

Keywords:
Bacterium, disinfection, E-coli, inorganic, oxidant, ozone

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Poster
Disinfection
PC 40

Application of the electrosedimentations in cleaning drinking water

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The present work is devoted to research of a condition of impurity of the Varzob River the main source of water supply of the Dushanbe city with the purpose of research of the opportunity of clearing of waters with application of a method of electro sedimentation. Results of physical and chemical and bacteriological analyses are presented

Keywords:
Electrosedimentation, Coli-index, E-coli, channel, cleaning, coagulant

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Poster
Disinfection
PC 72

Photocatalytic inactivation of *E. faecalis* in secondary wastewater plant effluents

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Photocatalytic inactivation of *Enterococcus faecalis* using TiO$_2$ suspensions was investigated and compared to the inactivation of the most commonly used faecal indicator strain *Escherichia coli*. In contrast to the inactivation in pure deionized water, disinfection of effluents from the biological process of an urban wastewater plant showed a longer initial lag phase and higher survival fractions after several hours of irradiation. Moreover, the fluctuation of the composition of the effluents strongly affects the overall inactivation rate. Additionally, it was found that *E. faecalis* was significantly more resistant than *E.coli* towards the photocatalytic treatment in secondary wastewater plant effluents. These results could be related to the differences in the cell wall structure of both microorganisms and the interactions with the chemical substances present in the wastewater. The main conclusion of this work is that attention must be paid when transferring results obtained for model organism to real bacteria consortia and from laboratory experiments with deionized water to effluents from wastewater plants.

Keywords:
Disinfection; *Enterococcus faecalis*; *Escherichia coli*; photocatalysis; wastewater

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Poster
Disinfection
PC 131

Microbiological Contamination. Treatment with Isolate and Combined Disinfection Agents: UVC, H_2O_2 and UVC/H_2O_2

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A generalized kinetic model resulting from several significant modifications of the originally known as the Series Event Model has been applied to describe three different disinfection processes and compare their efficiencies. The work was performed in a well-defined, versatile batch reactor employing *Escherichia coli* as a subrogate bacteria. The following systems were studied: (i) UVC radiation alone, (ii) hydrogen peroxide alone and (iii) UVC radiation combined with hydrogen peroxide. The kinetic parameters of the three models were determined. Within the range of studied operating conditions, the use of UVC alone has shown to produce the best results.

Keywords:
Disinfection; hydrogen peroxide; kinetic model; ultraviolet

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Poster
Disinfection
PC 207

Advanced Disinfection with UV/VIS, TiO_2 and H_2O_2 for *Clostridium perfringens* and *Enterococcus* sp. removal

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The aim of this work is to evaluate the bactericidal capacity of advanced oxidation treatments based on light UV/VIS, H_2O_2 and TiO_2 on two faecal indicators of obliged analysis in Europe according to the current legislation on quality of water for human consumption: *Clostridium perfringens* (including spores) and *Enterococcus* sp. Both indicators are Gram + bacteria, and moreover, *C. perfringens* has an anaerobic metabolism and a capacity of generating resistance forms, being its vegetative cells more sensitive to the action of oxidant species formed in these advanced oxidation treatments.
The vegetative cells of *C. perfringens* are inactivated quickly after the treatments carried out, being the most effective the photolysis/H_2O_2 treatment with 8.38 units log of inactivation. The photocatalysis is the most effective process for spores and Enterococcus, getting levels of inactivation of 1.30 units log for espores and 2.58 log for Enterococcus after 30 minutes of treatment.

Keywords:
Clostridium perfringens; Enterococcus; disinfection; photocatalysis; water quality

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Poster
Disinfection
PC 212

Electrochemical disinfection of secondary wastewater treatment plant (WWTP) effluent

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In this work the electrochemical disinfection of the effluent of a secondary wastewater treatment plant is investigated. In the experimental work, performed on-site with real effluents of the WWTP located in Vuelta Ostrera (Cantabria, Spain), boron-doped diamond electrodes were employed. The initial concentration of Escherichia Coli varied in the range $1.3x10^4$ – $5.2x10^5$ cfu/mL. The influence of two variables was investigated: i) The applied current density was varied in the range J= 40 – 120 A/cm2, showing first order kinetics of the E. Coli deactivation with relation to the applied current density; and ii) the chloride concentration was varied in the range 60-1000 mg/L, showing that increasing chloride content also enhanced the kinetics of the E. Coli inactivation. The latter parameter is particularly important in coastal areas, as in the case of study. Nevertheless, the concentration of trihalomethanes was maintained below 100 mg/L, so it can be concluded that the formation of disinfection by-products is not a disadvantage of electrochemical disinfection.

Keywords:
Electrooxidation; Wastewater disinfection; tertiary treatment

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Poster
Disinfection
PC 233

Decomposition of Gas-phase Trichloroethene by Advanced Oxidation Processes within Hg-coated Photoreactors

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The decomposition of gas-phase trichloroethene (TCE) in air streams by direct photolysis, the UV/TiO$_2$ and UV/O$_3$ processes with a low-pressure 254nm UV lamp in an annular photoreactor was studied. The experiments were carried out under various UV light intensities and reactor dimensions to investigate and compare the removal efficiency of the pollutant and the mineralization and dechlorination of organic intermediates by photolysis and advanced oxidation processes (AOPs). A photoreactor design equation for the photolysis of gaseous TCE in air streams by the 254nm UV irradiation was developed without and with the consideration of the reflection effect by combining the continuity equation of the pollutant and the empirical rate expression for the photolysis of TCE. By the proposed design scheme, the temporal distribution of trichloroethene at various operation conditions by 254nm UV photolysis can be well modeled. The UV/TiO$_2$ process was found to be superior in mineralization efficiency for the decomposition of TCE to it by the UV/O$_3$ process. However, the dechlorination efficiency for the decomposition of TCE by UV/TiO$_2$ process is comparable with it by the UV/O$_3$ process. The individual contributions to the decomposition of TCE by direct photolysis and hydroxyl radicals destruction in the UV/TiO$_2$/TCE and UV/O$_3$/TCE systems were differentiated to discuss the quantum efficiency.

Keywords:
direct photolysis, UV/TiO$_2$, UV/O$_3$, trichloroethene (TCE)

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Poster
Disinfection
PC 248

Disinfection optimization by a better control of ozonation process

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Currently, ozonation installations in French drinking water treatment plants are operated in order to ensure an ozone residual of 0.4 mg/L at the outlet of the contactor with a contact time of 4 minutes which guarantee, with regards to the USEPA tables, a 4 log virus inactivation. Veolia Water has launched a thorough study concerning hydraulics in ozonation

contactors which goals are (1) to reach the disinfection level desired through a better supervision of operating conditions, (2) to guarantee good hydraulic performances to reduce ozone production and ozonation-by products (bromates). The validation of these objectives is related to a relevant control of every ozonation tank with a Ct criteria considering from now their geometry, which condition their hydraulic efficiency. In comparison with CSTR method, the Ct_{10} method has been judged as the most relevant. Veolia is working with such a tank control, which definitely requires the determination of its hydraulic efficiency. Considering that numerical modelling of the ozonation contactors will be very long and expensive, the project team is working on the determination of an analytical model expression for hydraulic efficiency. The objective is to create an innovative tool which enables plant operators themselves to easily determine the hydraulic efficiency of inter or post ozonation tank.

Keywords:
Ct_{10}, CSTR, disinfection, hydraulic, ozonation, optimization

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Poster

Ozone/AOP/Water/Wastewater

PC 23

“Supercavitation” – A New Aeration Technology

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A newly-developed fine bubble aeration system, by which air is transferred under supercavitation conditions, shows a clearly better performance than traditional, well-known aerators that rely on the jet-pump principle. The performance can be compared to oxygen transfer rates achieved in membrane and foil plate aerators. A prototype supercavitation aerator installed at a sewage treatment plant revealed an air input rate, which was about one third lower than that of the replaced jet pump system. In spite of this low air input rate, the daily demand of pure oxygen for the additionally installed membrane aeration system went down by approximately 49 percent, from the original level of about 1 200 m^3/d to about 600 m^3/d – and this over a test period of more than seven months. With this new aerator and during the first three months of test phase already, more than 10 000 Euros had been saved because of the reduced pure oxygen consumption.

Keywords:
Mechanical aeration, Supercavitation, Energy efficiency

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Poster

Ozone/AOP/Water/Wastewater

PC 27

Ozone-based reclamation of an STP effluent

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The system ozone and hydrogen peroxide was used to reclaim wastewater from the secondary clarifier from a Sewage Treatment Plant (STP) of Alcalá de Henares (Madrid-Spain). The assays were performed by bubbling a gas mixture of oxygen and ozone, with ~ 24 g Nm^{-3} of ozone concentration, through a volume of wastewater samples for 20 minutes at 25 ºC . The removal of dissolved micropollutants such as Pharmaceutical and Personal Care Products (PPCPs) and Organic Carbon (TOC) was enhanced by adding periodic pulses of hydrogen peroxide while keeping pH above 8.0 throughout the runs. Removal efficiency ratios in the range of 7 – 13 mg O_3/mg TOC and 0.24 mg O_3 /ng micropollutants at 5 minutes of ozonation were assessed as reference data to reclaim wastewater from STP. The relation between the extent of TOC removed and ozone doses used was related by a second-order kinetic model in which the time-integrated ozone-hydrogen peroxide concentration was included.

Keywords:
Advanced Oxidation Processes, Kinetics, Reclaim Water, Ozonation, Water Pollution Control

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Poster
Ozone/AOP/Water/Wastewater
PC 42

Landfill leachates purification by H_2O_2/UV, O_3/H_2O_2, modified Fenton and modified photo-Fenton methods

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In this study the treatment of landfill leachate by H_2O_2/UV, O_3/H_2O_2, modified Fenton and modified photo-Fenton processes is reported. The ratio of COD/BOD_5 was 3.9-4.4. The modification of Fenton and photo-Fenton processes included the precipitation of humic substances after adjusting pH=3. Due to this precipitation COD decreased by 34% and BOD_5 by 7.1%. The modification significantly improved the efficiency and lowered reagents doses necessary to continue the process. Modified photo-Fenton process proved to be the most effective (98% COD removal). Fenton process was much more effective than other two processes up to 120 min of the treatment, while after longer times it was the lowest of all. After 30 min of Fenton treatment COD/BOD_5 ratio decreased to 2.3. The parameter referred to as 'efficiency of oxidants' was used to estimate the efficiency of all the processes - its value for the processes varied from 178 to 239%. In raw and treated leachate various substances were identified, including di-n-butyl phtalate, hydrocarbons, silanes and siloxanes.

Keywords:
Advanced oxidation processes, Efficiency of oxidants, Landfill leachate, Organic contaminants

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Poster
Ozone/AOP/Water/Wastewater
PC 45

The Impact of Groundwater Quality on the Removal of MTBE Using Advanced Oxidation Technology

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In this study, the removal of MTBE from contaminated groundwater using advanced oxidation technology was investigated. The UV/H_2O_2 treatment process was applied to remove MTBE from two types of Saudi groundwaters that have different quality characteristics with regard to their contents of inorganic species such as chloride, bromide, sulfates and bicarbonates (alkalinity). MTBE was spiked into these waters to a concentration level of about 250 µg/L. A 500 mL bench-scale forced-liquid circulation photoreactor was used to conduct the experiments. Two different UV lamps were utilized: 15 Watt low pressure (LP) and 150 Watt medium pressure (MP). Results of the study showed that the UV/H_2O_2 process removed more than 90% of MTBE in 20 minutes when the MP lamp was used at an MTBE/H_2O_2 molar ratio of 1:200. The results also showed that the various concentration levels of alkalinity, chloride, bromide and sulfates in the two types of groundwater have different impacts on the removal efficiency of MTBE by the UV/H_2O_2 process. Both types of groundwater behave similarly with respect to the fate of MTBE degradation by-products.

Keywords:

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Poster
Ozone/AOP/Water/Wastewater
PC 58

Molasses Process Wastewater Treatment by Electrocoagulation Combined with Hydrogen Peroxide

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Effluents arising from molasses fermentation are of dark brown colour and large organic content. Existing biological treatments can reduce the biological oxygen demand from these effluents, but are unable to decolourise or remove the colour associated chemical oxygen demand. This work evaluated the removal of the molasses process wastewater by electrocoagulation with iron anode, and the combined electrocoagulation/H_2O_2 process. The effects of pH, hydrogen peroxide addition amount and addition mode on colour and COD removal were investigated. It was found that the combined process greatly improved the removal efficiency, where almost 100% decolorization and about 85% COD removal efficiency were achieved with the addition of 500 mg/L hydrogen peroxide. The presence of hydrogen peroxide led to the formation of electro-Fenton process, which increased the treatment efficiency and reduced the specific energy consumption compared with the individual electrocoagulation. Therefore the combined electrocoagulation process has the potential to offer a simpler and more efficient wastewater remediation alternative.

Keywords:
Molasses process wastewater; electrocoagulation; hydrogen peroxide; combination; electro-Fenton

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Poster
Ozone/AOP/Water/Wastewater
PC 60

Enhanced removal of halogenated organics from industrial groundwater by sequential UV/H_2O_2 treatment and carbon adsorption

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The removal enhancement by a combination of UV/H_2O_2 degradation and GAC adsorption was investigated for the remediation of industrial groundwater heavily polluted by several halogenated organics. The UV/H_2O_2 process alone was able to remove all pollutants (90-97% in 30 min) but for the 1,2-dichloroethane, the most abundant one (initial concentration 25000 μg/L), the residual concentration (760 μg/L) was much higher than that set by the current legislation (3 μg/L). The employment of UV/H_2O_2+GAC allowed to reach the target residual concentration. Interestingly, it was found that GAC adsorption capacity was greater than expected. This was ascribed to the decomposition of residual H_2O_2 on the GAC giving rise to the formation of hydroxyl radicals that removed the residual organics. Therefore, the second step of the process consisted of a combination of heterogeneous oxidation and adsorption. This is of relevance for lowering the operation cost of the groundwater remediation process.

Keywords:
groundwater; chemical industry; 1,2-dichloroethane; VOC; UV/H_2O_2; activated carbon

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Poster
Ozone/AOP/Water/Wastewater
PC 67

Oxidative Elimination of Trace Organic Contaminants from Wastewater Effluents by Ozone and Peroxone Process

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The removal efficiency of organic contaminants from different classes of compounds such as diclofenac, iopamidol, tributyltin chloride and n-butyl phosphate from wastewater effluents by use of O_3 and the combination of $O_3 + H_2O_2$ (the peroxone process) was investigated. In pilot plant scale study, each substance at the concentration level of approximately 25 - 100 μg/L was spiked into the secondary wastewater effluents (DOC_0 = 9 -11 ppm). Ozone dose applied was 1 - 2 mg O_3/mg DOC_0 in the presence and absence of H_2O_2 in the range of 1 – 2 mg/mg DOC_0. Elimination of the probe compounds differs from one substance to another under the experimental conditions. Diclofenac molecule contains an amine group in addition to an activated aromatic ring which could lead to a successful elimination by O_3 as well as by peroxone process, whereas iopamidol which possesses an aromatic ring with electron withdrawing iodine substituents in the molecule is less efficiently degraded at the same O_3 dose (1 mg/L). Since tributyltin chloride and n-butyl phosphate have aliphatic substituents in their molecules, the degradation of these two substances is not markedly enhanced by the addition of H_2O_2. The elimination efficiency is increased only by increasing O_3 dose.

Keywords:
Organic contaminants, Oxidation, Ozone, Ozone+H_2O_2, Wastewater effluents

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Poster
Ozone/AOP/Water/Wastewater
PC 70

Impact of UV/H_2O_2 pre-treatment on the structure and adsorption of hydrophilic natural organic matter

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Hydrophilic rich raw water was pre-treated by UV/H_2O_2 at a dose of 21 to 65 kW h m^{-3} and 0.5 to 2 mM H_2O_2. This was not effective for reducing bulk DOC levels but a shift to smaller organics was observed. FTIR analysis also showed the formation of carboxylic acids and ketones. Batch and rapid small scale column test were undertaken using sterile granular activated carbon. The combination of UV/H_2O_2 and GAC using coagulated water resulted in an increased DOC removal and also significantly longer bed volumes. There is a need though to quench the H_2O_2 before the GAC process as it reduces overall performance.

Keywords:
Activated carbon, advanced oxidation process, disinfection by-products, NOM removal, rapid small scale column test

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Removing textile mill effluent recalcitrant COD and toxicity using photocatalysis

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The potential of the H_2O_2/UV process for improving quality of an industrial textile effluent before biological treatment was evaluated in the laboratory using a multivariate experimental design to determine the effects of pH, H_2O_2 dose and reaction time on colour, COD and toxicity removal efficiencies. Increasing reaction time (from 10 to 120 min) and H_2O_2 dose (from 0 to 5 mmol.L^{-1}) significantly improved removal efficiencies, while increasing pH (from 4 to 10) had a negative effect on colour and toxicity removals. Laboratory H_2O_2/UV treatment of the mill effluent under optimum conditions (pH7, 5mmol.L^{-1} H_2O_2, 120 min) resulted in decreases in colour (70%), COD (21%) and toxicity (67%), without lowering BOD. H_2O_2 was consumed within the first 30-60 min, while the effluent average oxidation state stabilized after 60 min. Decreasing reaction time to 60 min resulted in similar colour (63%) and COD (20%) removals but lower toxicity removal (44%). Spectrophotometric monitoring of the optimized reaction indicated partial destruction of residual aromatic azo dyes. H_2O_2 and residual peroxide and average oxidation state of the effluent Effluent biodegradability (BOD/COD) increased by 28% after the H_2O_2/UV treatment. Improvements observed in effluent quality are expected to enhance combined AOP-biological treatment efficiency of the mill effluent.

Keywords:
Acute toxicity, COD, colour, multivariate analysis, photocatalysis, TOC

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Poster
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Treatment of terephthalic acid wastewater by ozonation with UV, H_2O_2, Fe^{2+} in different combinations

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Terephthalic acid (TPA) wastewater from terephthalic acid manufacturing process was treated by several advanced oxidation processes (AOPs). UV assisted ozonation (UV/O_3), catalytic ozonation (O_3/Fe^{2+}), photo-chemical oxidation ($UV/O_3/H_2O_2$), ozone assisted photo-fenton ($UV/O_3/H_2O_2/Fe^{2+}$) systems were investigated for the COD removal efficiency. The $UV/O_3/H_2O_2/\ Fe^{2+}$ system was most efficient for the removal of COD among the tested AOPs. Even here a stepwise addition with pH control in the $UV/O_3/H_2O_2/Fe^{2+}$ system enhanced the COD removal efficiency around 20 % compared with one step addition. The step wise addition method showed a COD removal efficiency of 90 % at 240 min, and TPA, IPA, BA present in phthalic acid wastewater were completely decomposed within 150 min. Combination of various oxidant systems ($UV/O_3/H_2O_2$, $UV/O_3/H_2O_2/Fe^{2+}$) showed the enhancement of COD degradation. The pseudo first-order rate constant for all the five optimized systems were evaluated and compared.

Keywords:
Terephthalic acid wastewater; advanced oxidation process; ozone; COD removal efficiency, first order rate constant

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PC 105

Advanced Oxidation Processes for the Removal of Natural Organic Matter: Design and Construction of a Treatment Rig

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A treatment rig incorporating several advanced oxidation process (AOP) methods (utilising ozone, peroxide, UV, ferrate (Fe(VI)), and photo-Fenton's reagent) has been designed and is being constructed at a laboratory scale suitable for simulating plant conditions. The rig will be used to study the removal of natural organic matter (NOM) from waters by various AOP methods, in various combinations, with the overall goal of removal of DBP, particularly emerging DBP, precursors.

Keywords:

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Poster
Ozone/AOP/Water/Wastewater
PC 126

Treatment of Slaughterhouse Wastewater - Kinetics of Degradation Applying UV-Radiation or H_2O_2/UV

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In some Brazilian regions, surface water has become scarce e.g. semi arid climate areas and densely populated and industrial areas, where water over exploitation and/or fluvial pollution has been more common. Advanced oxidative processes (AOP) provide treated water as a source of reuse water even with the characteristics of drinking water enabling water reuse practices also in food industries. The secondary wastewater of a slaughterhouse was the water source for a tertiary treatment study evaluating the kinetics of the photo-induced degradation of color and UV_{254} under UV radiation with and without the addition of H_2O_2. The proximity of the *k'* values of color and UV_{254} degradation by UV indicates that the compounds responsible for color may be the same content measured by UV_{254}. The UV/H_2O_2 treatment was 5.2 times faster than simple UV in removing aromatic compounds. The degradation kinetics of aromatic compounds in both treatments followed a pseudo-first order law. The pseudo-first order constant for UV/H_2O_2 and UV treatments were $k'_{UV_{254}} = 0.0306$ min^{-1} and $k'_{UV_{254}} = 0.0056$ min^{-1}, respectively.

Keywords:
Advanced oxidative processes (AOP); hydrogen peroxide (H_2O_2); kinetics; UV

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Poster
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PC 140

The Influence of Reaction Conditions in the Oxidation of Organic Compounds of Nuclear Laundry Water by Ozone

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This paper presents the summary degrading organic compounds of nuclear laundry water by ozonation in different conditions of pH, hydrogen peroxide and ultraviolet radiation. The degradation of organic compounds was analysed by chemical oxygen demand (COD), total organic carbon (TOC) and biochemical oxygen demand (BOD). The optimal degradation conditions were at pH 7 with ozone, UV radiation and hydrogen peroxide addition. The transfer of ozone increased significantly thus resulting in decreased treatment time compared to ozone treatment alone. The reductions of COD, TOC and BOD were 46%, 32% and 70%, respectively.

Keywords:
Hydrogen peroxide, nuclear laundry water, ozonation, pH, ultraviolet radiation

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Poster
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Investigations on Ozonation of Tannery Wastewater as a Post Treatment Step

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Although foam is a rather neglected topic in the area of river basin management, it can lead to serious political problems with local stakeholders when occurring in residential areas. In laboratory scale experiments ozonation proved to be an appropriate measure to reduce foaming substances in the effluent of a tannery's wastewater treatment plant. Up to 50 % additional COD reduction and more than 70 % of the foam potential emission on river catchment scale could be eliminated.

Keywords:
COD reduction, foam reduction, ozonation, tannery wastewater

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Poster
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PC 157

Ozone-based treatment of a municipal secondary effluent

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Ozone-based processes were performed on the outflow of a membrane bioreactor from the municipal wastewater treatment plant of Grasse (France). The study analyses the effectiveness of conventional ozonation and ozone combined with hydrogen peroxide in terms of dissolved organic matter (DOM) removal. The influence of both reaction temperature and pressure was studied. Under the same operating and experimental conditions, the removal of DOM by ozone was higher at alkaline pH than at neutral and acidic pH. Indeed, ozone treatments at pH 3, 7 and 11 achieved 35 %, 37 % and 89 % of COD removal after 2 hours. Reaction temperature influenced the COD removal kinetic but not the COD removal rate. Addition of hydrogen peroxide during the ozonation greatly improved the DOM removal. After 60 min., conventional ozonation led to 52 % of COD removal, 46 % of mineralization and 55 % of UV$_{254}$-absorbency elimination, whereas with hydrogen peroxide addition COD, TOC and UV$_{254}$ removals reached 100 %, 57 % and 86%, respectively. Presence of hydrogen peroxide also improved the reaction rate of DOM removal. DOM elimination by indirect oxidation pathway, favored both at basic pH and in presence of hydrogen peroxide, was very effective partly because hydroxyl radical inhibitors content was low.

Keywords:
Advanced Oxidation Processes; Hydrogen Peroxide; Organic Matter; Ozone; Secondary effluent

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Poster
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PC 160

Advanced oxidation processes for NOM removal from groundwater used as drinking water supply

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To improve the quality of water, in this study a pilot-scale evaluation of how the conventional treatment process could be upgraded was conducted. The pilot system used consisted of coagulation, sedimentation, sand/anthracite-filtration (SF) and adsorption on granulated activated carbon (GAC) (treatment train A). Evaluation of three oxidative pre-treatments was performed: treatment train B – pre-ozonation (2.2 g O_3/m^3); treatment train C – H_2O_2/O_3 process (2.2 g O_3/m^3; $H_2O_2 : O_3 = 1:2$) and treatment train D – H_2O_2/O_3 process (2.2 g O_3/m^3; $H_2O_2 : O_3 = 2:1$). Treatment efficacy was followed on the basis of: DOC content, UV$_{254}$ absorbance, SUVA and by-products formation. DOC and UV$_{254}$ absorbing material removal was largely improved in treatment trains involving pre-oxidation with ozone and H_2O_2/O_3 process with a 1:2 $H_2O_2:O_3$ ratio, compared to the treatment without oxidative pre-treatment. A larger amount of H_2O_2 (2:1 $H_2O_2:O_3$ ratio) was less favourable for enhancing the efficacy of further treatment processes in terms of NOM removal, compared to the application of ozone and a 1:2 $H_2O_2:O_3$ ratio in the pre-oxidation step.

Keywords:
Drinking water, NOM removal, ozone, H_2O_2/O_3 process, pilot plant

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Graywater treatment Using UV-Titanium Ball-Tower and membrane

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In this study, wastewater of kitchen, bathroom and laundry was defined as graywater. Graywater was treated by titanium ball, micro filtration membrane and UV-Titanium ball. Removal efficiency of COD, suspended solids, turbidity, color and *E.coli* was studied to reuse as water of fire fighting, landscape, chamber pot and car washing. The pH was 7-8 Removal efficiency of each factor using titanium ball was the same as following things: COD (95%), suspended solids (96%) turbidity (97%), TN(62), TP(60), VSS(98) *E.coli* (2%). Removal efficiency of each factor by using micro filtration membrane was the same as following things: COD (99%), suspended solids (98%) turbidity (100%), TN(60), TP(50), VSS(99) *E.coli* (100%). The characteristic of graywater was enough to establish sustainable water circulation system to reuse wastewater of apartment. TB(Titanium Ball)-membrane system was the satisfaction of standards of reusing water in Korea: below COD 20 mg/L, below turbidity 2 NTU, below suspended solids 5 mg/L, no detection of *E.coli.*

Keywords:
graywater, titanium ball, membrane, micro filtration

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PC 204

POPs degradation in natural waters using a V-UV/UV/TiO_2 reactor

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The M300 water purifier which is a V-UV/UV/TiO_2 reactor has been investigated for the removal of different pollutants in different water qualities. The para-chlorobenzoic acid (pCBA) has been used as a model pollutant since it has been reported to be an ideal compound for UV AOPs studies because it displays slow reaction rates with UV, but rapid oxidation kinetics with OH radicals. V-UV was found to be the most efficient process within this unit for the pCBA degradation and no photocatalysis degradation has been found. The water quality was found to largely affect the efficiency of the system. Indeed, both DOC and total inorganic carbon lowered the HO radicals concentration in the system, but DOC did it to a larger extent. Two micro-pollutants, atrazine and sulfamethoxazole, was successfully degraded in the system. However, their removal efficiency was also very water quality dependent. The UV254 absorbance of the water affects the photolysis of the sulfamethoxazole which has a high molar extinction coefficient and quantum yield at 254nm, while the DOC is mainly competing with the pollutants for the HO radicals.

Keywords:
vacuum UV; UV; photocatalysis; micro-pollutants; pCBA; natural waters

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Poster
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PC 211

Photocatalytic oxidation of grey water over titanium dioxide suspensions

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Grey water reuse is an attractive alternative to the sustainable management of water especially under water scarcity situations. Grey water from two different sources, a sports centre and a household, was treated with TiO_2 photocatalysis. Dissolved organic carbon (DOC) from the sports centre grey water was reduced approximately 70% in 50 minutes. Moreover, acetic acid, formic acid and oxalic acid were detected in the treated effluent. Two types of laundry grey water from a household (high strength and low strength) were also treated. For high strength grey water, DOC remained constant during the photocatalytic process, although 67.47 % of anionic surfactants were removed. For low strength laundry grey water, DOC was reduced up to 52.75% and anionic surfactants removal was practically complete. In both cases, decomposition compounds such as acetic acid and formic acid were detected in the treated effluent.

Keywords:
grey water, reuse, photocatalysis, TiO_2

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Poster
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Partial O_3 and O_3/UV treatment of a phenolic wastewater: effect on biodegradability and toxicity

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The removal of persistent organic pollutants is a crucial step for the purification of wastewater. In this work, the capability of O_3 and O_3/UV to enhance the biodegradibility of the model component phenol is evaluated. In order to quantify the toxicity, two alternative techniques for analysis are considered: ATP bioassay and respirometry. The results show that the toxicity is strongly influenced by the kind of sludge used. As ATP-bioassay, unlike respirometry, does not measure the inhibition of micro-organisms derived from a biological active sludge unit, further testing with ATP bioassay was excluded.
The results of the partial O_3-treatment on phenol show an improvement in BOD/COD ratio and toxicity. The pH, ozone concentration, phenol concentration and the reaction time all feature a clear impact on the efficiency of the oxidation process. Under optimal conditions an improvement in BOD/COD ratio of 96% and a negligible toxicity is reached. Coupling the ozone-oxidation UV radiation leads to similar values for the optimal BOD/COD ratio and toxicity, however, the required residence time is strongly reduced.

Keywords:
Advanced oxidation processes; Biodegradability; Biological oxygen demand; Chemical oxygen demand; ozone; ozone/UV; respirometry, ATP bioassay

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Poster
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Enhancement of the water reuse by the application of AOP's on an industrial laundry wastewater

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During the last years the laundry sector has been confronted with important challenges concerning the water treatment. Stricter norms and a rising fresh

water costs make a more profound effluent purification, coupled with water reuse, more and more necessarily. In this paper, the potential contribution of the integration of partial chemical oxidation in realising these challenges, has been examined. This study comprises experimental work, as well as simulations for different water networks including economical aspects.

For the wastewater under study, the Fenton reagent, O_3, peroxone and UV/O_3 with a partial dose of 10% are used. From the pilot-scale experiments, the combination UV/O_3 has shown to improve the BOD/COD ratio by 70%, which makes a further treatment in a biological unit possible. The improved BOD/COD ratio for the UV/O_3 combination exceeds the increase with respect to pure O_3 by approximately 20%. These observations clearly confirm the synergetic effects of combining UV and O_3 for this wastewater. All other selected techniques show a less significant increase in BOD/COD ratio.

Finally a case study shows on the one hand that water reuse can lead to the necessary cost savings and on the other hand that the integration of partial chemical oxidation can be economically profitable. The expected increase of fresh water and groundwater costs will proportionally favour the economic feasibility of partial chemical oxidation.

Keywords:
Advanced oxidation processes; Biodegradability; Biological oxygen demand; Chemical oxygen demand; water pinch analyses; water reuse

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Poster
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PC 238

Removal of odorous organic compounds by ozonation in adsorbed phase

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Removal of malodorous organic compounds has been a major objective of water professionals for a few years. Regulations are becoming increasingly strict and conventional treatments techniques are not efficient enough. In this study, an advanced oxidation process coupling adsorption and ozonation is studied. The oxidation of butan-2-one adsorbed on two high silica zeolites was investigated. This oxidation was studied at different ozone loading, showing different results according to the solid: a partial regeneration of 35% was reached for ZSM-5 whereas with Faujasite Y, the ozonation lead to a higher regeneration, of about 80% .The analysis of exit gases shows the absence of ozone and the presence of CO_2, H_2O and trace by-products.

The adsorbent keeps its retention capacity even after several ozonation cycles. It was demonstrated that after three consecutively cycles of MEK adsorption–ozonation with both zeolites, the adsorbed quantities obtained are not changed. Zeolites are not damaged by the ozonation and no poisoning of adsorbent/catalysts occurred during the several ozonation phases. The efficiencies are dependent on the competitive mechanisms of ozonation reactions, adsorption and desorption.

The influence of several parameters such as the feed concentration of O3, MEK, relative humidity and the reactor residence time, was also studied.

Keywords:
adsorption, odours, ozonation, VOCs, zeolites

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Poster
Ozone/AOP/Water/Wastewater
PC 239

Photochemical Oxidation of Phenol in Olefins Unit Effluent by UV/H_2O_2 and Photo-Fenton Processes in Iran

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In this research, advanced oxidation processes (UV/H_2O_2, UV/H_2O_2/Fe(II) and UV/H_2O_2/Fe(III)) were investigated in bench scale experiments for degradation of phenol in olefin plant effluent of Tabriz petrochemical company. The study demonstrates that the photo-Fenton process, (a mixture of hydrogen peroxide and ferrous or ferric ion), was the most effective treatment process under acidic conditions and produced a higher rate of degradation of phenol at a very short radiation time. It accelerates the oxidation rate by 5-7 times the rate of the UV/ H_2O_2 process. The reaction was influenced by pH, the input concentration of H_2O_2 and the amount of the iron catalyst and the type of iron salt. The experimental results show that the optimum conditions were obtained at a pH value of 3, with 7 mmol/1 H_2O_2, and 0.4 mmol/1 Fe(II) for the UV/H_2O_2/Fe(II) system and 7 mmol/l H_2O_2 and, 0.3 mmol/1 Fe(III) for the UV/H_2O_2/Fe(III) system. As for the UV processes, UV/H_2O_2/Fe(III) showed the highest degradation rate.

Keywords:
Advanced Oxidation Processes; hydrogen peroxide; Phenol; photo-Fenton reaction; UV radiation

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Poster
Ozone/AOP/Water/Wastewater
PC 256
Combination of Ozonation and Biodegradation for Enhanced Elimination of Aqueous Chlorinated Phenols

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Chlorinated phenols (CPhs) are toxic compounds, often found in industrial effluents; these contaminants are difficult to be decomposed in the wastewater. Combination of chemical and biological treatments has shown good results in the phenols and phenolic derivatives decomposition. Synthetic residual water contaminated with individual CPhs (4–chlorophenol (4-CPh), 2,4–dichlorophenol (2,4– DCPh)) were treated by a combination of an ozonation followed by an aerobic biodegradation. A previously adapted mixed microbial consortium was used. The biodegradation of CPhs using free cells in a batch reactor was evaluated. In this case, low contaminant removal efficiencies (25-40%) were observed. CPhs at two pH values (7 and 12) were ozonated and subsequent biodegradation showed better results than only biodegradation treatment. The optimal ozonation condition was selected at pH 12, since the short reaction time (5-8 minutes) and the organic acids complete biodegradation during 20h.

Keywords:
Chlorophenols; ozonation; biodegradation

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Poster
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PC 258
Industrial Applications of Advanced Oxidation Technology

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Industrial applications of advance oxidation processes installed in various types of industry are shown by several examples. As commercial decisions do not base on scientific aspects, but on performance and cost specification it is focused on realised examples due operative advantages for the user. For touching the whole field of application chemical parameters, flow rates and approximate operation expenses are indicated as far as allowed. The installations presented are usually supplied on a Turn-key base and include the full scope of supply within the defined interfaces. The given examples are placed all over the world.

Keywords:
Advanced oxidation, COD – Elimination, Enviolet® -oxidation, Operational costs, UV-Oxidation

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Poster
Sludge
PC 65

‘LOTUS Project’ Leading to the Recycling Society with Sewage Sludge in Japan

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The lack of sludge dumping sites, increasing cost for sludge recycling and the social demand for the reduction in the emission of green house effect gas have been getting challenging issues for each municipality. “Biomass Nippon Strategy” and the commitment to attain the goal of the Kyoto Protocol urge national government to encourage local governments to internalize the concept of recycling and the measures against global warming in their sewerage works in Japan.

The Ministry of Land, Infrastructure and Transport (MLIT), that had launched SPIRIT21 Project (Sewage Project, Integrated and Revolutionary Technology for 21st Century) in 2002, decided to start a new R/D project named “LOTUS Project” (Lead to Outstanding Technology for Utilization of Sludge Project) as a part of SPIRIT21 Project. LOTUS project focuses on sludge processing technologies for practical and economical recycling and fuel use.

Keywords:

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Poster
Sludge
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Improve Sludge Dewaterability for Sequential Ozonation – Aerobic Treatment

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Chemical treatment processes such as ozonation have mostly been considered as an efficient way for bio-solids minimization. The improvement of sludge dewatering was more a welcoming side-effect in these sequential processes. However, some times the loaded ozone dose to the sludge has a negative effect on dewaterability. This work address the most important finding concern the effect ozone on sludge dewaterability in single ozonation processes as well as in a sequential ozonation biological processes. It was found that the maximum sludge dewaterability was achieved with ozone dose at 0.05 gO3/gTSS. This value was found to be less that the required ozone dosage that leads to sludge disintegration. However, it was observed that the sequential ozone and aerobic treatment allows further strong improvement of dewatering efficiencies.

Keywords:
Biological treatment, dewatering, ozonation; sludge

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Poster
Sludge
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Heavy metals removal from anaerobically digested sludge by Fenton process and phosphorus immobilisation

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Heavy metals removal from anaerobically digested sewage sludge and phosphorus immobilisation into the sludge were investigated through batch experiments using oxidising agents under acidic condition at pH 2.5. The addition of hydrogen peroxide to the sludge eluted Cd, Cu and Zn from the sludge more than that of acid only and its initial concentrations required for the maximum elution efficiency were 0.1 % for Cd and Zn and 0.5 % for Cu, respectively. The addition of ferric sulphate improved the elution efficiency of Cu. Ferric sulphate addition under an initial hydrogen peroxide concentration of 0.02 % gave rise to more effective elution of Cu from the sludge than that of either hydrogen peroxide or ferric sulphate. This enhancement would be due to the decomposition of insoluble copper compounds with hydroxyl radicals produced by Fenton reaction between hydrogen peroxide and ferrous ion formed in the sludge. On the other hand, the addition of acid and/or hydrogen peroxide caused the elution of phosphorus together with heavy metals. However, the addition of ferric sulphate (1g Fe/L) could immobilise phosphorus into the sludge and most of which was retained as bioavailable form.

Keywords:
Anaerobically digested sewage sludge; heavy metals removal; phosphorus immobilisation; Fenton process

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Poster
PPCP/EDC
PC 22

MTBE-Degradation by hydrodynamic induced cavitation

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Hydrodynamic induced cavitation generate imploding cavitations bubbles which can lead to degradation or even mineralisation of water constituents without addition of any chemicals. This technology overcome the problems of ultrasound irradiation by the local production of a cavitation cloud close to the sonotrodes.

In the presented paper hydrodynamic cavitation can be stabilized downstream the nozzle depending on the ambient pressure conditions. If the pressure is kept low, the imploding cavitation bubbles generate new cavities, analogous to a chain reaction, and elevate the radical synthesis inside the apparatus. During the pilot tests MTBE and ETBE were degraded and complete mineralisation started at a time delay of app. 20 minutes. The specific energy-demand for MTBE-degradation lies in the range of app. 200 Wh/ppm in the investigated concentration range of about 30 ppm.

Keywords:
Hydrodynamic Cavitation, MTBE-Degradation, Radicals

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Poster
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A Comparison of Ultrasound-based AOPs for the Removal of X-Ray Contrast Media

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The degradation of specific iodinated X-ray contrast media (ICM) compounds (viz: diatrizoate, iomeprol, iopromide, and iopamidol) by ultrasound (US) irradiation in aqueous solution, with and without the presence of hydrogen peroxide or ozone, has been studied. Experiments were carried out at a constant US frequency of 20 kHz, at two power intensity values of 17.6 and 200.1 Wcm^{-2}, and at five power densities up to 0.235 Wml^{-1}. Zero-order kinetic rate constants for the ICM degradation by US alone were

calculated under certain sonication conditions. Pyrolysis appeared to contribute approximately 30%, and radical attack 70%, of the overall ICM degradation performance. The effect of US intensity on compound degradation (at a given power density) was found to play a negligible role, whereas US power density was found to be a major factor controlling the overall oxidation process under these conditions. The compound degradation by US alone was relatively minor, but the addition of hydrogen peroxide in the sonication process gave some improvement with a doubling in the degradation performance at the greatest applied peroxide concentration. The combination of gaseous ozone and US was found to be very effective in degrading ICM compounds and an almost complete compound removal could be achieved.

Keywords:
Iodinated X-ray contrast media; ultrasound; hydrogen peroxide; ozone; AOPs

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Removal of EDCs from WWTP effluents by means of advanced oxidation

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Municipal sewage and WWTP effluents are considered to be a major source of pollution, regarding the occurrence of endocrine disrupting compounds (EDCs) in the environment. Although removal potential of many EDCs by conventional WWTPs is recognised, literature data are not easily comparable. Besides, in order to reach very low concentrations, a further treatment might be sometimes required. Positive results can be achieved by tertiary chemical oxidation, nevertheless, technical-economic suitability is still to be fully demonstrated. In this work, two estrogen-like susbstances were considered: nonylphenol (NP) (and its parent compounds) and bisphenol A (BPA). The experimental work was conducted at Verona (Northern Italy) WWTP (370,000 p.e.): after a 15 days sampling campaign, which was carried out in order to calculate mass balance of target compounds, chemical oxidation tests were performed on effluent by means of UV/H_2O_2 process and ozonation. Technical-economic feasibility of these solutions is discussed.

Keywords:
AOPs, cost, endocrine disrupting compounds, kinetics, municipal wastewater

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Poster
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Degradation of Bisphenol A using UV- and UV/H_2O_2-processes

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Bisphenol A (BPA; 4,4'-Isopropylidenediphenol) is a substance mostly used in the plastic industry. It is used in the production of epoxy resins, poly-carbonate fire retardants or as a stabilizer and an antioxidant in numerous types of plastics. BPA is introduced into the environment via municipal and industrial wastewater. Due to its hydrophobic properties, BPA has the potential for a sorption on an activated sludge during the biological wastewater treatment processes. The degradation of BPA by means of UV-radiation and in the UV/H_2O_2-process with the presence and absence of hydrocarbonate ions (HCO_3^-) as hydroxyl radicals ($OH^{\cdot}$) scavengers was the aim of this study. The first order rate constants of the BPA photodegradation were located between 0.10 min^{-1} (UV/H_2O_2 - process with the presence of HCO_3^-) and 0.27 min^{-1} (UV/H_2O_2 - process). The calculated quantum yield values of BPA photodegradation varied from $7.67*10^{-4}$ (UV/H_2O_2 with HCO_3^-) to $1.99*10^{-3}$ (UV/H_2O_2).

Keywords:
Bisphenol A, UV-radiation, UV/H_2O_2-process, the first order kinetic, quantum yield

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Poster
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Removal of Radiocobalt from EDTA-complexes Using Oxidation and Selective Ion Exchange

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Removal of radiocobalt from an ethylenediaminetetraacetic acid (EDTA) complex of Co(II) (aqueous solution containing 10 µM of Co(II) and 10 µM of EDTA traced with ^{57}Co) was studied. The combination of different oxidation methods and the sorption of ^{57}Co on a selective inorganic ion exchange material were studied. The oxidation methods comprised ultraviolet (UV) irradiation with and without H_2O_2, as well as ozonation individually and combined with UV irradiation. Also the possible contribution of Degussa P25 TiO_2 photocatalyst was studied. Without oxidation only minor sorption of ^{57}Co (7 %) on CoTreat was observed. Best results were achieved combining ozonation, UV irradiation and Degussa P25 TiO_2 with approximately 94 % sorption of ^{57}Co. High values for the ^{57}Co sorption were also achieved by ozonation (~ 88 %) and UV irradiation (~ 90 %). However, the addition of H_2O_2 during the UV irradiation decreased the sorption of ^{57}Co to ~ 84 %. The surplus of EDTA compared to Co(II) was also tested using 10 µM of Co(II) and 50 µM of EDTA. Only a slight decrease to ~ 88 % sorption of ^{57}Co was detected compared to the value (~ 90 %) obtained with 10 µM of EDTA.

Keywords:
EDTA; ion exchange; oxidation, ozone, radiocobalt, ultraviolet

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Poster
PPCP/EDC
PC 108

Degradation of pharmaceuticals in water by visible light photocatalysis

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This work reports about preparation and screening of nanocrystalilne ZnO coated on porous clay granulates for visible light photocatalysis. It can be shown, that this new ZnO-catalyst is able to eliminate different steroidal and non steroidal antiphlogistica in water by arificial and natural day light. By use of clay supported semiconductors (TiO_2, ZnO) there were obtained the same trend reported using of particles in dispersion: ZnO is more efficiently for visible light catalysis as TiO_2. The advantage of supported ZnO-catalyst suggested in this paper is its use in fixed bed or tube reactors to remove micropollutants from process water.

Keywords:
day light catalysis; diclofenac; pharmaceuticals in water; prednisolon-21-hydrogene-succinate; visible light photocatalysis; ZnO-supported catalyst

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Poster
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PC 112

Photodegradation of glyphosate in water by the UV/H_2O_2 process

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Glyphosate is an organophosphate herbicide, which is the most widely used in the world. In Argentina, over 13 million ha of arable land are dedicated to the production of transgenic, glyphosate-resistant (GR) soy. This production has been accompanied by an increase in the use of glyphosate (over 60 million L between 1998 and 1999).

The United Nations estimates that less than 1 % of used pesticides in agriculture actually reach the crops. The rest ends up contaminating the soil, the air and, mainly, the water. Due to the lack of availability of on-site treatment technologies, only a small amount of this waste is currently treated.

The combination of hydrogen peroxide and UV radiation seems to be a suitable option to decrease glyphosate concentration to acceptable limits. In this work the effects of initial pH, hydrogen peroxide initial concentration, and incident radiation in the glyphosate degradation were studied. The experimental device employed was a cylinder irradiated with a tubular, germicidal lamp. The small bath reactor was part of a recycle.

The results have shown that the best conditions for degradation are: pH 7-10 and hydrogen peroxide concentration of 2.20-7.97 mM (75-271 mg/L). In addition, the identification of same intermediates was possible and a degradation path is suggested.

Keywords:
Glyphosate; degradation; reactions paths; UV/ hydrogen peroxide

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PC 137

Occurrence and Removal of PPCPs and EDCs in the Detroit River Watershed

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The occurrence of 51 pharmaceuticals and personal care products (PPCPs) and endocrine disrupting compounds (EDCs) in the Detroit River Watershed (DRW) was investigated. Also, the efficiency of local water treatment plants (WTPs) in removing these pollutants was evaluated. Samples were collected from various locations in the DRW, including the discharge of a sewage treatment plant (STP), downstream of the STP on the Detroit River, the intakes of the WTPs, and treated drinking water. Of the 51 target substances analyzed, 12 were not detected in any of the samples, while 14 were detected consistently in all samples from the STP effluent. The concentration of target chemicals was two to four orders of magnitude higher in the STP effluents than at the intakes of the WTPs. In total, 10 substances were detected in at least 10% of the drinking water samples. Two compounds, PFOA and PFOS, were found in 90+% of the drinking water samples.

Keywords:

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PC 141

Effect of advanced oxidation processes on Nonylphenol removal with respect to chlorination in the drinking water treatment

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The presence of nonylphenol compounds in water has to be controlled due to be included in the list of Priority Substances and classified as endocrine disrupters. In this study, natural water from Ebro river and fortified with nonylphenol compounds (4n-nonylphenol and technical nonylphenol) is used as sample in order to approach to real situation in drinking water treatment plants. The aim of this work is to compare conventional disinfection and the following advanced processes (O_3, O_3/H_2O_2, O_3/TiO_2 and $O_3/H_2O_2/TiO_2$) used for the removal of nonylphenol compounds present in natural water. Furthermore, a study of the by-products (THMs) generation as a consequence of natural organic matter presence is carried out. Preoxidation by chlorine completely degrades 4n-nonylphenol and technical nonylphenol. Respect to advanced oxidation processes, it can be seen that the best AOPs correspond to O_3/H_2O_2 process achieving an average removal of 55% although the differences among the processes were not very important. Furthermore, the use of post-chlorination guarantee the total removal of these compounds. Taking into account the current Spanish legislation (Royal Decree 140/2003) the conventional disinfection doesn't observe the maximum concentration of $\sum$THMs (100 $\mu g\ l^{-1}$) in water from now on.

Keywords:

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Advanced Oxidation Processes for the Elimination of Drugs Resisting Biological Membrane Treatment

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The recalcitrant pharmaceutical compounds carbamazepine, clofibrinic acid diazepam, and diclofenac were monitored in municipal wastewater by ESI-LC-MS and -MS-MS in positive and negative mode. While biological treatment by conventional and membrane bioreactor failed, the advanced oxidation methods using ozone (O_3), O_3/UV or hydrogen peroxide in combination with UV (H_2O_2/UV) successfully achieved their complete elimination. Target compounds could be confirmed as permanently present pollutants in Aachen-Soers wastewater in concentrations between 0.006 and 1.9 $\mu g\ l^{-1}$ prior to AOP treatment resulting in a complete elimination.

Keywords:
Advanced Oxidation Process (AOP), Biological wastewater treatment, Degradation products, Mass and tandem mass spectrometry, Polar pharmaceuticals

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Degradation of Sulfamethoxazole and Chlortetracycline using a UV, Ozone and Electron beam

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Recently, the occurrence of antibiotics in the aquatic environment as well as in finished drinking water has raised a concern about their potential impact on environmental and public health. Antibiotics are found in surface and ground waters which indicates their ineffective removal by conventional water treatment technologies. Advanced oxidation processes (AOPs) have received considerable attention for antibiotic removal. This study were conducted to evaluate the degradation and mineralization of antibiotics (sulfamethoxazole and chlortetracycline) using ozone, UV, and electron beam.

The results of this study showed that ozone, UV and electron beam were very effective for the removal of sulfamethoxazole and chlortetracycline in aqueous solution. Besides, the electrical energy consumption based on the EE/O parameter (the electrical energy required per order of pollutants removal in 1m^3 wastewater) was used to quantify the energy cost associated with different AOPs (UV, Ozone, Electron beam) for degradation of antibiotics. In view of the electrical energy efficiency, the electron beam was better than ozone and UV.

Keywords:
Sulfamethoxazole, chlortetracycline, UV, ozone, electron beam

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Poster
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Efficiency, costs and benefits of AOPs for removal of pharmaceuticals from the water cycle

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Different advanced oxidation processes (AOP) were developed for the treatment of highly loaded waste water streams. Optimisation of removal and improvement of efficiency was realized on a laboratory, semiworks and pilot plant scale. The persistent cytostatic drug cyclophosphamide was selected as a reference substance regarding elimination and evaluation of the various oxidation processes because of its low degradability rate. The investigated processes are cost-efficient and suitable regarding the treatment of waste water streams since they lead to efficient elimination of antibiotics and antineoplastics. A total reduction of toxicity was proven by means of the umuC-test. However, in order to reduce pharmaceuticals from the water cycle, it must be considered that more than 80 % of the pharmaceuticals are coming from private households. Therefore, advanced technologies should be installed at the end of waste water treatment plants. Ozonisation and activated carbon are technically and economically feasible.

Keywords:
AOP, LC-MS/MS, ozone, pharmaceuticals, waste water treatment

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Poster
PPCP/EDC
PC 210

Experience with an Ozonation Pilot Plant for further Treatment of Municipal Wastewater

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The presence of endocrine disrupting compounds (EDCs), pharmaceuticals and personal care products (PPCPs) in the effluent of municipal wastewater treatment plants raises the discussion on potential methods for further treatment. Ozonation proved to be a suitable technology in experiments on laboratory and pilot-scale. While ozonation represents best available technology in water treatment hardly any experience is available with regard to full-scale ozonation of the effluent of wastewater treatment plants. The dynamic matrix of effluent as to the chemistry and flow variations is only one of the challenges. For process control the spectral absorption coefficient at 254 nm was investigated. In the present study the ozonation of tertiary effluent of a two-stage activated sludge plant was investigated on pilot-scale. First results are given for the removal of micropollutants and disinfection. For a specific ozone consumption of 0.9 – 1 g O_3/g DOC_0 the removal efficiency of the analysed micropollutants ranged between 40 and > 99%. The estrogenicity of the tertiary effluent could

also be decreased. In order to investigate potential negative impacts of an ozonation step on the effluent standardized ecotoxicology tests were made. No increase in ecotoxicology of the ozonated samples could be detected. Hygienic water quality parameters for bathing waters regulated in the European bathing water directive could be met for both *Escherichia coli* and the *Intestinal enterococci*. Overall, ozonation proved to be a promising technology for the investigated micropollutants and hygienic parameters.

Keywords:
Ozonation; municipal wastewater; advanced treatment

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Reduction of biocide-polluted wastewater by the oxidation processes O_3 and H_2O_2/O_3

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The aim of this research work is the study and testing of various oxidation processes for refractory compounds decomposition for the purpose of reducing the concentration and toxicity of biocide wastewater from Slovene phytopharmaceutical factory. The experimental work was focused on the reduction of environmental load caused by toxic wastewater that originated from the production of isothiazolones, Kathon 886 F and Kathon LX. Lab scale experiments employing two AOP processes, ozonation (O_3) and Peroxone (H_2O_2/O_3), were applied to reduce the concentration of involved active components, methylisothiazolone (MI), chloromethylisothiazolone (CMI) and dichloromethylisothiazolone (DCMI). The reduction of biocide wastewater load for the performed oxidation processes was evaluated by the ecological parameters such as pH, COD, BOD, TOC, AOX and toxicity (Daphnia magna). The active isothiazolones' components concentrations were measured via HPLC prior to and after the treatment.

The H_2O_2/O_3 oxidation procedure by O_3 flow rate 1g/h, at pH value 10 and with the addition of 5 ml H_2O_2 (0,3 M) proved as the most effective treatment, where there was a significant removal of all the analyzed parameters: COD 91%, TOC 54% and AOX 98% according to the initial values. At the same time, the active isothiazolones' components were almost completely removed (99%). The toxicity of biocide-load wastewater with initial EC_{50} = 0.38%, decreased to EC_{50} (24h) >100% and EC_{50} (48h) = 76%.

Keywords:
Biocide wastewater; chloromethylisothiazolone (CMI); dichloromethylisothiazolone (DCMI)); Peroxone (H_2O_2/O_3); Kathon; methylisothiazolone (MI); ozonation (O_3); phytopharmaceutical factory

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Poster
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Ozone applied to treatment and disinfection of hospital effluent

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The objective of this work was the investigation of the performance of ozone as a tertiary treatment of a hospital effluent biologically treated. The quality of final effluent was evaluated by physicochemical and microbiological parameters. The toxic potential of the ozone treatment was investigated in bioassays using *Daphnia similis*. Applied ozone doses ranged from 15 to 135 $mg.L^{-1}$ and the most significant reduction was observed in color and UV_{254} absorbance with maximum efficiency of 97% and

51%, respectively. COD concentration decreased in a linear correlation with the increasing of residual ozone present in solution and maximum abatement was 55%. However, higher residual ozone concentration and higher hydraulic detention times did not represent higher disinfection effectiveness. The disinfection efficiency was dependent on organic matter content and it was verified a linear correlation between total coliforms, *E. coli* inactivation and UV$_{254}$ decaying. In this manner, the parameter UV$_{254}$ absorbance seems to be a useful tool to monitor the disinfection in wastewaters with complex organic matrix as hospital effluents. The acute toxicity increased after elevated ozone doses, probably due to the production of toxic intermediates.

Keywords:
Disinfection, hospital effluent, ozone, toxicity

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Poster
PPCP/EDC
PC 228

Comparison between Several AOPs and Wet Oxidation Technologies for the Removal of Industrial Antibiotics

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In this work, the photocatalytic degradation of the antibiotics oxolinic acid, chlortetracycline and thiamphenicol using ozone and ozone:UV as a function of pH and antibiotic concentration was studied. The analysis was planned as a Response Surface, in order to determine the best affordable experimental conditions to the chemical depletion of these industrially used antibiotics at salmon farms. Results shown complete elimination of the two firsts compounds before one hour, with the sulphide-containing substrate being more resistant for photocatalytic removal.

Keywords:
Ozone: UV, photocatalysis, industrial antibiotics, AOPs, salmon farms

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Poster
PPCP/EDC
PC 230

Decomposition and Detoxification of Antibiotics by Ionizing Radiation

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One considerable concern for antibiotics is the potential development of antibiotic-resistant bacteria in the environment, even at low concentrations. Kinetic experiments were conducted to compare two kinetic models for radiolytic decomposition of various antibiotics such as cephradine, amoxicillin, sulfamethazine, tetracycline, and lincomycin. All the antibiotics were completely decomposed at 1-4 kGy. The biological toxicities of the antibiotics after irradiation were also clearly reduced. Batch kinetic experiments with the initial aqueous concentrations of 2, 6, 8, 20 mg/L showed the decomposition of antibiotics using gamma radiation followed a pseudo first-order reaction, and the dose constant increased with lower initial concentrations. For the comparison of kinetic models, the Monod equation was used. The kinetic parameters of maximum reaction rates (k_{max}) and half-velocity coefficient (K_s) are obtained. The k_{max} values ranged from 0.29 to 0.99 µM/Gy. The K_s values for antibiotics decreased in the order of: cephradine > lincomycin > amoxicillin > sulfamethazine > tetracycline. Radiolytic decomposition of antibiotics by gamma radiation was well described by both a pseudo first-order reaction and the Monod equation. The inhibition experiments were performed to investigate the inhibition effects of the anions in municipal wastewater on the radiolytic decomposition of the antibiotics. The experimental results showed that nitrate and nitrate had significant inhibition effects, but relatively insignificant effects were observed for the other anions such as phosphate, chloride, and sulfate.

Keywords:
radiation, antibiotics, kinetics, inhibition

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Poster
PPCP/EDC
PC 235

Enhancement of carboxylic acids degradation with Sulfate Radical generated by persulfate activation

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The aim of this work was to investigate the generation of sulfate radical for the removal of two carboxylic acids in aqueous solution: acetic and citric acids.

The kinetic of degradation of these two carboxylic acids was studied as a function of the pH of the solution. The results of kinetics and mineralization were also compared with the H_2O_2/UV system.

The study performed on the pH impact shows that a maximum degradation of acetic acid occurred at pH 5. Above this pH, competitive reactions with the carbon mineralized inhibit the reaction of $SO_4^{\cdot-}$ and also $OH^{\cdot}$ with the solute. In the case of citric acid, pH has only a little effect on the kinetic of citric acid degradation. The determination of the mineralization yields shows several differences based on carboxylic acids, photochemical chemical systems and pH. The $S_2O_8^{2-}$/UV system provides a better yield of mineralization of the acetic acid compared to the H_2O_2/UV system.

Keywords:
Mineralization; Oxidation; Sulfate radical; Acetic acid; Citric acid

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PC 243

Degradation of Sulfamethoxazole in Wastewater Using Ozonation

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Sulfamethoxazole (SMX) is an antibiotic widely used by both humans and animals. Once excreted, it makes its way to wastewater treatment plants where the treatment processes cannot significantly remove it. In this work, 60 mg/L and 100 µg/L solutions of SMX in both reverse osmosis (RO) water and wastewater were treated with ozone. The degradation profile of SMX and its degradation products were monitored as a function of ozone dose in both matrices. No difference was observed in the ozone dose required for the concentration to fall below the limit of detection in RO water and wastewater, and the same peaks (degradation products) were obtained for both concentrations. Solutions with an initial concentration of 60 mg/L required 331 mg/L of ozone and eight degradation products were detected during the treatment.. Solutions with an initial concentration of 100 µg/L required 55 mg/L of ozone to fall below the limit of detection and only four degradation products were detected. The four peaks obtained during experiments at low concentration were observed at the same retention times as four of the peaks obtained in higher concentration samples. The hypothesis that these are the same products is currently under investigation.

Keywords:
Degradation Products; ozone; pharmaceutical; sulfamethoxazole; toxicity; wastewater

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Fate of Triclocarban during Soil Aquifer Treatment

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- No abstract submitted. -
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Heterogeneous Photocatalytic Degradation of the Antiseptic Triclocarban

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- No abstract submitted. -
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Oxidation of sulfamethoxazole by UVA radiation and modified Fenton reagent: toxicity and biodegradability of by-products

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Improvement of sulfamethoxazole biodegradability using a modified Fenton's reaction has been studied. The modification consists of replacing hydrogen peroxide with atmospheric air and adding copper sulphate as a reaction promoter. Two series of experiments were carried out. The first (Series 1) was conducted using only the catalysts with aeration. In the second series (Series 2), cycles of UVA radiation and aeraton were used. During UVA radiation, the removal of sulfamethoxazole proceeds less rapidly than in only aerated solution. After 1.5 h of these two processes, the SMX degradation was 23% in Series 2 and 59% in Series 1. The opposite trend was observed for mineralization and the removal of DOC was about 5% higher in Series 2 than in Series 1.

The FTIR spectra of the extracts of reaction products yielded by four organic solvents of varying polarity revealed a wide diversity of functional groups in the post-reaction mixture in comparison to the extracts from sulfamethoxazole solution. Based on FTIR analysis, several oxidation products of sulfamethoxazole are proposed. Apparently, hydroxyl radicals initially attack sulphonamide bonds, resulting in the formation of sulfanilic acid and 3-amino-5-methylisoxazole.

Irrespective of the reference organism used in toxicity tests, the post-reaction mixture in the Series 2 was more toxic than the post-reaction mixture in Series 1. In contrast, the biodegradability calculated as BOD_5/DOC ratio, was higher for post-reaction mixture 2 and amounted to 0.43.

Keywords:
Bioassays, FTIR, modified Fenton's reaction, Sulfamethoxazole, UV – radiation

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Poster
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PC 265

Innovative oxidation techniques for elimination of active substances from pharmaceutical production

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Active pharmaceutical ingredients cause great problems in wastewater from the production process and its conditioning. Known wastewater treatment procedures and also Advanced Oxidation Process-applications as the PEROXON process and the UV-PEROX-method often do not lead to success.
Therefore, innovative solutions were investigated and the determined active substance degraded.
Target of these investigations were to work out an effective advanced oxidation process-application based on the combination of electrochemical, photochemical and catalytic reactions to achieve the environmental harmlessness of this water.
Best results were achieved with an alike electro-photochemical FENTON-reaction based on cathodically produced hydrogen peroxide.

Keywords:
cathodic hydrogen peroxide, FENTON-reaction, pharmaceutical ingredients

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Modeling the reaction kinetics and product identification of linuron decay by UV/O_3 process

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The degradation of a phenylurea herbicide, linuron (LNR), which has been classified as a possible human carcinogen, was investigated by using UV/O_3 process. The decay rate of LNR by UV/O_3 boosted up from 0.154 to 0.711 min^{-1} as the initial pH increasing from 3.0 to 10.0. It was also found that the apparent rate constants of LNR decay increase linearly with the concentration of ozone while they decrease from 1.44 to 0.242 min^{-1} as the concentration of LNR increasing from 0.0304 mM to 0.160 mM. A linear model was successfully developed for the prediction of LNR decay at different initial [O_3], [LNR] and pH level in the UV/O_3 process. *N*-demethylation, *N*-demethoxylation, and chlorine substitution have been found to be the main degradation mechanisms of LNR by UV/O_3 process at the first step. A primary decay pathway was proposed on the basis of five identified intermediates.

Keywords:
Linuron; ozone; rate constant; intermediates; decay pathway

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Poster
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Eliminination of pharmaceuticals from treated wastewater by uv-oxidation

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** *IFZ, Justus-Liebig-University Giessen, Giessen, Germany*
*** *UVitt GmbH, Taunusstein, Germany*

Micropollutants like pharmaceuticals are often hardly removed in conventional wastewater treatment plants. Advanced oxidation processes (AOP) like uv-oxidation are capable of eliminating these micropollutants. A special uv-reactor, producing its own ozone, was used for uv-oxidation of micropollutants from conventionally treated wastewater from the wastewater treatment plant of Giessen, Germany. The uv-reactor contained 3 amalgam uv-lights (each having 60 watt) that produce ozone in the gas chamber and emit uv-light into the water running in the inner tube. The ozone enriched gas is injected into the water stream circulating in the system. The whole system was run in a batch mode. In the gas phase ozone concentrations of 0.7 g/m³ were reached. Carbamacepine, naproxen and diclofenac were already eliminated after a treatment time of 20

minutes and hormones after 15 minutes below detection limit respectively.

Keywords:
uv-oxidation, pharmaceuticals, hormones, wastewater

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