Ozone and Related Oxidants
for Water Treatment

December 2 – 3, 2013
Shanghai, China

Programme and Book of Abstracts

With the support of
The European African Asian Australasian Group of the International Ozone Association is organizing an International Conference entitled Ozone and Related Oxidants for Water Treatment in Shanghai, China. This event continues a long series of successful conferences organised worldwide to provide an international forum for all concerned with fundamental, engineering and applied aspects of oxidation technologies involving ozone and related oxidants. IOA-EA3G Shanghai 2013, organised in cooperation with Tongji University is a unique opportunity to enhance your knowledge about the potentialities offered by ozone and related oxidants in all fields of the water treatment in relation with the current and next challenges.

**Scope and objectives**

The earth’s water supply remains constant, but man is capable of altering the cycle of that fixed supply. Population increases, rising living standards, food consumption and industrial and economic growth place greater demands on our natural environment. Human overuse of water resources and contamination of freshwater are stressing the water resources in the terrestrial water cycle. Our activities affect the quantity and quality of natural water resources available to current and future generations. Health risks associated with contaminated water and wastewater, continuous degradation of aquatic environment and water scarcity issues are contributing to the growth of the use of advanced technologies for water treatment. This event will provide an overview of the current state of knowledge and latest advances regarding the use of Ozone and Related Oxidants for providing solutions to meet this goal and contribute to a sustainable water management.

The topics of interest connected to the Conference theme include but are not limited to the combinations of:

- Ozone oxidation
- Advanced oxidation
- Drinking water
- Process water
- Urban wastewater
- Industrial wastewater
- Water reuse
- Water recycling
- Disinfection, micro-organisms
- Reactions, kinetics, by-products
- Persistent pollutants, micropollutants
- Hydraulics, Hydrodynamics, mass transfer
- System design, process
- Case studies

**The Organizer and the Host**

The International Ozone Association is a non-profit organization dedicated to the development of educational and scientific activities to respond at the best to the needs of industry and research community in the field of ozone and derived oxidants.

The Association operates through three Regional Groups. The EA3G Group manages membership and develops activities in Europe, Africa, Asia and Australasia.

Since its foundation in 1973, the IOA is at the forefront in connecting professionals around the globe involved and interested in ozone-related issues including scientists, researchers, engineers, system designers, technologists, equipment manufacturers, consultants, users and members of governmental agencies.

Typical topics covered in the activities program are ozone generation, secondary oxidant generation, gas mass transfer, chemical reactions of ozone in gas and liquid phases, engineering aspects, water treatment for disinfection and pollutants removal, oxidation for food processing, for pulp bleaching, for products manufacture, and conditioning, development of analytical procedures and materials, development of equipments for ozone use, development and applications of advanced oxidation processes, safety and health effects.

www.ioa-ea3g.org

Tongji University is one of the leading universities directly under the State Ministry of Education in China. It offers degree programs both at undergraduate and postgraduate levels. The university has School of Sciences, School of Architecture and Urban Planning, School of Civil Engineering, Mechanical School, School of Environmental Science and Engineering, School of Material Science and Engineering, School of Electronics and Information Engineering, School of Transportation, Medical School, School of Liberal Arts and Law, School of Foreign Languages, School of Economics and Management, School of Software Engineering, school of Ocean and Earth Science. In addition, there are Institute of Further Education, Institute of Higher Technology, Institute of Vocational and Technical Education, Institute of E-Education, Women's College, Institute of Automobile Marketing and Sino-German Institute which is authorized by Chinese and German governments to run postgraduate courses. There are also six university hospitals located in different campuses.

The university now registers over 50,000 students at all levels from certificate and diploma courses to Bachelors Degrees, Masters, PhD programs and post-doctoral attachments. There are over 4200 academic staff for teaching and/or research. As one of the state leading centers for scientific research, the university has 22 state key laboratories and engineering research centers.

http://sese.tongji.edu.cn/
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SPECIAL ACKNOWLEDGEMENTS AND CONTRIBUTIONS

The success in the organization of this event results from the strong involvement of many individuals and from the generous contributions of corporate sponsors.

The Organizers would like herewith to acknowledge the support given by the following partners:

Host of the conference and local organizer

http://unep-iesd.tongji.edu.cn/

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GENERAL INFORMATION

> Language
The official language will be English.

> Conference venue
The Conference venue is: 902 Zonghe Building, Tongji University, Shanghai, China.

> Registration
Registration will be managed by Tongji University organizers. The fee are as follows:
- Registration full rate: 2000 RMB
- Registration IOA member rate: 1500 RMB
- Registration Student rate*: 1300 RMB

These registration fees will cover scientific and technical sessions, book of abstracts, lunches, coffee breaks and technical tour.
*Valid Student ID is required for this registration.

> Welcoming desk
It will be opened during the conference as follow:
- Monday 2nd December 9:00 – 17:00
- Tuesday 3rd December 8:30 – 11:40

> Coffee and Lunch breaks
Complimentary coffee and drinks will be available at the scheduled break times. Each day, the lunch will be offered as part of the registration fees.

> Arriving by public transportation
Metro Line 10 - Tongji university Station

> Tourism
Visit the Official Shanghai China Travel Website:
http://www.meet-in-shanghai.net/

> Liability and insurance
Registration for the Conference implies that the delegate agrees that neither the Organizers assume any liability whatsoever. Delegates are requested to make their own arrangements for medical, travel and personal insurance.

> Disclaimer
The Organizers may at any time, with or without giving notice, in their absolute discretion and without giving any reason, change the Conference programme and withdraw any invitation to attend. In any case, neither the organizers nor any of their officers employees, agents, members or representatives shall be liable for any loss, liability, damage or expense suffered or incurred by any person, nor will they return any money paid to them in connection with the Conference unless they are satisfied not only that the money in question remains under their control, but also that the person who paid it has been unfairly prejudiced (as to which the decision shall be in their sole and unfettered discretion, and when announced, final and conclusive).

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The two-day conference will feature scientific and technical presentations, one poster presentation with introduction platform, discussions and networking opportunities. Near 20 presentations were selected by the Programme Committee and arranged according to the following sessions:

### Monday 2\textsuperscript{nd} December

<table>
<thead>
<tr>
<th>Time</th>
<th>Event</th>
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</thead>
<tbody>
<tr>
<td>9:00-10:00</td>
<td>Registration</td>
</tr>
<tr>
<td>10:00-10:30</td>
<td>Opening Ceremony</td>
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<tr>
<td>10:30-12:00</td>
<td>Session 1. Ozone applications</td>
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<tr>
<td>12:00</td>
<td>Lunch</td>
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<tr>
<td>13:30-15:30</td>
<td>Session 2. Advanced Oxidation</td>
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<tr>
<td>15:30</td>
<td>Coffee break</td>
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<tr>
<td>16:00-17:00</td>
<td>Session 3. Ozone mass transfer contacting systems</td>
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### Tuesday 3\textsuperscript{rd} December

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<th>Time</th>
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<tr>
<td>8:30-9:50</td>
<td>Session 4. Industrial Water</td>
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<td>9:50</td>
<td>Coffee break</td>
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<td>10:20-11:20</td>
<td>Session 4. Industrial Water (cont’d)</td>
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<td>11:20-11:40</td>
<td>Conclusions</td>
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<td>11:40</td>
<td>Lunch</td>
</tr>
<tr>
<td>13:00-18:00</td>
<td>Technical visits</td>
</tr>
</tbody>
</table>

> **Technical visits**

Access is allowed by kind permission of the plant operators and owners and upon registration only. Valid passport is required.

**Shanghai Chemical Industrial Park Natural Treatment System, Shanghai, China**

Located on the coast of Hangzhou Bay, the 3000 hectare Shanghai Chemical Industrial Park (SCIP) consists of more than a dozen modern petrochemical industrial facilities. Based on the special demand of the client, our master planning professionals designed a water treatment system to purify industrial wastewater effluent for recycling within the industrial park and discharge to Hangzhou Bay. The unique characteristics of the wastewater require a rigorous, engineered approach to water quality improvement and as the design lead for the project, we created a 30 hectare Natural Wastewater Treatment System, one that will treat over 22,000 m\(^3\)/day of partially-treated industrial wastewater.

**Taicang No.3 water treatment plant. Jiangsu Province.**
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<th>Time</th>
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<tr>
<td>9h00-10h00</td>
<td>Registration</td>
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<tr>
<td>10h00-10h30</td>
<td><strong>Opening ceremony</strong></td>
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<td><strong>IOA and Conference introduction</strong></td>
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<tr>
<td></td>
<td>Prof. Santiago Esplugas (IOA-EA3G President Elect, Spain)</td>
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<td></td>
<td><strong>Research in Tongji University</strong></td>
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<td></td>
<td>Prof. GAO Naiyun (China)</td>
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<tr>
<td>10h30-12h00</td>
<td><strong>Session 1. Ozone applications</strong></td>
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<tr>
<td></td>
<td>Chair Person: Prof. DAI Xiaohu</td>
</tr>
<tr>
<td>10h30-10h50</td>
<td>1.1 Challenges to meet essential human needs: Why and what for ozone and related oxidants can serve?</td>
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<tr>
<td></td>
<td>S. Baig, M. Roustan (IOA Past President and IOA-EA3G Vice-President, France)</td>
</tr>
<tr>
<td>10h50-11h10</td>
<td>1.2 Ozonation and adsorption for the control organic matter and micropollutants discharges from urban wastewater effluents</td>
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<tr>
<td></td>
<td>B. Domenjoud, S. Esplugas, S. Baig (Spain, France)</td>
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<tr>
<td>11h10-11h30</td>
<td>1.3 Reuse of ozone vent gas for aeration at a wastewater treatment plant</td>
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<td></td>
<td>Y. Lu, S. Shi, R. B. Marx, W. Rong, M. Fabiyi, A. Gupta (China, USA)</td>
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<tr>
<td>11h30-11h50</td>
<td>1.4 Organophosphorous flame retardants oxidation by ozone: water matrix effects</td>
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<td></td>
<td>J. Cristale, X. Yuan, R. Falcao, S. Lacorte, C. Sans, Z. Qiang, S. Esplugas (Spain, China)</td>
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<tr>
<td>11h50-12h00</td>
<td>Discussions</td>
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<td>12h00</td>
<td>Lunch</td>
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<tr>
<td>13h30-15h30</td>
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<td>Chair Person: Prof. ZHOU Qi</td>
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<tr>
<td>13h30-13h50</td>
<td>2.1 Cobalt Doping Red Mud Catalytic Ozonation for Degradation Bezafibrate from WasteWater</td>
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<td></td>
<td>H.N. Li, L.L. Han, B.B. Xu, F. Qi, D.Z. Sun (P.R. China)</td>
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<tr>
<td>13h50-14h10</td>
<td>2.2 Study on Catalytic Effect of Activated Carbon in the Ozonation of Reactive Black S</td>
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<td>H. He, D. Wu (P.R. China)</td>
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<td>14h00-14h30</td>
<td>2.3 Heterogenous catalytic ozonation of organic pollutant in water with mesoporous manganese oxide as catalyst</td>
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<td>M. Sui, L. Sheng, W. Jie (P.R. China)</td>
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<tr>
<td>14h30-14h50</td>
<td>2.4 Factors affecting UV/H2O2 inactivation of Bacillus subtilis spores in drinking water</td>
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<td>Y. Zhang, Y. Zhang (P.R. China)</td>
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<tr>
<td>14h50-15h10</td>
<td>2.5 Ozone and Ozone Based AOP for the Removal of Taste and Odour and Emerging Organic Substances in Drinking Water Plant</td>
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<td>J. Wang, A. Ried, Z. Shao, M. Ma (Germany, China)</td>
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<tr>
<td>15h10-15h30</td>
<td>Discussion</td>
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<td>15h30-16h00</td>
<td>Coffee break</td>
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<tr>
<td>16h00-17h00</td>
<td><strong>Session 3. Ozone mass transfer contacting systems</strong></td>
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<td>Chair Person: Prof. ESPLUGAS Santiago</td>
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<tr>
<td>16h00-16h20</td>
<td>3.1 Evaluation of mass transfer and gas-liquid equilibrium of high concentration gaseous ozone</td>
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<tr>
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<td>T. Mizuno, H. Tsuno (Japan)</td>
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<tr>
<td>16h20-16h40</td>
<td>3.2 How to make the contact between ozone and waters?</td>
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<tr>
<td></td>
<td>S. Baig, M. Roustan (France)</td>
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<tr>
<td>16h40-17h00</td>
<td>3.3 Effects of ozone on live fish logistics</td>
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<td>H. Liqun Hou, T. Chen, G. Yuk-sing Chan (Hong Kong)</td>
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<td>Time</td>
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<tr>
<td>8h30-8h50</td>
<td><strong>4.1 Synergistic chemical / biological oxidation coupling ozonation and biofiltration for advanced treatment and reuse of industrial wastewaters</strong></td>
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<tr>
<td>8h50-9h10</td>
<td><strong>4.2 Removal of Active Pharmaceutical Ingredients (APIs) from Wastewater—a review of existing treatment solutions</strong></td>
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<td>9h10-9h30</td>
<td><strong>4.3 Decolorization of Effluent water from Pulp and Paper Mill in Thailand by Ozonation</strong></td>
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<td>9h30-9h50</td>
<td><strong>4.4 Application of ozone oxidation of secondary effluent in wastewater treatment plant</strong></td>
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<tr>
<td>9h50-10h20</td>
<td>Coffee break</td>
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<tr>
<td>10h20-10h40</td>
<td><strong>4.5 The Color Removal of Brewery Wastewater with Ozonation in Thailand</strong></td>
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<td>10h40-11h00</td>
<td><strong>4.6 Ozone to Control Bulking and Foaming in Municipal Waste Water Treatment Plants</strong></td>
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<tr>
<td>11h00-11h20</td>
<td><strong>4.7 Application of 2 stage Ozone/Hydrogen Peroxyde AOP system for mixed effluent wastewater treatment</strong></td>
</tr>
<tr>
<td>11h20-11h40</td>
<td>Conclusions</td>
</tr>
<tr>
<td>11h40-12h45</td>
<td>Lunch</td>
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COMPLEX PROBLEMS REQUIRE RADICAL SOLUTIONS

As a world leader in ozone oxidation systems, OZONIA designs and manufactures ozone generators, UV systems and AOP solutions incorporating the most sophisticated electronics technology available.

Ozone and AOP, thanks to their high oxidation potentials, have proved to be the most efficient solution for the removal of the most recalcitrant pollutants.

PRODUCT HIGHLIGHTS

OZAT® CFV Series
> High production rates from 1.24 to 25.7kg O₃/h from oxygen
> High ozone concentration at full-load
> Robust non-glass dielectrics
> Robust industrial quality for reliability and long service life
> Skid mounted with a small footprint for easy integration
> Complete containerized systems available

For more information please visit our website at:
WWW.OZONIA.COM
sales@ozonia.com
The International Ozone Association
The International Ozone Association is a non-profit educational and scientific organisation dedicated to the collection and dissemination of information on, and to promote research in, any and all aspects of ozone and related oxygen species technologies.

In 1973, the professionals from industry and research sectors created the International Ozone Association as network dedicated to support the growth of ozone application in all fields. Since its foundation, the IOA is at the forefront in connecting professionals around the globe involved and interested in ozone-related issues including scientists, researchers, engineers, system designers, technologists, equipment manufacturers, consultants, end users and members of governmental agencies.

The Association groups together almost 1300 members representing the world’s leading edge of ozone and related oxidants specialists from various disciplines through three regional groups.

The Association is thus in the first position to help professionals interested in any ozone related topics by offering them many services: publications, taylor-made events, promotion of research programs, quality assurance papers, regulations overview...

Ozone and its applications
The use of ozone was made possible through the development of ozone generators mainly based on corona discharge applied to oxygen-containing gas. The latter directly installed on the use site permit to make the most of the oxidizing properties of ozone in various fields since the beginning of nineties.

Ozone can serve in any case where an effective oxidizing action is required on natural, organic, inorganic, mineral, biological, gaseous, liquid or solid substances: disinfection (destruction of pathogenic germs in water, gas, equipment, packaging...), pollutants removal with biodegradability increase, decolorization, COD abatement, VOCs elimination, reduction in toxicity, degradation of specific compounds (from water, air, surface...), conversion and purification of products (chemicals, natural products), therapy purpose...

- Water purification: drinking water, bottled water, swimming pools, industrial wastewaters cooling towers, groundwater remediation, wastewater re-use.
- Air purification: gas emissions from industry, conditioning system.
- Pulp bleaching for chlorine-free production of paper.
- Organic synthesis.
- Aquaculture and fish farming.
- Food processing: rinsing water, food preservation.
- Surface treatment: semiconductor manufacture, inorganics production.
- ...

Ozone based process
Ozone is generated using air or pure oxygen and electric energy. Typical ozone plant includes system for air or oxygen supply, generator, reactor equipped with gas diffusion device, equipment for monitoring and destruction of ozone in excess into oxygen.

Topics covered in the Association activities
The self-managed EA3G group represents the living strength of IOA in about 40 countries. Its mission is to develop activities to respond at the best to the needs of the regional industry and research community in the field of ozone, derived oxidants and comparable oxidants.

Topics covered in the activities program include: ozone generation, gas mass transfer, chemical reactions of ozone in gas and liquid phases, engineering aspects, water treatment for disinfection and pollutants removal, oxidation for food processing, for pulp bleaching, for products manufacture and conditioning, development of analytical procedures and materials, development of equipments for ozone use, development and applications of advanced oxidation processes, ozone safety and health effects.
Current programme: A conference focused on Ozone and Related Oxidants for Water Treatment

Organised with the objectives:

- To provide an overview of the current state of knowledge regarding the use of ozone and related advanced oxidants
- To interface with scientists, researchers, students, engineers, users, technical experts, representatives of leading organizations from various disciplines,
- To share the latest information on research topics, current issues, technologies under development, new applications, full-scale experiences and equipments and products,
- To find solutions to address scientific and technical challenges.
- To support the development of ozone-related activities in China thanks to local collaborations and finally the enlargement of the IOA network.

The final programme includes 21 presentations arranged on four major topics:

- Ozone applications
- Advanced oxidation
- Ozone mass transfer contacting systems
- Industrial Waters

Literature

The following selection of papers published in Ozone: Science & Engineering illustrates the knowledge in ozone science and the expertise degree of professionals that you can meet through IOA.


Ozone has been used increasingly popular in drinking water treatment of waterworks in Yangtze River Delta of China. Among the flow diagram of drinking water treatment processes, there are two processes applied ozone, pre-ozonation and post-ozonation-biological activated carbon (O3-BAC) for micro-polluted source water treatment.

Our group have been studying on Ozone (O3) and Ozone based oxidation processes for several years. During the ozone based oxidation processes, combined Ozone with peroxide process (O3/H2O2) and combined Ozone with biological activated carbon process (O3-BAC) and O3 pretreatment were studied in depth for pollutant removal. Our research is focused on several subjects, such as, taste and Odor compound removal by O3 and O3/H2O2, pharmaceutical and personal Care Products (PPCPs) removal by O3 and O3/H2O2, precursors of halogenated nitrogenous disinfection by-products removal in O3-BAC) system, Huangpu River water treatment by microfiltration with O3 pretreatment, and so on.
CHALLENGES TO MEET ESSENTIAL HUMAN NEEDS:  
WHY OZONE AND RELATED OXIDANTS CAN SERVE?  

S. Baig, M. Roustan  
IOA Past President and IOA-EA3G Vice-President, France

Key-words: Ozone, Water, Energy, Agri-food

The world’s population is growing by about 80 million people a year and will reach 8 billion by 2030 with 60 % of urban dwellers. Together with population growth and urbanisation, growth in globalisation and wealth is forcing rapid changes such as industrialisation and extensive agriculture, these last in association with rising living standards and changing food and water consumption patterns. This unprecedented expansion poses an array of critical challenges related to the sustainable use of natural resources for provision of basic human needs such as safe drinking water, food, energy, materials. While protecting the environment and human health through adequate control of pollution discharge and development of green processes for the industry fields of agri-food, production & transformation process, energy and water treatment. This introduction will provide an overview of opportunities offered to ozone and related oxidants for providing solutions to meet these challenges.

The use of ozone was made possible through the development of ozone generators mainly based on corona discharge applied to oxygen-containing gas. The latter directly installed on the use site permit to make the most of the oxidizing properties of ozone in various fields since the beginning of nineties. Ozone can serve in any case where an effective oxidizing action is required on natural, organic, inorganic, mineral, biological, gaseous, liquid or solid substances: disinfection (destruction of pathogenic germs in water, gas, equipment, packaging…), pollutants removal with biodegradability increase, decolorization, COD abatement, VOCs elimination, reduction in toxicity, degradation of specific compounds (from water, air, surface…), conversion and purification of products (chemicals, natural products), therapy purpose...

In water treatment field, ozone was used as early as 1893 for disinfection of drinking water in Holland. Full scale ozone application in water treatment goes back to 1904 with the installation for drinking water production in Nice, France. By 1980, there were over 1100 water treatment facilities utilizing ozone, mostly in Europe. Ozone treatment of drinking water is well established in Europe and now grows in North America. Ozone has been used in the USA since 1979, beginning with a water treatment plant in Monroe, Michigan. It was implemented in Quebec, Canada, in the early 1980s and is now gaining in popularity in other provinces. Ozonation for drinking water provides several key benefits such as disinfection and Disinfection By-Product Product control. Use of ozone is increasing because very often, several benefits are achieved at the same time. This ability to achieve multiple benefits has increased ozone’s role in current water treatment practice. Europe has pioneered the development of ozone application in the production of drinking water that has over 2000 references. The North American continent has taken over from the 1970s in the field of disinfection of urban wastewater as an alternative to chlorination.

Today, the increase in the number of treatment plants worldwide equipped with an ozonation facility has been supported by several factors: the significant progress on the performance of ozone generators, advances in the design of ozone contactors, demonstration of the effectiveness of ozone to meet various objectives.
Challenges to meet essential human needs: Why and what for ozone and related oxidants can serve

Sylvie Baig¹, Michel Roustan²
1- IOA Past President
Degremont Head of Scientific Innovation
2 – IOA-EA4G Vice President
INSA Toulouse, Emeritus Professor

Basic human needs

- Food and water are obvious fundamental needs to keep the body alive, because body needs nutrients and water to work properly.
- Health care. Its implementation is crucial for life.
  - Healthy food and water
  - Well living
    - Industry production
    - Energy
  - ...”

COMMON CHALLENGES

- Worldwide supply
  - Supply of needed quantities
- Food and water bodies preservation
  - Preservation and distribution
- Safety and health issues
- Sustainability

“Meeting the needs of the present without compromising the ability of future generations to meet their own needs” - Human Principles – Expo 2000, World Commission on Environment

Water demand

- One third of the world population faces physical/economical water scarcity.
- Water Stress Index: Withdrawal/Availability ratio

Impact of climate change

- Warmer air, warmer water, ecosystems, water quality
- Change in hydrological cycle, location and amount of precipitation; increased extreme events frequency and strength
- Sea level rise and boundary changes; Change in ocean characteristics

Excessive withdrawal from surface waters and underground aquifers
Pollution of fresh water resources
Inefficient use of freshwater

Global evaluation

1995
2025
Who uses freshwater

- First is agriculture, industry is the second largest user of water. - 4,500 km³ withdrawal/year
- Industrial use of water increases with country income. The amount varies widely from one type of industry to another.

<table>
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<th>Industrial use</th>
<th>Agricultural use</th>
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<td>Consumptive</td>
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</tr>
<tr>
<td>World</td>
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<tr>
<td>Low- and middle income countries</td>
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</table>

Some key figures and drivers

- The world population will increase by 40 to 50% by 2050.
- This population growth is coupled with industrialization and urbanization.
- The whole will result in an increasing demand for water and will have serious consequences on the environment.

- Worldwide supply
- Safety and health issues
- Sustainability
- Over the global availability issue, needs for agriculture, industry and domestic uses will possibly compete.

Water Scarcity - Technical challenges

- Application field of Ozone & Related Oxidants
- Stormwater runoff
- Combined Sewage Overflow
- Resources remediation
  - Groundwater
  - Surface waters
- Policies & Regulations
- Economics
- Risk management
- Carbon footprint
- Technologies for
  - Temporary units / High flows
  - Advanced Treatment
  - Reuse
- Alternative resources
  - Desalination
  - Reuse
  - Fit for use
- Drilling
- Transport
Emerging Contaminants - Advanced treatment

- Mechanisms involved:
  - Key parameters:
    - Volatilization through mixing and aeration: Henry's Law constant (volatility)
    - Adsorption onto suspended solids and sludge: Octanol-water partition coefficient (hydrophobicity)
    - Biological degradation: Solubility, size, structure (biodegradability)
    - Photodegradation at water surface: UV absorption
    - Chemical oxidation: Structure, type, and dose of oxidant
    - Molecular rejection:
      - Molecular weight, molecular radius and length, ionic strength, charge, octanol-water partition coefficient
- Current Advanced treatment:
  - Biological processes with high sludge retention time:
    - NBR - EN
    - MBR
  - Membrane filtration:
    - Nanofiltration
    - Reverse Osmosis
  - Adsorption (Activated carbon)
  - Chemical oxidation:
    - Ozonation
    - AOPs

Need to evaluate both the fate of the parent compounds as well as conjugates and bioactive by-products.

Water and Energy

> World energy needs will grow by 84% over 2007-2050.
> 24.3% CAGR for water treatment equipment in oil & gas, 2010-2016.
> Fossil fuels, Oil & Gas, will still represent more than 60% of primary energy supply involving:
  - More efficient recovery from existing fields (Enhanced Oil recovery)
  - Exploitation of unconventional resources (Oil sands, Very deep offshore production, Shale gas)
> All with potential high environmental impact.

Water is of prime importance for industry

> Water is used as utility in non-strategic processes: cooling, steam generation, sanitation, fire network.
> Water is essential upstream of manufacturing/extraction process: material transport and washing.
> Water has many uses in the manufacturing/extraction process itself (solvent, raw material, equipment cleaning...). In this last application, criteria for water quality depend directly from the industrial process and are production-specific.
> Water related cost can reach up to 25% of the total production cost.
> Water, a highly valuable asset and key element for production sustainability.

- Industry creates more pressure on water resources from the impacts of wastewater discharges and their pollution potential than by the quantity used in production.
### Industrial water cycle – Stakes

- **Process water**: Production adaptation to salinity & organics, variations in raw water, temporary limits for crisis management.
- **Wastewater treatment**: More stringent discharge limits, low costs for recycling/reuse, valorisation under material/energy, reduction of sludge production, reduction of chemicals use.
- **Utility water**: Alternative resource/reuse, better use of waste heat, management of ecotoxins, green process.

### Usual treatment technologies - Ozone

- **Drinking water**: Surface water, seawater, groundwater, wastewater.
- **Process water preparation**:
  - Clarification
  - Filtration
  - Demineralisation
  - Degassing
  - Conditioning
  - Disinfection

- **Wastewater treatment**:
  - Stream-specific solutions:
    - Biological treatment of readily degradable streams
    - Controlled stripping of VOC containing streams
    - Evaporation of brines
    - Carbon adsorption or chemical oxidation of refractory organics

<table>
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<th>Technology area</th>
<th>Technology need</th>
<th>Major driver</th>
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<td>Biological treatment</td>
<td>Reliable treatment regarding the high variability of influents (load and composition) on each industrial sector</td>
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<td>Membrane</td>
<td>Treatment for fouling reduction</td>
<td>Cost</td>
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<td>Modification of membrane surface to limit scaling and fouling</td>
<td>Technology</td>
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<td></td>
<td>Ceramic membranes with catalytic properties</td>
<td>Technology</td>
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<td>Increase of membranes capacity by nanotechnologies</td>
<td>Cost</td>
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<td>Selective separation</td>
<td>Functionalized membrane</td>
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<td></td>
<td>Highly Selective adsorbent easy to regenerate</td>
<td>Business</td>
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<tr>
<td>By-product valorization</td>
<td>Selective separation of valuable mineral compound (e.g. metals)</td>
<td>Cost</td>
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<tr>
<td></td>
<td>Selective separation of organics compounds</td>
<td>Cost</td>
</tr>
<tr>
<td>Salt removal</td>
<td>Salt separative treatment integrated in industrial re-use strategy in order to limit corrosion and scaling</td>
<td>Business</td>
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**Technology needs**

<table>
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<tr>
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<th>Major driver</th>
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<tr>
<td>Brine treatment</td>
<td>Energy saving membrane concentrative treatment</td>
<td>Cost</td>
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<tr>
<td></td>
<td>Energy saving distillation processes</td>
<td>Cost</td>
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<td></td>
<td>Low fouling selective membrane for electrodialysis treatment</td>
<td>Cost</td>
</tr>
<tr>
<td></td>
<td>Evaporation / Crystallization (precipitation or thermal) processes with by-product control</td>
<td>Cost</td>
</tr>
<tr>
<td>Refractory COD</td>
<td>Cost effective oxidative treatments with control of by-products</td>
<td>Regulations</td>
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<tr>
<td>Persistent organics</td>
<td>Combined processes for adsorption, biodegradation and/or oxidation</td>
<td>Regulations</td>
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<td>treatment</td>
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<tr>
<td>Process intensification</td>
<td>Improvement of kinetics, reduction of size units</td>
<td>Technology</td>
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</tbody>
</table>

**Key issues in agri-food chain – Ozone field**

- Depletion and contamination of natural resources
- Pollution and food contamination
- Impacts on
  - Environment
  - Human health

**Challenges in the agri-food industry**

Way forward “Food for life”

- Processes, products and tools that improve health, well-being and longevity.
- Processes, products and tools that build consumer trust in the safe food chain.
- Processes, products and tools to support sustainable and ethical production.
**Foodborne illnesses**

- **Causing agents**
  - Microorganisms
    - Bacteria
    - Viruses
  - Contaminants
    - Persistent Organic Pollutants (POPs)
    - Metals ...
  - Naturally occurring toxins
    - Mycotoxins (aflatoxin, ochratoxin A)
  - Unconventional Agents
    - Prions

Even in industrialized countries, up to 30% of the population of people have been reported to suffer from foodborne diseases every year. Food contamination creates an enormous social and economic strain on societies.

- **Bacteria infection**
  - Salmonellosis,
  - Campylobacteriosis, E. Coli...

- **Organic contaminants**
  - DEHP, D(2-EthylHexyl) Phtalate – 600 000 t/yr in EU – food packaging
  - Bisphenol A – 3.8 Mt/yr – polymer materials

**Ozone in agri-food**

- **Disinfection and organics removal**
  - Agricultural products
  - Food products
  - Equipments
  - Water
  - Air

- **Along the agri-food chain**
  - Production
  - Processing
  - Storage
  - Transport

**Food safety**

- **Antimicrobial agent**
  - Bacteria
    - Listeria monocytogenes
    - Bacillus cereus
    - Staphylococcus aureus
    - Enterobacteriaceae
    - Pseudomonas aeruginosa
    - Candida tropicalis
  - Yeast
    - Candida albicans
    - Zymosechyzomyces bailii
  - Spores
    - Aspergillus niger
  - Viruses
    - Human enteroviruses
    - noroviruses
    - hepatitis A, vesiculoviruses
    - infectious bovine rhinotracheitis virus

- **Degradation of active molecules**
  - Pesticides
  - Mycotoxins

**Ozone in agri-food, back- and foreground**

- **Crop protection**
  - Development of a Systemic Acquired Resistance (SAR) during growing

- **Fruits and vegetables**
  - Surface decontamination and Storage
    - Lettuce, Baby carrot, Apple, Grape, Peach, Tomato ...

- **Meat and Sea food**
  - Processing
    - Surface decontamination and Storage
    - Red meat, Poultry, Fish, Shrimp ...

- **Antioxidant enrichment**
  - Grape juice

- **Sanitation**
  - of food processes
    - Clean-In-Place
      - Dairy, Wine, Brewing industry ...
Challenges and opportunities

- Water and food supply vs population growth
- Food and water resources preservation
- Safety and health issues
- Sustainability

All drive innovation in application of ozone and related oxidants for water and agri-food applications.

The drivers identified for new technologies cover issues addressed within IOA

- Water scarcity: water reclamation, natural water conservation
- Crop growth, Food safety along the chain
- Contaminant control: pathogens, toxics, bulk pollution

Research & Development aspects
- Fundamentals
- Contactors
- Energy requirements

Thanks for your attention
www.io3a.org
www.ioa-ea3g.org
Introduction

Limiting the micropollutants discharge in the environment has become a new issue in connection with organic pollution; good status of surface water and groundwater bodies must be preserved or recovered. Conventional municipal wastewater treatment plants (WWTP) has been demonstrated a major source of continuous emission of deleterious organic substances (1, 2). Upgrading the existing WWTP with the implementation of advanced technologies as tertiary treatment appears essential to protect receiving water bodies.

Material and Methods

This work compares ozonation and activated carbon technologies in basis of the removal of persistent micropollutants contained in a municipal biotreated wastewater effluent. The micropollutants covered particularly include the priority substances of the European Water Framework Directive (2000/60/EC). Moreover, the conventional aggregate parameters used for the characterization of organic pollution in wastewaters (COD, DOC, UV
d, BOD5, etc.) were also controlled during the treatments. On one hand, it allows the determination of the final global water quality after treatment. On the other hand, it permits the evaluation of the extent of the limitations of micropollutants removal induced by the presence of the bulk of organic matter. Finally, organic matter fractionation methods based on size exclusion (LC-OCD) and substances polarity (XAD) were employed to deeply characterize the organic matter involved in the different stages of the treatments.

Samples were taken in at the outlet of the biological treatment from several municipal urban wastewater facilities Ozonation experiments were performed at lab-scale in semi-batch mode. Activated carbon adsorption experiments were performed in batch mode at lab-scale with powdered activated carbon (PAC) and also at pilot-scale using a GAC filtration column in down-flow mode.

Results

Both technologies showed to be suitable to remove the major part of the organic micropollutants investigated as illustrated in Figure 1. Ozonation as well as GAC filtration technologies were shown to be effective in removing from urban secondary effluents most of the micropollutants regulated by the European Directives. At low ozone doses close to 20 mg/L, only the HCHs were shown to be ozone recalcitrant among the substances tracked and detected (3).

In the case of adsorption application, the substances with molecular weight below 1,000 Da, which represent 80 to 90 % of the DOC, are absorbed simultaneously with the micropollutants using activated carbon. High organic matter loaded would strongly limits the life time of the GAC.
In the case of ozone application at ozone doses below 30 mg/L, micropollutants oxidation mainly occurs during degradation of aromatic, low biodegradable and high molecular weight compounds which constitute 20 to 50% of the COD. This organic fraction was converted into more biodegradable, less aromatic and smaller substances (Figure 2).

**Figure 2. BOD5/COD kinetics during ozonation of municipal secondary effluents.**

**Conclusion**
Depending on the chemical make-up of water pollution, the best technological solution can either be ozone oxidation or activated carbon adsorption. Cost comparison and Life Cycle Assessment study will draw the final selection of the best solution.

**Key-literature**

**NOTES**
REUSE OF OZONE VENT GAS
FOR AERATION AT A WASTEWATER TREATMENT PLANT


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** PRAXAIR, Inc., 7000 High Grove Blvd, Burr Ridge, IL 60527, USA

Keywords: ozone, vent gas, pure oxygen

Introduction
The use of ozone for tertiary treatment at wastewater plants is increasing in popularity due to the rising demand for effluent that can be reused. As a strong oxidant, ozone is an effective disinfectant that produces discharge water free of known toxic disinfection byproducts with the exception of those that result from ozonation of high-bromine waters. Ozone is a cost-effective means to achieve color removal without the addition of chemicals, or generation of chemical sludge.

As ozonation of filtered secondary effluent enables reuse, ozone is popular in areas of “water stress” where usage rates are high relative to water flows and storage in natural systems such as lakes and rivers. In China, the annual water usage represents 20% of the total available supply, however, due to acquisition cost constraints and pollution, the nation’s water supply deficit has been estimated at 40 billion cubic meters in 2000 (U.S. Department of Commerce, 2005). The motivation to use vent gas for aeration is based on the fact that oxygen-based aeration typically uses less power on-site compared to air based aeration systems. Electrical power is a major operating cost of wastewater treatment facilities. More than half of the plant’s electrical power is typically used for aeration (Redmon, 2011). While modern fine-bubble diffuser systems have a typical clean water aeration efficiency (SAE) of 4.2 kg/kWh (Redmon, 2011), the I-SOTM oxygen-based aeration has an SAE with oxygen of up to 6.2 kg/kWh under typical conditions (Praxair, 2003). An additional advantage to oxygen-based aeration is the low capital cost of surface based or floating oxygen aerators compared to the conventional submerged diffusers.

The paper will present an economic analysis of the application of O3 vent gas for aeration, which enabled significant reduction in the capital and operating cost for aeration at the plant, offsetting the cost of O3 for tertiary treatment. Key to the realization of an economic benefit was the combined ozonation and vent gas system modified to maximize O2 purity in the vent gas as well as net flow of vent gas to the aeration system.

Material and Methods
A municipal wastewater plant was originally designed to treat a combination of municipal and textile wastewater (120,000 m³/d) with Class IB effluent limits (see Table I). The main treatment plant is an oxidation ditch reverse AAO plant. Due to color removal and reuse requirements, the plant installed an ozone-based tertiary treatment system.

In 2009, when the facility needed to increase its capacity to 150,000 m³/d, the vent gas use was studied. So, the plant (expansion) was designed to utilize vent gas from an ozone contactor for aeration in the secondary process. The capacity of the existing oxidation ditch plant was increased from 120,000 m³/d to 150,000 m³/d with the construction of additional secondary trains and clarifiers based on a reverse A2O process (Anoxic, Anaerobic, Oxic) for biological nutrient removal. The incremental flow (30,000 m³/day) is treated using a high purity oxygen (HPO) reverse A2O process for which the oxygen source is vent gas from a tertiary ozonation system. Ozonation of the filtered secondary effluent from the whole plant uses about 1.7 mtpd of ozone (at 10% w/w). The vent gas contains about 15 mtpd O2. After losses of oxygen due to oxygen dissolution into the tertiary effluent and ventilation losses, there is a net yield of 10 mtpd O2 that is applied to the aeration zone of the A2O process.

The low pressure vent gas stream is dissolved using Praxair’s I-SO™ oxygenating systems which are in-situ, floating mechanically agitated contacting systems that are able to induce gas flows using a high strength vortex generated by the rotational action of a helical impeller.

Results and Conclusions
Ozonation of the filtered secondary effluent from the whole plant uses 17 mtpd pure oxygen at the current flow rate of 150,000 m³/d and, following ozone generation and contacting, yields 10 mtpd oxygen in vent gas. The oxygen-rich vent gas (75-85% pure oxygen) promises to reduce the capital and operating cost for aeration compared to air-based aeration. The vent gas supplies pure-oxygen aerators, which have higher standard aeration efficiency (SAE, kg O2/kWh) for oxygen transfer compared to air based systems. The projected power savings results in a net savings in operating cost with no incremental operating cost for the pure-oxygen from the vent gas.
References

1. Praxair, Inc. 2003. Internal communication on clean water testing results for the I-SO™ as performed at Philadelphia Mixing Solutions, Ltd., Palmyra, PA.

NOTES
ORGANOPHOSPHOROUS FLAME RETARDANTS OXIDATION BY OZONE: WATER MATRIX EFFECTS

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Keywords: Micropollutants, Ozonation, Wastewater, hydroxyl radicals

Introduction

The term flame retardant (FR) does not refer to a specific class of chemicals but to a function, and different chemicals, with different properties and structures, are included in this group. Among others, Organophosphorus Flame Retardants (OPFRs) deserve special attention since they are High Volume Production Chemicals, they are widespread in the environment, especially in aquatic system and are toxic or neurotoxic [1]. Industrial and wastewater treatment plants (WWTPs) discharges [2] and releases from materials [3] are indicated as a source of flame retardants to the aquatic environment. Ozonation is very effective in eliminating micropollutants that react fast with ozone \( (k > 10^3\text{M}^{-1}\text{s}^{-1}) \), but there are also ozone refractory \( (k < 10^{-1}\text{M}^{-1}\text{s}^{-1}) \) micropollutants such as some organic phosphates, among others. Yet, they could be degraded upon ozonation to some extent, and this is due to •OH radicals generated in the reaction of ozone with organic matter in wastewater.

The objective of the present study was to determine the degradation of a set of 8 OPFRs in water by ozonation. The flame retardants studied were: Aliphatic: tributyl phosphate (TBP), tris(2-butoxiethyl) phosphate (TBEP), tris(2-etilhexil) phosphate (TEHP); Chlorinated: tris(2-chloroethyl) phosphate (TCEP), tris(2-chloro-1-methylexil) phosphate (TCPP), tris(1,3-dicloro-2-propyl) phosphate (TDCP); and Aromatic: triphenyl phosphate (TPhP), tricresilphosphate (TCP). The contribution of the formation of •OH generated upon the reaction of ozone with the water matrix is also included.

Material and Methods

Ozonation was assayed for the removal of 50 ppb of the 8 OPFRs spiked in 3 different types of water: MilliQ water, MilliQ water with 10 mg.L\(^{-1}\) of humic acids, and a secondary effluent from a wastewater treatment plant. The ozone containing stream (10 gO\(_3\) Nm\(^{-3}\)) was injected at a flow rate of 60 L h\(^{-1}\) to attain various transferred ozone doses (from 0.05 up to 600 mgO\(_3\) L\(^{-1}\)). The duration of each experiment was set between 60 and 120 minutes.

All the samples were analyzed with HPLC-MS/MS. Apparent removal kinetic constants of the analyzed OPFR were obtained by fitting the data to first order kinetic expressions, and they were used to compare the different degradation rates of the compounds. Other physical-chemical parameters, like TOC, DOC, COD, pH and alkalinity were also determined.

Results

In this study, the molecular ozone reacts quickly with the organic compounds having nucleophilic moieties such as aromatic rings, and the functional groups bearing oxygen atoms like TBP, TBEP, TCP, and TPhP. On the other hand, TCPP, TDCP, TCEP, and TEHP with the chloride atoms and saturated aliphatic branched chains were difficulty for ozone to oxide. Therefore the target 8 OPFRs could be divided into two groups in basis of the chemical structures (see Figure 1-A).

Figure 3. Removal of OFRs achieved by ozonation in MilliQ water (A) and humic acid solution (B).
Moreover, experimental results showed that in comparison with O₃ in Milli-Q water, O₃ with humic acid led to faster degradations of target compounds such as TBP, TCP, TPhP, and TBEP. More than 90% of TBP, TBEP, TCP, and TPhP were degraded by O₃ within 10 min. Meanwhile the removal efficiencies of TCPP, TDCP, and TEHP could reach 30% after 2 h reaction. Natural organic matter (humic acid) may as the pioneer of active substances, induced the production of •OH and other active substances, which can improve the degradation of target compounds. Also, humic acid could affect the ozone stability and lead to hydroxyl radicals generation during the reaction. Indirect oxidation of O₃ via hydroxyl radicals is therefore promoted in humic acid solution which would be responsible of the faster degradation of 8 OPFRs observed. Results of ozonation in secondary effluents showed that the treatment efficiencies decreased compared with that in Milli-Q water and humic acid solution, but the degradation of target compounds still followed the similar tendency. This discrepancy may be ascribed to the effect of some radical scavengers in the real wastewater (HCO₃⁻, due to the high value of initial inorganic carbon 75.08 mg.L⁻¹) decreased the concentration of hydroxyl radicals and the competition between the bulk of organic matter and the target compounds for hydroxyl radicals. It is also possible that some compounds may combine with dissolved organic matter in the wastewater, which can result in the less concentration of freely dissolved compounds, exhibiting with lower degradation rate.

Conclusion
Recalcitrance-grade of the OPFR's is related to their chemical structure. Moreover, an increased degradation via the •OH route can be observed in low DOC content water but this improvement is overloaded for the scavenging capacity of secondary wastewaters.

Acknowledgement
The research leading to these results has received funding from the People Programme (Marie Curie Actions) of the European Union's Seventh Programme FP7/2007-2013/ nº 318926.

Key-literature
COBALT DOPING RED MUD CATALYTIC OZONATION FOR DEGRADATION BEZAFIBRATE FROM WASTEWATER

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Abstract
Red mud (RM) is an alkaline residue generated in large amounts in the extraction of aluminum from bauxite [1]. The storage and maintenance of RM is a challenging environmental problem due to its alkaline character and containing many kinds of toxic heavy metal [1]. In general, RM are mainly constituted by Fe, Al, Si and Ti oxides and oxyhydroxides, which can be used in water treatment, such as coagulant [2], adsorbent and catalyst in activation peroxymonosulfate [1].

In this study, cobalt doping red mud (i.e. Co/RM) was used as a catalyst in catalytic ozonation for degradation BZF in aqueous solution. The performance of bezafibrate degradation and mineralization in aqueous phase by Co/RM was evaluated. The removal effectiveness of catalytic ozonation BZF in the presence of RM and Co/RM is shown in Fig.1. The efficiency of BZF was only 36.9 % in the sole ozonation. BZF cannot be effectively removed by this short contact time (30 min) by the sole ozonation process (SOP). Co/RM catalytic ozonation not only degraded bezafibrate, but also mineralized the corresponding intermediates successfully, in either ultrapure water or effluent of wastewater.

![Reaction condition: (A) batch ozonation, \([O_3]_0=0.5\) mg/L, \([BZF]_0=2.76\) \(\mu\)M, [catalyst]=50 mg/L, water pH=6.68; (B) continue ozonation, \([O_3]_0=0.38\) mg/L, \([BZF]_0=0.2\) mM, [catalyst]=1.0 g/L, water pH=6.68.](image)

**Fig.1 Performance (A) and mineralization (B) of ozonation, RM or Co/RM catalytic ozonation**

Then, the surface and structure properties of Co/RM were characterized by BET, XRD and UV-Vis analytical methods. After cobalt modification, the surface area was significantly increased from 7.66 to 57.87 m²·g⁻¹. Also, The pore structure had also changed significantly after the modification, indicating that the role of either micropore or mesopore was different. Though the result of XRD pattern could not support the crystallites of cobalt oxides, UV-Vis spectrum showed the presence of \(\text{Co}_3\text{O}_4\) in Co/RM. It was also found that \(\text{Co}_3\text{O}_4\) forming the active components on the surface of RM by addition of cobalt in red mud, enhanced the catalytic activity.

The ozone decomposition rates in absence of BZF by the sole ozonation and RM or Co/RM catalytic ozone decomposition was observed (Fig. 2(A)). Co/RM exhibited a stronger ability on catalytic ozone decomposition (over 83.3 % in 10 min). The presence of TBA inhibited the reaction involved with RM or Co/RM, confirming that the catalytic ozone decomposition generated ·OH. Fig. 2(B) shows the corresponding effective ozone consumption ratio (\(\eta\)) during ozonation alone and catalytic ozonation by RM or Co/RM. In Co/RM catalytic ozonation, \(\eta\) value exhibited the lowest effective ozone consumption, suggesting that the lower \(\eta\) value in catalytic ozonation was due to the fate ozone decomposition and the BZF degradation in catalytic ozonation was dominated by the ·OH oxidation not the molecule ozone reaction.

The leaching of toxic heavy metal from catalyst in this process was very low, and the heterogeneous reaction dominated the BZF decay, which made the reuse of catalyst highly feasible. Furthermore, 22 intermediates generated in this process were identified and the degradation pathway was proposed.
Reaction Condition: $[O_3]_0=0.5 \text{ mg/L}$, $[\text{BZF}]_0=2.76 \mu\text{M}$, [catalyst]$=50 \text{ mg/L}$, [TBA]$=500\text{mg/L}$, water pH$=6.68$.

Fig. 2 (A)-Catalytic ozone decomposition in the absence of BZF or with TBA, (B)- Ozone utilizing efficiency ($\eta$) in degradation BZF by different process.

Acknowledgements
This work was carried out with the support of the National Natural Science Foundation of China (No. 51378063, 51108030 and 41273137), Beijing Natural Science Foundation (No. 8132033), the Specialized Research Fund for the Doctoral Program of Higher Education (No. 20100014120001), and China Post Doctoral Science Foundation (No. 201104060 and 2012M520006).

Key-words: Bezafibrate; Catalytic ozonation; Red mud; Co/red mud

References
STUDY ON CATALYTIC EFFECT OF ACTIVATED CARBON IN THE OZONATION OF REACTIVE BLACK 5
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Keywords: RB5; heterogeneous catalysis; activated carbon; O\textsubscript{3}; decolorization; mineralization

1. Introduction
Dye wastewater is in the characteristic of large amount, variable water quality, complex compositions and high content of toxic organic matter and is bio-refractory in the environment. Dye wastewater untreated or treated with low degree will have a great impact on the aquatic ecosystem and its boundary conditions and is toxic to the microorganisms. Although dye wastewater that treated by biochemical treatment can meet the discharge standard, it can also lead to water pollution. With the improvement of sewage discharge standard, it is necessary to develop new technologies to improve the mineralization.

Due to strong oxidizing property of O\textsubscript{3} and HO\cdot, as a kind of AOPs catalytic ozonation has increasingly become a hot topic at home and abroad. Nowadays, improving the generation of HO\cdot to improve the removal ability of organic matters by certain means is getting worldwide attention. This paper is to explore catalytic effect of activated carbon in the oxidation of reactive black 5 by O\textsubscript{3}.

2. Materials and Methods
2.1 The Experimental Apparatus and Process

\begin{center}
\includegraphics[width=0.5\textwidth]{catalytic_ozonation_experiment_flow_chart.png}
\end{center}

Picture 1 Catalytic ozonation experiment flow chart
1 pure oxygen tank; 2 ozone generator; 3 flowmeter; 4 reactor, net capacity 2L; 5 ozone adsorption liquid, ozone concentration is measured by Iodimetry

2.2 Reagents and Instruments
H\textsubscript{2}SO\textsubscript{4}(98%); KI(AR); Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}(AR); NaOH(AR); HCl(AR); RB5(technical grade)
Leici pH5-2F pH meter, Shanghai Jingke; ozone generator (CG-3-10g, Qingdao Guolin); TOC-L CPHCN200, Shimadzu; TU-1810 UV-Vis spectrophotometer, Persee.

2.3 Analytical Method
The influent of the reactor is 200mg/l simulated dye wastewater prepared in the laboratory, and the reaction time is 1h, TOC and remained dye concentration are referred to judge the removal effect of dye by catalytic ozonation.

3. Results and Discussion
The effect of activated carbon dosage on the removal of dyes is shown in picture 1 as below:

\begin{center}
\includegraphics[width=0.5\textwidth]{dye_concentration_change.png}
\includegraphics[width=0.5\textwidth]{decolorization_rate.png}
\end{center}

Picture 1. curve of dye concentration changing with time under different activated carbon dosage
Picture 2. histogram of decolorization rate of RB5 in 10min

2.2
From picture 1 we can see, ozone alone has certain effect on dye decolorization; activated carbon of low dosages (0.5g/l, 1g/l) have inhibitory effect on dye decolorization, the decolorization rates of groups which carbon dosage is 0.5g/l, 1g/l are lower than ozonation alone group in 10min, and the less the dosage of activated carbon, the less the decolorization rate. The remaining dye concentration of RB5 of 0.5g/l activated carbon group is larger than other three groups during all reaction time, thus we can conclude that the decolorization is not that effective in low activated carbon dosage, which may due to ineffective decomposition of ozone in low activated carbon dosage, hence the utilization efficiency of ozone decreases; or due to the HO· O3 decomposes is not selective, thus only a small proportion of them react with chromophoric group, however, O3 reacts first with chromophoric group which means it reacts selectively. The dye removal rate of high activated carbon dosage (5g/l, 10g/l) groups is better than low activated carbon dosage (0.5g/l, 1g/l); the decolorization rates of high activated carbon dosage (5g/l, 10g/l) groups reach 87.56% 89.76%, both higher than 82.98% 72.82% and 82.59% of low activated carbon dosage groups 0g/l 0.5g/l 1g/l. So the amount of activated carbon shows a significant impact on the dye removal, of which high amount is favorable, low amount is not conductive. The effect of activated carbon dosage on the removal of dye is also analyzed in the perspective of TOC removal rate.

From picture 3 we can see activated carbon dosage impacts the removal of TOC significantly, especially under high activated carbon dosage. The removal rate of TOC under low activated carbon dosage (0.5g/l, 1g/l) are almost the same with that under ozonation alone; with the amount of activated carbon increase to 5g/l 10g/l, the TOC removal rate increases fast, reaching 56.67% and 86.61%, showing high mineralization rate of dye. Comparing the indicator of TOC and decolorization, the activated carbon dosage influences TOC removal rate more significant, this may because activated carbon accelerate the generation of HO.[3], while the acceleration under low activated carbon dosage is negligible.

Because of the porous structure, activated carbon shows strong adsorption ability. So here we compare the removal effect of both catalytic ozonation and adsorption.

Within 1h adsorption, the remaining RB5 are 146.8mg/l, 132mg/l under 5g/l, 10g/l activated carbon groups and the dye removal rate are 24.72%, 32.98%; under the same activated carbon dosages, the catalytic ozonation can reach 100% and even the time needed is less than 1h; similarly, the TOC removal rate of adsorption by 5g/l, 10g/l activated carbon are 20.50%, 40.58%, however, under the same activated carbon dosage, TOC removal rate of catalytic ozonation reach 56.67% and 86.61%. From both the removal of TOC and decolorization, catalytic ozonation exerts better performance than adsorption, this may be due to the adsorption enrichment zone led by the strong adsorption ability of activated carbon[4].
4. Conclusion

4.1 Activated carbon shows catalytic effect on the removal of RB5, especially under high amount and adsorption amounts to only a small proportion. Thus, activated carbon is an effective catalyst in the RB5 removal.

4.2 Activated carbon shows significant performance under high dosage, from the viewpoint of engineering application, high dosage means high running cost. Therefore, it is urgent to increase the efficiency of the generation of HO· decomposes by O3, our next step is to prepare stable and efficient carbon based catalysts.

Reference

HETEROGENEOUS CATALYTIC OZONATION OF ORGANIC POLLUTANT WITH ORDERED MESOPOROUS MANGANESE OXIDES AS CATALYST

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Keywords: ordered mesoporous material; manganese oxide; hydrogen peroxide; oxidation; norfloxacin

Abstract: Heterogeneous catalytic ozonation is a very attractive oxidation method in remediation of wastewater containing organic substances. Manganese oxide (MnOx) has been found to be active for the decomposition of ozone in aqueous solution to enhance the generation of hydroxyl radicals (HO•) [1]. Manganese oxides as catalysts are often loaded on porous materials (e.g. GAC, SBA-15, and mesoporous Al2O3 [2]) based on the consideration that higher specific surface area and porous structure favored the catalytic activity. However, the unavoidable leaching of manganese from the surface of the support may deteriorate its catalytic activity.

In the present study, manganese oxide with ordered mesoporous structure (om-MnOx) was prepared and introduced into ozone oxidation process. Few works have ever focused on the catalytic performance of ordered mesoporous transitional metal oxide. It’s expected the ordered mesoporous structure and up to 97.33 m²/g of specific surface area may provide manganese oxide favorable catalytic activity on ozone. Norfloxacin (NFX), one of the quinolones, which are among the most important classes of synthetic antibacterial agents, was chosen as model target organic pollutant. Awareness on antibiotics found in the environment has increased in the last decade. Most antibiotics are incompletely metabolized during therapy [2]. NFX is widely used in human and veterinary medicines [3]. It’s difficult to biodegrade NFX in aqueous solution, thus, chemical oxidation has been considered [4].

The ordered mesoporous MnOx was prepared by a hard template method, in which SBA-15 as hard template and Mn(NO3)2 as manganese source, while the calcination condition was modified. As a reference, the manganese oxide without ordered mesoporous structure, designated as no-MnOx, was prepared. The prepared materials were characterized by XRF, TEM and BET. Figure 1 shows the TEM image of om-MnOx, and parts of the important physicochemical properties of MnOx were listed in Table 1. pH of the reaction solution was adjusted using 0.1 M NaOH and HCl but was not buffered to avoid the effect of buffer salt on the catalyst’s properties. NFX was analyzed using an ultra high-performance liquid chromatography system (ACQUITY UPLC H-Class).

![Fig. 1. TEM images of on-MnOx (a), and om-MnOx (b).](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>MnOx content (wt%)</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>no-MnOx</td>
<td>97.4</td>
<td>0.90</td>
<td>0.0076</td>
<td>--</td>
</tr>
<tr>
<td>om-MnOx</td>
<td>99.4</td>
<td>97.33</td>
<td>0.44</td>
<td>15.14</td>
</tr>
</tbody>
</table>

The catalytic activity of om-MnOx on ozone was evaluated in pure water. Ordered mesoporous manganese oxide was proved to possess marked catalytic activity towards ozonation on the degradation of NFX. The existence of om-MnOx greatly improved the removal efficiency of NFX in the ozonation system. With the presence of MnOx mesoporous material, the degradation efficiency of ozone on NFX was found to be three times of the degradation efficiency of ozonation alone. The influence of the catalyst dosage, pH,
bicarbonate concentration on om-MnOx catalytic ozonation was investigated. The degradation efficiency of NFX by om-MnOx heterogeneous catalytic ozonation showed the trend of first increased and then decreased with the increasement of catalyst dosage. Acidic conditions were found to favor the degradation of NFX. The catalytic activity of om-MnOx was also tested in real water sample. The degradation efficiency of NFX by om-MnOx catalytic ozonation was observed to decrease in Yangshupu Water Plant tap water. The reaction mechanism of MnOx mesoporous material catalytic ozonation was explored by adding the inhibitor t-butanol and ESR technology. The oxidation of NFX didn't be inhibited when t-butanol was added. And an unknown seven-line signal was detected by ESR technology in the om-MnOx catalytic ozonation system.

References
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FACTORS AFFECTING UV/H₂O₂ INACTIVATION OF BACILLUS SUBTILIS SPORES IN DRINKING WATER

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This study aims at estimating the performance of the Bacillus subtilis spores inactivation by the UV treatment with addition of H₂O₂. The effect of factors affecting the inactivation was investigated, including initial H₂O₂ dose, UV irradiance, initial cell density, initial solution pH and various inorganic anions. Under the experimental conditions, all the B. subtilis spores inactivation exhibited a pseudo-first-order kinetics pattern. The results revealed that the H₂O₂ played dual roles in the reactions, while the optimum reduction of 5.88 lg was received at 0.5 mM H₂O₂ for 10 min. The inactivation effect was affected by the UV irradiance, while better inactivation effect was achieved at higher irradiance. An increase in the initial cell density caused a decrease in the inactivation efficiency. A slight acid condition at pH 5 was considered as the optimal pH value. The inactivation effect within 10 min followed the order of pH 5 > pH 7 > pH 9 > pH 3 > pH 11. The effects of three added inorganic anions were investigated and compared, including sulfate (SO₄²⁻), nitrate (NO₃⁻) and carbonate (CO₃²⁻). The sequence of inactivation effect within 10 min followed the order of control group > SO₄²⁻ > NO₃⁻ > CO₃²⁻.
OZONE AND OZONE BASED AOP FOR THE REMOVAL OF TASTE AND ODOUR AND EMERGING ORGANIC SUBSTANCES IN DRINKING WATER PLANT

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SUMMARY
Nowadays more and more water utilities worldwide are facing the challenges to control taste and odour compounds and/or other emerging organic contaminants in the water with their existing treatment processes. Advanced Oxidation Processes (AOPs) are one of the recommended treatment approaches, of which the key is producing highly reactive hydroxyl radicals (OH•) that can rapidly react with most organic compounds in the water. A comprehensive Ozone based AOP (Ozone/Hydrogen Peroxide) pilot study has been conducted in a drinking water plant in Asia. The compounds of interest included Taste & Odour (T&O) compounds, Endocrine Disrupting Compounds (EDCs), Pharmaceuticals and Personal Care Products (PPCPs) and etc. The impact of various O3, H2O2 dosages and hydraulic retention time (HRT) on the removal efficiencies of contaminants has been studied systematically. The test results are very promising. That can be even used for China’s water utilities as reference and may support their decision-making for plant upgrading design or improve the emergency handling ability of the water utilities on contamination accidents.

KEYWORDS: Ozone, AOP, T&O, EDC, PPCP, Drinking Water Treatment.

INTRODUCTION
A drinking water plant in Asia uses blended reservoir water as their source water. The water plant has currently pre-chlorination, coagulation/flocculation, sedimentation, filtration and post-chlorination processes (Figure 1). Currently, the produced water quality can totally meet the WHO Guidelines for Drinking Water Quality. Even though the water plant would like to have their first-hand Ozone and Ozone based AOP (O3/H2O2) test data under real water conditions, So that the data could support their decision making for plant upgrading design or emergency measures to handle contaminants issue in the future.

MATERIALS AND METHODS
The containerized pilot was manufactured and supplied by Xylem Water Solutions Herford GmbH, Germany. It is designed with adjustable water flow, Ozone and Hydrogen Peroxide dosages. On the test day, the pre-mixed contaminant stock solutions were diluted with the filtered water in the spiking tank to get the

![Diagram](image-url)
anticipated working solutions and final spiking levels. The grab water samples then were collected and used for analysing in the lab. The inlet water quality can be classified as low-scavenger (low TOC, low alkalinity, low Fe and Mn) and moderate-bromide concentration water.

RESULTS AND DISCUSSIONS

Table 1 shows some test data of representative contaminants by different Ozone and H₂O₂ combinations under fixed 5 min HRT. It indicates all the EDCs, such as Estrone, Estradiol, 17α-ethynylestradiol and Bisphenol A, can be effectively degraded by dosing 2 mg/L Ozone alone. For the other compounds such as MIB and Geosmin, the so-called T&O compounds, higher Ozone dosage or Ozone based AOP are necessary to achieve a high removal rate such as 90% or more. Another noted that ozonation removed higher percentage Geosmin than MIB.

Table 1. Removal of compounds by different Ozone and H₂O₂ combinations with 5 min HRT

<table>
<thead>
<tr>
<th>O₃ dose (mg/L)</th>
<th>Low</th>
<th>Moderate</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>H₂O₂ dose</td>
<td>w/o Optimized</td>
<td>High</td>
<td>w/o Optimized</td>
</tr>
<tr>
<td></td>
<td>0.2-0.5</td>
<td>0.5-1.0</td>
<td>0.7-1.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>Conc. N= [ng/L]</th>
<th>% Average Removal Efficiency and Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MIB</td>
<td>219±11</td>
<td>68±4</td>
</tr>
<tr>
<td>2</td>
<td>Geosmin</td>
<td>103±11</td>
<td>81±2</td>
</tr>
<tr>
<td>3</td>
<td>DEET</td>
<td>1538±6</td>
<td>83±1</td>
</tr>
<tr>
<td>4</td>
<td>Ibuprofen</td>
<td>1391±9</td>
<td>81±1</td>
</tr>
<tr>
<td>5</td>
<td>Estrone</td>
<td>1182±4</td>
<td>97±2</td>
</tr>
<tr>
<td>6</td>
<td>Estradiol</td>
<td>1054±4</td>
<td>99±0</td>
</tr>
<tr>
<td>7</td>
<td>17α-ethynylestradiol</td>
<td>1026±4</td>
<td>98±1</td>
</tr>
<tr>
<td>8</td>
<td>Bisphenol A</td>
<td>953±4</td>
<td>97±1</td>
</tr>
</tbody>
</table>

*Green: < method detection limit; Blue: > 90% removal rate

Figure 2 shows the treatment results of MIB and Ibuprofen under different HRTs. It shows for the relatively easy removable compound such as Ibuprofen, the reduction rate was not significantly impacted by HRT either for Ozone or for AOP treatment. Meanwhile for the relatively difficult removable compound such as MIB, the HRT played a significant role, especially for the “Ozone only” process. It indicates that with the addition of H₂O₂, or in other words with the production of •OH radicals, both the reaction kinetics and the removal rates have been significantly increased. Carefully comparing the trend curves of "3 mg/L O₃ + 0.5-1 mg/L H₂O₂" and the "3 mg/L O₃ + 2-4 mg/L H₂O₂"”， it looks like the "high H₂O₂" concentration could further accelerate the reaction velocity, but could not improve the final removal rate anymore. It can be explained that the production of •OH radicals probably started very rapidly at the beginning when both dissolved Ozone and Hydrogen Peroxide in the water are available. After the decomposition of all the Ozone in the water, the excessive H₂O₂ alone could not improve the production of •OH radicals anymore. The trend lines illustrates the vast majority of reactions by AOP (Ozone and H₂O₂) had been occurred within the first 2.6 min.
As most of the full scale drinking water plants use conventional Ozone only treatment with much longer HRT, such as 10 min or even longer, for the purpose of comparison, the HRT was extended to 10 min again. Figure 3(a) shows the MIB removal behaviour under different combinations and HRTs. For example, with 3 mg/L Ozone, the removal rate achieved 80% after 5 min HRT and increased to 90% after 10 min HRT. With addition of 0.8 mg/L H₂O₂, the removal rate achieved even 94% after short HRT of 2.8 min. To achieve 90% reduction rate for MIB, "3 mg/L Ozone with 10 min HRT" or "3 mg/L Ozone plus 1 mg/L H₂O₂ with 3 min HRT" will be the two possible design options.

Figure 3(b) shows 1,4-Dioxane is more resistant to Ozone than MIB. For example, with 3 mg/L Ozone, the removal rate achieved 46% after 2.8 min HRT and increased to 68% after 10 min HRT. With addition of low level H₂O₂, the removal rate achieved 76% after 2.8 min HRT and continued to rise slowly to 86% after 10 min HRT. With 5 mg/L Ozone, the removal rate achieved 87% after 10 min HRT. In combination "5 mg/L Ozone + 0.6 mg/L H₂O₂", 88% reduction rate has been achieved after 2.8 mg/L already. In this case, if achieving 80% reduction rate for 1,4-Dioxane is the treatment goal, "5 mg/L Ozone with 10 min HRT" or "3 mg/L Ozone plus 1mg/L H₂O₂ with 5 min HRT" will be two possible options.

CONCLUSIONS

Conclusively, both Ozone and/or Ozone based AOP are appropriate for the removal of the organic compounds. However, using AOP, i.e. with the addition of Hydrogen Peroxide, the required Ozone dosage and the required HRT will be significantly reduced for the same percentage removal of organic compounds, especially for the resistant organic compounds such as 1,4-Dioxane and MIB. That will lead to smaller footprint design and more energy efficient operation.

The other advantage of ozone based AOP is, the addition of a low level Hydrogen Peroxide can mitigate the formation of Bromate in the treated water. For instance, it is recommended to water utilities to use Ozone based AOP than Ozone alone if their source water contains a moderate or high bromide concentration (>50 µg/L), but still needs to apply ozonation process to treat the organic contaminants in their water. Ozone based AOP can better control the bromate level below 10 µg/L which is required by some countries National Drinking Water Standards, including China.
RECOMMENDATION TO CHINA’S UTILITIES

China’s water utilities face very serious challenges with the deterioration of water quality. On the whole, there are two types of water pollution incidents. One type is the accumulative effect of pollutant discharge over a long period which eventually causes severe water pollution at a certain time point. The drinking water source pollution in Wuxi by algae in Tai Lake occurred in May 2007 is an example for that. Another type is when a great volume of pollutant is discharged within a short time period into the water body from an unexpected accident. The Songhua River toxic spill which occurred in November 2005 is a typical example for that.

In order to solve the water deterioration problem and supply high quality water – safe and tasty – to their residents, the so-called advanced treatment process, Ozone alone followed by Granular Activated Carbon (GAC) has been rapidly accepted and widely applied in China in recent years. It is now possibly the time to start to study the possibility how to optimize this application, for instance, “Ozone + Hydrogen Peroxide” followed by GAC with reduced retention time for both oxidation process and filter process. That may help China’s utilities to solve the problems such as land acquisition in metropolis area. For example, according to the current standards for Drinking Water Quality, China, it is recommended to have an ozone contact time for at least 12 minutes. There is also informative guideline for MIB and Geosmin in the standard, 10 ng/L of each. However, with the Ozone AOP, we can achieve this goal in much short retention time, for example 5 minutes or even lower. The figure below gives a rough comparison for this new idea compared to the conventional ozone application in terms of CAPEX, OPEX and footprint requirement based on a water flow of 7600 m³/h. So, the water utilities and water experts in China may have interest in the future to do detailed study in this field.

- Option 1: 5 mg/L Ozone only, 12 minutes retention time
- Option 2: 3 mg/L Ozone, 1 mg/L H2O2, 5 minutes retention time

![Figure 4. Comparison of CAPEX, OPEX and Footprint](image)

REFERENCES

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NOTES
EVALUATION OF MASS TRANSFER AND GAS-LIQUID EQUILIBRIUM OF HIGH CONCENTRATION GASEOUS OZONE

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Introduction

When ozone water treatment technology is applied, gaseous ozone is once produced and then introduced to water, generally. Because of this feature, the evaluation of mass transfer and gas-liquid equilibrium of ozone between gas and liquid phase is necessary. Particularly, the evaluation of high concentration of gaseous ozone is required, because the higher concentrations of ozone gas can be produced due to the improvements of ozone generator recently. This study examined overall mass transfer coefficients and gas-liquid equilibrium coefficients under the higher concentration of supplied gaseous ozone up to 100 mg/L and variety of conditions; pH ranging from 2.7 to 7.8, temperature from 15 to 30 °C, and inorganic carbon concentration from 0 to 30 mgCl/L. Both of the experimental and modeling approach was applied and data at the transient and steady state were offered to the evaluation.

Experiment

All ozonation experiments were conducted with a semi-batch type reactor whose cross-section area, effective height and effective volume were 52 cm², 21 cm and 1100 cm³ (1.1 L), respectively. The experiments were conducted under the conditions; pH ranging from 2.7 to 7.8, temperature from 15 to 30 °C, inorganic carbon concentration from 0 to 30 mgCl/L and supplied gaseous ozone concentration from 15 to 100 mg/L. The data were obtained under the both of transient and steady state.

Ozone absorption model

We assumed that the fluid-dynamic behavior of liquid is completely mixing and that of gas is plug flow. The mass transfer of gas in head space was not included in the mass balance equation because of the pre-investigation. The main parameters consisting of mass balance equations were overall mass transfer coefficient ($K_{L,a}$) (1/min.), gas-liquid equilibrium coefficient ($m$) ((mg/L-liquid)/(mg/L-gas)), and rate of ozone self-decomposition ($r$) (1/min.). Rates of ozone self-decomposition were obtained as the second order reaction of dissolved ozone (Mizuno et al., 2007a & b).

Results and Conclusions

Table 1 shows overall mass transfers ($K_{L,a}$) in this study and gas-liquid equilibrium coefficients ($m$) at the temperatures of 15, 20 and 30 °C. The $m$ at 15 and 20 °C was obtained from the experimental data of steady state, and that at 30 °C was evaluated by model. The temperature dependence of $m$ was obtained as follows and this agrees with Sander's collecting data (1999); $m = -0.0067T + 0.4474$ ($R^2=0.998$).

<table>
<thead>
<tr>
<th>temperature (°C)</th>
<th>15</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{L,a}$ (1/sec)</td>
<td>0.00319 ± 0.00012</td>
<td>0.00330 ± 0.00021</td>
<td>0.00370</td>
</tr>
<tr>
<td>$m$ (-)</td>
<td>0.348 ± 0.009</td>
<td>0.310 ± 0.0008</td>
<td>0.246</td>
</tr>
</tbody>
</table>
Figure 1 shows the time course of dissolved ozone concentration at transient state. Good agreement between experimental and model results during whole time was obtained. All of the data of steady state results, offered to the verification of the model, shows the good agreement for both of dissolved ozone concentration and exhaust ozone gas concentration as well. Sensitive analysis elucidates that rate constants of ozone self-decomposition strongly affect on the absorption of ozone.

Key Words: Ozone, Absorption, Mass transfer, Gas-liquid equilibrium coefficient, Solubility, Ozone self-decomposition

References

NOTES
1/ Introduction

Ozonation of water and wastewater is typically carried out by dispersing gas, which contains ozone, into the liquid phase. Different methods of gas dispersion are applied in practice and the most popular are diffusers (e.g. porous elements), static mixers, injectors etc. The contact between the two phases accompanied by an ozone mass transfer is realised in OZONE REACTORS.

This paper deals with the ozone transfer from the gas phase to the liquid phase (waters). Indeed a very high rate of ozone utilisation is required in any industrial contactors in order to optimize the ozone amount applied, thus to save energy for ozone generation.

The first part of the paper presents different types of contactors used to perform ozone transfer, with mention of their advantages and disadvantages. The second part reviews the fundamental concepts necessary for the design of ozone contactors: mass transfer, chemical reaction and hydrodynamics. These concepts are illustrated by examples of ozone reactor design.

2/ Main types of ozone reactors

Ozone is produced in a gas phase and must be dissolved in water. In practice various ozone contactors are available for the realisation of the contact between the gas (O₃) and the liquid (water).

Conventional fine bubble diffuser contactor

It is the most widely used technology for the O₃ transfer because it is operated without addition of energy input. The gas phase is normally discharged from the ozone generator at a pressure of 0.7 to 1 bar and dispersed as bubbles (2 to 3 mm in diameter) by porous ceramic diffusers placed at the bottom of the contactor. Several different contactor configurations, baffle arrangements and flow patterns are used (2) (3). The majority of this conventional contactor employs two or three chambers or cells of contacting, separated by single or double baffles. Nevertheless some of them can use 6 stages (and more), in order to reach near plug flow behaviour. The height of the water is in the range 4-7 m. The O₃ mass transfer efficiency depends on the operating conditions, but the range is 75-92%. The mean residence time of the water can vary from 6 to 20 min. The range of volume in this contactor varies from 80 to 500 m³.

Injectors and static mixers

When water flows rapidly through a pipe and past a small orifice, a Venturi effect (vacuum) is created and gas is pulled through the orifice into the water stream. With an injector device, a very fine gas-liquid emulsion is generated (containing very small gas bubbles) which permits to achieve a high O₃ mass transfer. After the injector the gas liquid emulsion enters the reaction vessel, which is designed for each specific application. Then, the two-phase flow goes i) either to the degassing separator where the gases and the water are separated (the gases are discharged by a degas valve at the top of the separator), ii) either enters the reactor ozone (bubble column), iii) either enters directly the pipe where water is circulating. A static mixer (SM) is constituted of a pipe in which some portions of helicoid or geometrical elements are inserted and create the mixing of the phases. Ozone is injected just before the inlet of the static mixer. A degassing column is generally associated to the static mixer in order to achieve the separation of the two phases. The hydraulic residence time in the degassing column is comprised between 30 and 100 seconds, but it can be adjusted in function of the ozonation process.

These two systems of ozone injection can be used as a side stream contacting device: a portion of the full water flow rate is pumped through one system. A high dissolved ozone concentration can be obtained at the outlet and then this side stream is efficiently mixed with the main flow of the water in the pipeline. The main advantage is the conservation of the flow line pressure.

Deep U Tube

The system is composed of two vertical concentric tubes of approximately 20 meters deep. Water flows downward through the inner tube. Ozone is injected into the water stream near the top of the inner tube and flows downward with the water. After reaching the bottom of the tube, the water-ozone mixture flows upward through the annular tube. The shear stress caused by the high velocity flow in the inner pipe leads to the formation of bubbles with a diameter comprised between 2 and 4 mm. The efficiency of ozone transfer is in the range 95-99%.
3/ Modelling of water/wastewater ozone reactors

Modeling of ozone reactors need the knowledge of the three fundamental concepts: mass transfer, chemical reaction kinetics and hydraulics. The theoretical approach of the gas-liquid mass transfer permit to identify the important parameters which govern the ozone transfer: mass transfer coefficient, interfacial area. The hydraulic performance is based on the determination of the residence time distribution curve (RTD) obtained by tracer test. Several models have been proposed for the description of water flow through ozone bubble contactor. The most commonly used is the J tanks in series model \((J = 1 \text{ CSTR} \quad J = \infty \text{ Plug Flow})\).

The reactions of \(O_3\) with organic or mineral compounds in water are generally of overall second order. The values of the constant \(k_2\) vary in a very large domain depending on the nature of the molecule. Due to the complexity of a water matrix, a water can be characterized by i) the instantaneous ozone demand \((X \text{ mg/l})\) which corresponds to the very fast reactions, ii) a moderated consumption defined by a first order decay kinetics \(k_d\).

The coupling of these concepts constitutes the sound basis for ozone reactor design.

Key-References

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NOTES
EFFECTS OF OZONE ON LIVE FISH LOGISTICS

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Keywords: Ozone, fish, stress, Oxidation Reduction Potential

About 40% of the global aquatic fish yields were consumed by Chinese in China; this urged the sustained fast development in the aquaculture business in China. Since 2008, the quantity of aquaculture production in China has already exceeded the quantity of harvested yield from open seas and rivers. Chinese prefer consumption of fish which are really live and fresh before cooking. Driven by the market, in addition to better technique and management to maintain the quality of aquaculture produce, there is an urgent need to improve the technology in live fish logistic to minimize fish loss in transportation.

To reduce transportation cost in long range road traffic, live fish will be kept in tank with minimal quantity of water and the fish to water mass ratio will be about 1:1. As a common practice, fish tanks in the logistic vehicles will be purged with pure oxygen and the water temperature has to be reduced to less than 10°C to minimize fish activities. This article reports a case study of ozone applications for long range road transportation of live fish. The results indicated that ozone is mostly important to safe guide the insecurity in fish logistics and to control the nitrite level in tank water.

NOTES
**SYNERGISTIC CHEMICAL / BIOLOGICAL OXIDATION COUPLING OZONATION AND BIOFILTRATION FOR ADVANCED TREATMENT AND REUSE OF INDUSTRIAL WASTEWATERS**

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**Keywords:** industries, advanced wastewater treatment, hard COD, discharge, reuse, reverse osmosis, brine, pre-treatment, ozonation, biofiltration.

**Introduction**

Protection and restoration of natural water resources is a priority in most industrialized countries and in some developing countries to ensure sustainable use of water. Economic incentives such as cost of water withdrawal, the "polluter pays" principle and the more and more stringent regulatory requirements stimulate on one hand the widespread application of advanced finishing treatments to control the release of persistent organic pollution and on the other hand the development of industrial effluent reuse. The main barriers to these developments are of technical and economical orders.

Ozonation application for water treatment began in the early 1900s with drinking water treatment, has spread worldwide and today grows in the industrial wastewater treatment field (Rice, 1997). Once dissolved in water, ozone may react with many organic compounds according to two ways: by direct reaction as molecular ozone or by indirect reaction through formation of secondary oxidants like free radical species (Hoigné, 1988). In practice, both mechanisms may occur depending on the chemical make-up of the water pollution. Because of its high reactivity, treatment lines for industrial wastewaters commonly involve ozone for extensive COD removal after biological treatment as an end treatment (Baldes and Becker, 1993; Hausler et al., 1995; Hostachy et al., 1993; Roche et al., 1995). These ozone treatments may cause high costs when performed to achieve important oxidation yields of organic pollutants. However, low ozone doses can ensure sufficient chemical changes of biorefractory compounds to enhance the wastewater biodegradability. To provide considerable cost advantage, partial ozonation can then be applied prior to a second aerobic biological treatment (Carini et al., 1998; Medley and Stover, 1983; Tuhkanen, 1997, Baig, 2001).

**Context and technical challenges**

Of particular interest is the recent development of such integrated oxidation process in China. The Chinese oil refining industry currently faces strong challenges: a crude oil refining market in fast growth with limited water resource and very stringent regulations in terms of discharge limits. In order to treat the waste water streams generated by the different production processes of the PetroChina refinery (ten million tons per year) and ethylene plant (800 000 tons/year) recently built in Chengdu, Sichuan province, the petrochemical plant was featured with 60.000 m³/d as capacity for the waste water treatment plant. The main challenge consisted in the design of a powerful wastewater treatment line in order to reuse 50% of treated water in the industrial process. This reclaimed water, used as process water in cooling towers, requires a specifically level of total dissolved solids (600 mgTDS/L) and chlorides (30 mgCl/L) thus involving the implementation of reverse osmosis system (RO, 30.000 m³/d capacity). Because of the final disposal of wastewaters in sensitive area, the authorities specifically required discharge limit of 60 mg/L for the chemical oxygen demand (COD). In order to meet these requirements and address RO application drawbacks, special attention was paid to the RO pre-treatment and the brine treatment (10.000 m³/d capacity) to reduce the hard COD content.

**Approach and results**

The Oxyblue process™ combining ozonation and biofiltration was included in the water line to reach a reliable reverse osmosis operation for the wastewater reuse and to meet the strict discharge requirements for the brine.

The synergy in chemical biological oxidation for organic matter removal proceeds from two interdependent stages:

- Ozonation provides an increase in biodegradability, through controlled reaction between persistent organic matter and ozone through kinetics and ozone dose
- Biofiltration achieves next high performing biological aerobic treatment (Biofor™).
Process conditions were determined at lab scale according to usual experimental protocols with ozonation studied in batch mode and next biological process in SBR mode.

Figure 2 shows for example, the results of experiments conducted under similar conditions with sample tests at 5 °C or 20 °C from the RO brine of initial COD 212 mg/L. COD generally decreases exponentially in accordance with a conventional reaction pseudo-first order with respect to the COD. Indeed, kinetic plots highlight two successive steps with decreasing kinetic constants and with transition occurring at 30% COD reduction corresponding to ozonation duration of 30 min. The decrease in kinetic reflects the intermediate formation of more difficult to oxidize products. Indeed the COD reduction during the first fast kinetic stage causes an increase of the BOD₅ concentration of the effluents as shown in biological tests.

Conclusions
Demonstration of the viability of the benefits of ozonation and biofiltration coupling (Oxyblue™ process) on these wastewater streams made during tests proved COD removal by 40% on the RO pre-treatment line and by almost 60% on the brine line. These results are consistent with background experience from early built plants in France and Austria in agrifood and pulp & paper industrial sectors (Kaindl, 2008).

Key literature
REMOVAL OF ACTIVE PHARMACEUTICAL INGREDIENTS (APIS) FROM WASTEWATER – A REVIEW OF EXISTING TREATMENT SOLUTIONS

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Abstract
This paper discusses the process development work and full-scale performance of advanced treatment using ozone to remove Active Pharmaceutical Ingredients (APIS). This paper summarizes pilot- and full-scale results taken from selected projects installed at Pharmaceutical Industry, hospitals and municipal waste water treatment plants. The plant treating pharmaceutical waste water is located in Ireland. This facility is among the first full-scale pharmaceutical manufacturing sites to build and operate a treatment system specifically designed to remove APIs from industrial wastewater. The major unit processes at the WWTP include: (1) equalization and pH control; (2) biological treatment; (3) membrane filtration and (4) ozone oxidation prior to discharge to a local Publicly Owned Treatment Works (POTW). The effluent is suitable for reuse as make-up water for cooling towers. Although the biological treatment and membrane filtration has the ability to remove most of the API’s, this paper shows the effect of ozone and how it relates to the successful removal of active estrogen in the wastewater; in which MBR has little to no effect. This paper also focus on the relationship between the two unit processes (MBR + ozone) when operated in series to increase the efficiency of the full-scale operation and optimize the effective ozone dosage. The process combination MBR + ozone is selected as BAT for the treatment of hospital waste water. The oxidation with ozone is an efficient solution to implement in the effluent of municipal waste water treatment plants to reduce APIs.

Keywords: Ozone; biological treatment; MBR; membrane filtration; COD reduction; estrogen; wastewater; Active Pharmaceutical Ingredients (APIs); reuse

APIs in Wastewater
APIs and endocrine disruptors are a new class of environmental pollutants. Because pharmaceuticals are highly potent and biologically active compounds, they can have human health and environmental effects at concentrations as low as the part per trillion (ng/L) range. As an example, 17-β-estradiol (E2) reportedly causes feminization of male fish at levels as low as 10 ng/L and ethinyl estradiol (EE2) has similar effects at concentrations as low as 0.1 ng/L (Desbrow et al., 1998).

Figure 1 illustrates the occurrence of APIs in the wastewater cycle. APIs are present in wastewater discharges at hot spots like the production sites of pharmaceuticals itself and areas of intensive use like hospitals. Municipal wastewater plants are another spot where APIs are detected and maybe discharged to the environment. The concentration levels for APIs found in the wastewater discharge from hot spots are often at concentration that may have adverse human health and/or environmental impacts. Of particular concern are Pharmaceutical Manufacturing facilities where 100 to 1500 kg batches of hormones and steroids are produced and losses to wastewater can be as high as 2%. At these facilities the resulting peak loads or Predicted Environmental Concentrations (PEC’s) from wash waters containing these potent APIs are estimated to be in the range of 10 to 10,000 times the Predicted No Effect Levels (PNECs). Therefore, bench proven and robust treatment concepts are necessary to reduce the impact of APIs on receiving bodies such as lakes, rivers, oceans, or groundwater water. Figure 1 show 3 different discharge locations where treatment could take place to minimize the impact of APIs on water resources.
Removal of APIs requires more advanced technology and additional treatment steps than typically practiced in conventional industrial and municipal wastewater treatment. The API issue presents industry and regulators with unique challenges due to the large number of APIs (more than 3000 different substances), their different effects on the environment and human health and their specific behavior on treatment technologies because of various physicochemical properties (Desbrow et al., 1998; Ternes et al., 2003; Joss et al., 2004).

Figure 2 gives an overview about investigated treatment steps and concepts to improve the treatment efficiency on APIs removal. A conventional treatment including pretreatment, aerobic biology and clarification is not able to achieve stricter discharge limits for APIs. The most investigated and already proven techniques in full scale to advance the treatment are: oxidation with ozone, adsorption on GAC and filtration with membranes.

Membranes (e.g. UF membranes) can improve the biological process by operating in an MBR mode. The reduction rates for APIs are increased by using an MBR instead of conventional aerated biology. A further reduction of APIs requires membrane systems like NF/RO, adsorption techniques like GAC or oxidation techniques like ozone.

**Performance Results from Full-Scale Plants**

Full scale plant designs and performance results were analyzed from different locations:

- Pharmaceutical production site in Ireland
- Hospital waste water in Germany

**Pharmaceutical Production Site Ireland**

The average flow rate was 589 m$^3$/day (103 gpm). This corresponds to 107% and 84% of the WWTP's average and maximum hydraulic capacities respectively. The flow increased from 540 m$^3$/day (99 gpm) to 650 m$^3$/day (119 gpm) as the week progressed and this would be normal as production and cleaning operations increase from the beginning to the end of the week.

Under worst case conditions, the Chemical Oxygen Demand (COD) removal was 95% for MBR and 98% for MBR plus ozone; Biological Oxygen Demand (BOD) removal was 99.5% for MBR and 99.9% for MBR plus ozone; Total Suspended Solids (TSS) removal was 99% for MBR and aggregate API removal was 99.3% for MBR and 99.94% for MBR plus ozone. Figure 3 shows the results for gross organic removal and trace API removal.
Over the last ten years some studies have examined the special treatment of hospital wastewater directly at the source. The most relevant project is the European joint project “PILLS” (www.pills-project.eu) where six European countries cooperate to gather knowledge for this application. Within the project frame two large scale installations (Marienhospital / Germany and Isala hospital / Netherlands) are operated. Subsequently to a pilot study, which has been founded by the North Rhine Westphalian ministry of the environment (Pinnekamp 2009) another full scale plant is in operation at the Kreiskrankenhaus Waldbröl since 2010. In this demonstration plant hospital wastewater is treated by an advanced combination of MBR and subsequent ozone oxidation.

Figure 4 demonstrates the treatment efficiency of the ozone step downstream the MBR. 14 different pharmaceuticals were investigated. The ozone step can further reduce the most of the investigated compounds. Only substances like X-ray contrast media (e.g. Iopamidol, Diatrizat) are difficult to oxidize.

The DOC concentration in the effluent of the MBR system was in the range of 8 to 12 mg/l. Ozone doses between 7.5 mg/l to 30 mg/l were tested with reaction times of 7.5 to 15 minutes. An ozone dose of 12.5 mg/l and a reaction time of 15 minutes showed a reduction rate of > 90% for the investigated key compounds Bisoprolol, Carbamazepin, Diclofenac, Metronidazol and Ciprofloxacin. By using the reported range of ozone doses ecotoxicological effects after the ozone treatment (algae, daphnia, genotoxicity) could not be detected.
Conclusions

APIs originates from different source points including pharmaceutical production sites, hospital waste, and household waste. Hot spots with higher concentration levels are the raw wastewaters from pharmaceutical production sites and wastewaters generated at hospitals. Environmentally relevant concentration of APIs may also be in the effluents of municipal WWTPs.

Ireland established specific regulatory guidelines for wastewaters from pharmaceutical production sites. The treatment process combination of MBR followed by Ozone has proven its availability to fulfill the regulatory requirements. The in Ireland installed WWTP is meeting the original design goals to reduce APIs in the site’s final effluent and sets a new benchmark for full-scale pharmaceutical manufacturing wastewater treatment. In summary the WWTP reduces total APIs from the wastewater by 99.94%; reduces estrogenicity 1,000 fold to a level believed to be of no concern to human health or to the environment; and produces a non-toxic effluent. Additionally, it was shown that this treated effluent could be beneficially reclaimed as make-up water for cooling towers and potentially for other beneficial reuse purposes.

Other guidelines (e.g. EU water directive and California Draft Groundwater Recharge Regulations) are still under development but it is obvious that stricter regulations for pharmaceuticals will be promulgated in the future. Results from research projects and technology evaluations shows that the treatment combination of MBR followed by Ozone is preferred very effective solution for API removal and for other applications including hospital wastewater and municipal WWTPs.

The full-scale plant installations in Ireland and at hospitals demonstrate the robustness of the MBR and ozone systems. Important aspects as reliability/redundancy, aesthetic (noise attenuation and odor control), and safety devices could be meet in the final installation.

Ozone in particular is proven as an key step in removing the effects of APIs, particularly estrogens, that while below detection limits using LC or GC MS/MS, make their presence known in the more sensitive yeast estrogen receptor (YES) and similar biochemical tests (E-Screen eg). This is an enormously important and relevant finding of studies completed to date.

References


NOTES
DECOLORIZATION OF EFFLUENT WATER FROM PULP AND PAPER MILL IN THAILAND BY OZONATION

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Abstract
Currently, the effluent water from pulp and paper industry is a major problem in the country. Its high COD value and pigment contamination will cause significant environmental problems. One effective way to treat effluent water is use ozone. The effect of ozonation on color removal, COD, SS and pH of the effluent water from pulp and paper mill in Thailand was studied. From the experimental results show that ozonation can remove dark brown color about 56.97%. and the COD removal was 36.4%. The reduction of the SS and pH did not change significantly.

Key-words: Ozone, decolorization, Effluent water

Introduction
Dark brown color of effluent water from pulp and paper mills is a major problem for the environment, especially the psychological community [1]. It is found that the color of effluent water generated from the compound of lignin-degraded products and tanning during various pulping and bleaching operation, which cannot be removed by biological treatment processes [1, 2]. For several decades attempts have been made to remove the dark color from the effluents. Whereas, physical adsorption, chemical oxidation and biochemical methods [3,4]. Additionally, several researchers have investigated the efficiency of ozonation as a technique for treating pulp and paper mill effluent [5,6]. The advantages of ozone are that rapidly reacts with bacteria, viruses and protozoa over a wide pH range; stronger germicidal properties than chlorination; no chemicals are added to water; also efficient for organics degradation and inorganics removal; removes color, taste and odors.

In this study, the ozone technology was used as a post treatment after the biological process for decolorization of effluent water from pulp and paper mill in Thailand. The effect of ozone dosage on color, chemical oxygen demand (COD), suspended solids (SS) and pH were investigated.

Material and methods

Sampling and analysis the quality of effluent water
In this research, the actual pulp and paper mill effluent water were obtained from the pulp and paper mill located in Khonkaen, Thailand. The pulp and paper mill wastewater treatment system in this study is shown in Fig. 1. The activated sludge (A/S) system was used for biological treatment. The color of the effluent water collected is light brown to dark brown. Effluent water is composed of organic compounds such as lignin, cellulose and semi-cellulose. The average characteristics of actual effluent water are shown in Table 1.
Table 1 The average characteristic of actual pulp and paper mill wastewater and biological treated effluent

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Actual wastewater</th>
<th>Biological treated effluent</th>
<th>*Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6-8</td>
<td>7.6</td>
<td>5.5 – 9.0</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>1,000-1,500</td>
<td>170</td>
<td>** &lt; 400</td>
</tr>
<tr>
<td>SS (mg/L)</td>
<td>300-500</td>
<td>23</td>
<td>&lt; 50</td>
</tr>
<tr>
<td>Color (Pt-Co)</td>
<td>500</td>
<td>400</td>
<td>not objectionable</td>
</tr>
<tr>
<td>Color (AMDI)</td>
<td>600</td>
<td>495</td>
<td>not objectionable</td>
</tr>
</tbody>
</table>

* Pollution Control Department of Thailand (1996)
** for pulp & paper mill

From table 1, the parameters are based on standards set by Pollution Control Department of Thailand (1996). The results show that, all parameters except color remained within standards when treatment with biological method. When considering the color of effluent water showed a decrease about 20%. Although, the color of the effluent water had not been determined but the color of the effluent water can affect the mental health of the community.
Effect of ozone dosage to effluent water treatment

Fig. 2, pilot plant used in this decolorization is shown. Effluent water was pumped from a holding tank into the reactor with volume of 115 L until its level was approximately 3.6 m from bottom. The flow rate of wastewater from pump was 3 L/min with detention time in reactor about 38 min. Ozone dosage can adjust from 0 – 400 mgO₃/L. The ozone diffuser was placed at bottom of the reactor to mix ozone with water. The ozone was produced by ozone generator (FAC, model FAC-100G-OX, Innovation ideas Company Ltd., Thailand) with maximum ozone capacity 100 gO₃/hr. Oxygen compressed gas with purity of 95% was used to produce ozone. The effluent water was collected after biological treatment (activated sludge AS). The effect of different ozone dosages of 0, 20, 40, 80, 160, 320 and 400 mgO₃/L was investigated. The experimental parameters including color, COD, SS and pH were carried out.

Results and discussion
The effluent water was treated by ozonation process with the ozone dosage of 20, 40, 80, 160, 320 and 400 mgO₃/L, respectively. Fig. 3 shows the effect of ozone dosage on color removal of the effluent water. The result shows that the ozonation process can reduce the color of effluents with increasing ozone dosage.
Fig. 4 shows the effect of ozone dosage on effluent water color removal. The color of the effluent water was measured in terms of ADMI. ADMI color value was measured at a wavelength of 400-700 nm every 10 nm interval which covered all of the visible wavelength. The color of the effluent water was decreased from 495 to 213 ADMI units after ozonation process. Color removal efficiency was 56.97%. The results are consistent with the color of the effluents shown in Fig. 3.

The results of ozonation can be explained that the COD parameter represents organic compounds included lignin and tannin which were degraded by ozone. From Fig. 5, the COD concentration decreased from 170 to 108 mg/L in ozone dosage range of 0 - 400 mgO₃/L. COD removal efficiency was 36.47%. Reduction of color and COD are likely higher when ozone dosage increased. While, ozone dosage increased as a result of the increase in ozone exposure time longer.
Fig. 6 shows the effect of ozone dosage on SS and pH of effluent water. For the results of SS and pH showed that there were no significant changes after treatment with ozone. SS values were in the range of 15.5-23 mg / L and pH values were measured in the range of 7.9 to 7.7 in all ozone dosages.

Conclusions
Effluent water from paper mill in Thailand was treated by ozonation. The results showed that ozone dosage affected the reduction of color and COD, but not for the SS and pH values of the effluent water after treatment. Ozone dosage of 400 mg is effective in reducing the effluent water color was 56.97%. The COD concentration decreased from 170 to 108 mg/L

References

NOTES
**APPLICATION OF OZONE OXIDATION OF SECONDARY EFFLUENT IN WASTEWATER TREATMENT PLANT**

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**Introduction**

Situated in Shanghai Chemical Industry Park, the wastewater treatment plant of *Sino-French Water Development Co., Ltd* (SFWD-WWTP) receives and treats various types of industrial wastewater from different sectors like petro-chemistry, fine chemistry. Industrial wastewater is often characterized by complex organic substances, especially biologically-refractory, toxic substances and high color.

With the rapid development of petro-chemistry and fine chemistry, conventional biological treatment processes such as activated sludge cannot well handle those pollutants, and this can pose great risks towards environment. Besides, both chemical oxygen demand (COD) and color are two of the parameters which are rigidly controlled and regulated in Shanghai according to Shanghai Integrated Wastewater Discharge Standard (DB 31/199-2009). Therefore, a more efficient way needs to be figured out for SFWD-WWTP so as to meet the increasingly strict requirement, especially on color removal.

Ozone oxidation is often considered as a promising treatment process in terms of advanced treatment, since ozone is a powerful oxidant with a reduction/oxidation potential of 2.07V merely behind F2 (2.87V). Ozone has been utilized for decades in the field of water disinfection and wastewater treatment because of its satisfying removal performance and no pollutant selectivity and no secondary pollution problem. In SFWD-WWTP, ozone oxidation has been successfully applied as advanced treatment process of secondary effluent for the purpose of color and COD removal since the enforcement of updated discharge standard.

**Ozone oxidation process in SFWD-WWTP**

SFWD-WWTP, with a daily wastewater treatment capacity of 35000 m³, applies traditional biological treatment process (anoxic-aerobic treatment) followed by coagulation/flotation and newly installed ozone oxidation process. Designed by Degremont, the ozone oxidation process is based on Ozonia’s ozone generator by producing ozone through corona discharge. The first ozone generator (25kg/h, OZAT CFV-30, Ozonia) came into operation in 2011. The average treatment capacity of the first ozone oxidation system is about 24000 m³ per day with an average ozone feeding concentration of 23 mg/L. The average reaction time is set to be about 8 minutes.

In view of successful operation and satisfying removal performance of the first ozone generator, a second ozone generator (20kg/h, OZAT CFV-30, Ozonia) has completed final commissioning process in November 2013 to meet the needs of stricter regulation as well as increasing volume of existing and new clients’ wastewater, and it’s now under operation.
According to the figure above, the color removal rate before and after ozone oxidation treatment for the last two years (October 2011-October 2013) is 60~75%. This indicates that ozone oxidation can reduce the color from the wastewater in a significant way. The reason for this efficient removal performance lies in that color derives from some dissolved organic matters which are difficult to remove by conventional treatment process. Characteristic structures of these colored organic matters are double bond or aromatic ring. Hence, their chromophores are prone to be attacked by oxidants such as free radicals and ozone.

Besides, from the figure above, it can be observed that since July 2013, the color of ozone generator inlet and outlet is keeping increasing, which show that with the full development of Shanghai Chemical Industry Park, more wastewater with high color flows into SFWD-WWTP and that ozone oxidation is evidently necessary to remove color from the wastewater.
The COD removal rate through ozone oxidation during the last two years (October 2011-October 2013) is 20~25%. In SFWD-WWTP, ozone oxidation is designed to removal color from the wastewater. The figure shows that ozone oxidation can further reduce COD value of the biologically-treated wastewater. As a result, the application of ozone oxidation process can not only remove color from the wastewater in a significant way but also further reduce COD of the wastewater.

The mechanism of ozone oxidation can be classified in two categories – direct oxidation with ozone molecule and indirect oxidation with free radicals which are generated through combined ozone oxidation like O$_3$/H$_2$O$_2$, O$_3$/UV. In SFWD-WWTP, direct oxidation is currently sufficient in SFWD-WWTP to control COD of treated wastewater under regulated value. Indirect ozone oxidation can be an alternative to meet a stricter regulation in the foreseeable future.

Consumption

The cost of ozone oxidation process (only electricity fee and oxygen cost included) in SFWD-WWTP is about 0.3~0.6 RMB/m$^3$ wastewater, or 20~40 RMB/(kg COD removed).

Conclusion

After 3 years’ operation, the Degremont’s ozonation system in SFWD-WWTP has been proven to be cost-effective, well efficient, and highly reliable as the tertiary treatment process to remove color and COD of the wastewater. Additionally, with the development of petro-chemistry and fine chemistry, there will be an increasing volume of industrial wastewater with complicated biologically refractory components and high color. Hence, ozone oxidation can be an option to meet this challenge. The successful application of ozone oxidation process in SFWD-WWTP can serve as an example in the field of advanced treatment of industrial wastewater.

Key literature

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THE COLOR REMOVAL OF BREWERY WASTEWATER WITH OZONATION IN THAILAND

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Abstract
The ozonation of dark brown waste water from Thai brewery plant was investigated. The dark brown color caused by polymer called melanoidins. Melanoidins are difficult to degrade by biological processes but it can be reduced by ozonation. Ozonation was selected in this case study to eliminate the melanoidins and remove the color. The wastewater was collected after upflow anaerobic sludge blanket (UASB) reactor and activated sludge (AS) tank. Ozone was treated in wastewater using different ozone dosages. The color, biochemical oxygen demand (BOD₅), chemical oxygen demand (COD), total organic carbon (TOC) and fourier transform infrared spectroscopy (FT-IR) were analyzed. From the experimental results show that ozonation can remove dark brown color about 93%. The BOD and COD removal are 29% and 57%, while TOC removal is 1.4%. The FTIR spectra show that molecular structure was changed after ozonation.

Keywords: Color removal, Ozonation, Melanoidins, Brewery wastewater

Introduction
The major problem of wastewater in brewery plant after biological treatment (upflow anaerobic sludge blanket and activated sludge UASB-AS) was dark brown color from melanoidins. Melanoidins were formed when sugar from malt combine with amino acid. They were high molecular weight amino-carbonyl compounds produced by Maillard reaction are during thermal processing and preservation [1]. They can be produce serious environmental problems when melanoidins are discharged to surface water [2]. Ozonation was one of many methods to reduce the brown color [3] therefore, in this study we reported effect of ozone dosage on color removal, BOD₅, COD, TOC and molecular structure.

Materials and methods
Samples of wastewater before and after ozonation obtained from output of UASB-AS system were collected from ozone mixing tank. Ozone was produced from desiccant air dryer (Fusheng, model FD050, -70°C dewpoint ) obtained from air compressor (Atlas Copco, model GA55). The 12 units of ozone generator (FAC, model FAC-2.5 KG, ozone capacity 2.5 kgO₃/hr, ozone concentration 30 gO₃/NM³, Innovation Ideas Company Ltd., Thailand) were used in this brewery wastewater plant. Cooling towers were used to reduce the temperature of ozone chamber. The maximum ozone capacity of the plant is 30 kgO₃/hr. The overall system is shown in Figure1. Ozone dosage can adjust from 0 – 55 mg/L by increasing ozone capacity in each unit. Ozone was mixed with waste water in mixing tank using 288 units of ozone diffuser. The flow rate of waste water in mixing tank for color removal is 13,000 M³/day with detention time about 40 min.

Results and discussion
Photograph of wastewater before and after ozonation at different ozone dosages of 0, 16, 32 and 48 mgO₃/L is shown in Figure 2 a). Figure 2b) shows effect of ozone dosages on color removal. The color was decreased from 497 to 33 Pt-Co unit after ozonation process. Figure 3a) shows the effect of ozone dosage on BOD, COD and TOC. The results of ozonation can be explained that the COD parameter represents organic compound included melanoidins which was degraded by ozone. The COD concentration decreased from 100 to 43 mg/L in 48 mgO₃/L dosages while TOC concentration nearly constant around 38 mg/L. BOD was slightly effected by ozone. As seen in Figure 3b) the all BOD/COD ratios were less than 0.4 representing the wastewater was slowly biodegradable. Figure 4a and 4b show FTIR results before and after ozonation.
ozonation at ozone dosage 48 mgO$_3$/L. The results show the stretching vibration of C=O (carbonyl group) at 1734.37 cm$^{-1}$ that was shifted to 1734.14 cm$^{-1}$ and the peak of this point was decreased. The results show that the chemical structure of wastewater was changed.

![Figure 2](image2.png)

Figure 2 a) Photograph of wastewater before and after ozonation at different ozone dosages  
b) Color removal

![Figure 3](image3.png)

Figure 3 a) BOD, COD, TOC results b) Ratios of BOD/COD.

![Figure 4](image4.png)

Figure 4 FTIR spectrum of wastewater a) before ozonation b) after ozonation with 48 mgO$_3$/L

**Conclusion**

Ozonation of brewery wastewater in Thailand was studied in this work. According to the results, the ozone treatment of wastewater can effectively remove both COD and color. The color and COD removal were increased with increasing ozone dosage. The ozonation changed organic structure to smaller molecule.
References
OZONE TO CONTROL BULKING AND FOAMING IN MUNICIPAL WASTE WATER TREATMENT PLANTS

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Abstract
Ozone is known to be effective for achieving positive treatment effects on sludge characteristics. One of these effects is the reduction in excess sludge generation in wastewater treatment operations. This application is known for many years and full scale plants are installed and in operation. The economical success of this application strongly depends on the required ozone dose to reduce a certain amount of excess sludge expressed as kg O\textsubscript{3}/kg TS\textsubscript{removed}. Economic dosage rates below \( \leq 0.1 \text{ kg O}_3/\text{kg TS}_{\text{removed}} \) are proven in full scale plants.

In addition a significant reduction of bulking at the wastewater treatment operation as a result of the ozonation process is observed. Microbiological analyses indicate that this is as a result of the greater vulnerability of filamentous bacterial species to sludge ozonation. Investigations show a significant reduction in the population of all filamentous microbial species, with the most significant reductions being observed in \textit{Microthrix parvicella} and \textit{Nocardia} species. The dosage range of ozone required enabling foam reduction and bulking control is significantly lower than the dosage range for the excess sludge reduction. Ozone is an attractive alternative to chemicals to prevent the sludge bulking and improves in parallel the settlement behaviour of the sludge (reduced Sludge Volume Index SVI). Depending on operational conditions the SVI can be readily reduced from 300 to lower than 100 ml/g.

Keywords: Ozone; sludge; lysis; filamentous bacteria; improved settlement; foam reduction

Ozonation of RAS (Return Activated Sludge)
The most applied sludge ozonation processes are integrated in the return activated sludge line to reduce the growth of biomass and therefore to reduce the amount of waste activated sludge mass. Integration in RAS line means that a portion of activated sludge is treated by ozone in a bypass system and RAS is pumped back to the biological treatment step. Most common is the mixing of ozone and RAS with a venturi pipe. Some processes use a pressurized reactions system or a loop reactor to have a certain retention time. The following scheme shows the implementation on RAS treatment:

\begin{figure}
\centering
\includegraphics[width=\textwidth]{scheme.png}
\caption{Principle scheme for Sludge removal process by ozone}
\end{figure}

Bulking and foaming control on activated sludge systems
The effectiveness of solid-liquid separation in wastewater treatment operations can be affected by bulking and foaming (Wanner, 1994; Madoni et al, 2000). Bulking and foaming problems can be pervasive, affecting up to 50\% of biological wastewater treatment facilities (Madoni et al, 2000). It has always been recognized that poor settleability and bulking is associated with the presence of filamentous organisms. A wide variety of filamentous organisms such as \textit{Microthrix parvicella}, Eikelboom types 0041, 021N, 0092, 0675, Thiothrix, and norcadiaforms actinomycetes have been found in wastewater treatment systems. \textit{Microthrix parvicella} is extremely pervasive. In a survey of 167 plants in Italy, Madoni et al (2000), found \textit{Microthrix parvicella} to be the most common filamentous organism, and its presence was highly correlated with the incidence of both bulking and foaming problems. A variety of factors such as low DO, low F/M,
complete mix reactor conditions, septic wastewater and sulfide availability, nutrient deficiency and low pH have all been associated with filamentous bulking (Eikelboom, 1975)

**Effects of Ozonation on filaments**

Filaments have a high surface area to volume ratio, which allows them to thrive under nutrient deficient conditions. However, the high surface area of filaments also makes them particularly susceptible to chemical attack. When ozone is applied to sludge, the lysis process occurs through the oxidation of the cell wall of the bacterial cells by ozone. It is well known that the rate of chemical reactions is enhanced by reaction systems that have large surface areas. The high surface area to volume ratios of filaments makes them especially susceptible to ozone attack. Also, even where the absolute number of filaments might be lower than that of the floc formers in a system, filaments form extensive bridging networks within and across flocs. This implies that not only single, free floating filaments are susceptible to ozone oxidation, they are also likely to be attacked by ozone molecules that penetrate the interior of the floc.

The technical process of bulk control with ozone is comparable with the disintegration process. The technical integration on WWTP is similar to Figure 1. The major impact is the size of the ozone generator due to lower dosages. The ratio of RASozoned / RAStotal is in the range of 0.05 – 0.1 depending on the gas flow of the ozone generator and treatment effects.

**Case study I: Ozone for sludge reduction and foaming control in Italy**

The effect of sludge ozonation on filament control was tested at full scale as part of a sludge minimization project at the Lariana WWTP (25,400 m³/day) located in Bulgarograsso / Italy (Fabiyi et al 2007). The raw water is a mixture of industrial (mainly textile) and municipal waste water. The facility had been plagued by a significant foaming problem (see figure 2). Microbiological tests indicated that the filamentous organisms at the facility included Microthrix parvicella, Nocardiaforms, Thiotorix, Sphaerotilus and Nostocodia. The foam was stable and measured about 20 cm in height.

![Figure 2: Foam on aeration tank in Lariana before (left) and during (right) ozonation (Fabiyi 2007)](image)

The ozonation step was installed by Praxair (Lyso) in the RAS line and the ozone was mixed via a venturi pipe. The ozonated sludge was returned to both nitrification basins. The dosage for this project is 0.05 - 0.07 kgO₃/kgTS reduced, which is lower than former studies. The following figure 3 shows the effect of the ozonation on the abundance of different filament in the biological treatment step.

![Figure 3: Reduction of filaments during ozonation at Lariana WWTP (Fabiyi et al 2007)](image)

Nostocodia was completely eliminated in the system and did not recur throughout the test period. In the 10 week period following the commencement of the sludge ozonation tests, the average abundance levels of
Microthrix parvicella, Thiotrix and Norcadiaforms were reduced by 66%, 94% and 87% respectively. The operator observed significant reduction of foaming in the aeration basin process of the wastewater treatment operation as a result of the ozonation process. The foam layer was consequently reduced. Additional effects were observed like decrease of SVI, the improvement of dewaterability of the excess sludge and no changes in the overall COD and TN removal.

Case study II: Ozone for bulking control in Germany
Lyko et al (2012) describes the use of ozone for bulking control at one of largest WWTP in Germany. The WWTP of Bottrop was sized for 1.300.000 PE and has an inflow at dry weather of 4.25 m³/s (mixture of municipal and industrial waste water). The problem of bulking is a seasonal problem which happens during periods with low temperature.

The design includes three parallel activated sludge lanes. One of these lanes was equipped with an Ozonation step to treat approx. 6% of RAS with ozone. The RAS was pumped in the ozone plant where the ozone was mixed in by a venturi pipe. The treated RAS was returned to the denitrification basin. The most important process parameters are summarized in Table 1.

Table 1: Process parameter of ozonation at WWTP Bottrop (Lyko et al 2012)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value at line 3 of WWTP Bottrop</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozone in process gas</td>
<td>wt%</td>
<td>8</td>
</tr>
<tr>
<td>Ozone load</td>
<td>Kg O₃/h</td>
<td>3</td>
</tr>
<tr>
<td>Gas flow</td>
<td>Nm³/h</td>
<td>25</td>
</tr>
<tr>
<td>RAS for ozonation</td>
<td>m³/h</td>
<td>300</td>
</tr>
<tr>
<td>RAS total</td>
<td>m³/h</td>
<td>5,000</td>
</tr>
<tr>
<td>Operation time</td>
<td>-</td>
<td>1 or 2 week(s) per month</td>
</tr>
</tbody>
</table>

The applied ozone dosage was according to Table 1 approx. 0.00167 gO₃/gTSSozonedRAS. The operation of the ozone plant was discontinuously one week in operation and two weeks without operation.

Figure 1 shows the changes in lane 3 and the two reference lines before and after the implementation of an ozonation step.

Figure 4: SVI changing during ozonation at WWTP Bottrop (Lyko et al 2012)

After the start of the ozonation the SVI level in lane 3 is on a constant level below 100 mL/g compared with the reference line where the SVI increases at the end of AlCl₃-Dosing. Comparing ozone and AlCl₃-Dosing the first effect on the sludge could be observed at the ozone treated lane after only two days. The effect of AlCl₃-Dosing could be observed after 7-10 days. Additionally the MLSS in lane 3 could be increased to 3.5 g/L compared to 2.5 g/L in the reference lines. Since the sludge retention time of lane 3 is 17 days 14 days without ozonation are quite enough to control filamentous bacteria. The ozone generator was 1 week in
operation and one week out of operation. The operating costs with ozonation are 50% less compared to the AlCl3-Dosing.

Conclusion

Although a variety of methods exist which can potentially be utilized for foaming and bulking control, sludge ozonation can be an extremely effective means for mitigating foaming problems in wastewater treatment facilities. The case studies summarized in this paper have demonstrated the effectiveness of ozone for controlling foaming and bulking problems at wastewater facilities. The continuous application of ozone in a wastewater treatment facility constitutes both a corrective and preventative measure. When applied to a plant that already suffers from bulking and foaming problems, ozone addition eliminates filamentous organisms that are already within the process. However, once that baseline is addressed, the further application of ozone serves to provide a strong selection pressure in the system for floc formers.

One full scale operation proved the prevention of bulking even with discontinuous ozone dosing (1-2 weeks operation during a month). The effect on the settling behavior can be observed in a short time and the overall treatment process is not negatively influenced. The ozonation technology is quite easy in operation and the operational costs are comparable or even lower than the use of chemical.

The specific operation conditions for bulking and foaming control (low ozone doses and the option of discontinuous operation) offers the operator of a waste water treatment plant a safe and economical attractive option to manage the plant in case of bulking and foaming problems.

References


Madoni P., Davoli D., Gibin G. (2000), Survey of filamentous microorganisms from bulking and foaming activated sludge plants in Italy. Water Research 34(6), 1767-1772


NOTES
APPLICATION OF 2 STAGE OZONE/HYDROGEN PEROXYDE AOP SYSTEM FOR MIXED EFFLUENT WASTEWATER TREATMENT

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Keywords: Advanced Oxidation, AOP, Wastewater, Ozone, Hydrogen Peroxide, Color, COD

Introduction
Rapid population growth, industrial development and diminishing water resources necessitate advanced waste water treatment processes to protect limited water resources. Advanced oxidation processes (AOP) have proven to be an efficient means to break refractory organics and are more and more commonly used to answer water treatment challenges of tomorrow. This paper reviews the use of a 2 stage advanced oxidation process for color removal and COD reduction of a mixed effluent from industrial and municipal sources.

In 2005 the conventional treatment scheme of the WWTP of Dongducheon City, Gyeonggido, South Korea (fig. 1) had been upgraded with a tertiary ozone treatment step to treat the high degree of color mainly originating from the light industrial sector including dye production.

Table 1: Main wastewater characteristics at WWTP Dongducheon City 2005 ad 2012

<table>
<thead>
<tr>
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<tr>
<td>pH</td>
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<td>7.0…7.2</td>
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<tr>
<td>COD_{MnVII}</td>
<td>[ mg/l ]</td>
<td>&lt;= 50</td>
</tr>
<tr>
<td>Color</td>
<td>[ degree ]</td>
<td>50…150</td>
</tr>
<tr>
<td>Flow rate</td>
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<tr>
<td>Origin</td>
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<tr>
<td></td>
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In an on-site pilot testing program different approaches have been selected to improve the existing treatment scheme. Besides an increase of the applied ozone dose, also an AOP process using ozone and hydrogen peroxide as well as the use of a unique 2 stage process with ozone followed by an AOP using ozone and hydrogen peroxide was tested.

Methods
For the on-site tests a mobile AOP pilot rig mounted on a truck was used (fig. 2). The pilot rig allows testing of any combination of AOPs, i.e. O₃/H₂O₂, O₃/UV, O₃/UV/H₂O₂. Oxygen from an oxygen bomb is fed to an ozone generator, the ozone then introduced into the water through a venturi followed by a static mixer and reaction tank. Waste water is fed into the motive water loop that can either be operated in a once through mode or in a recirculation operation mode allowing very high ozone dosages. H₂O₂ is dosed into the motive water stream upstream the injector. Up to 3 reaction tanks, which can individually be connected to the system or bypassed, provide the required reaction time (fig. 3)
For the tests with ozone alone wastewater from the existing plant before ozonation was used and different ozone dosages tested in the test rig. For the tests with a 2 stage process (O₃ followed by O₃/H₂O₂) ozonated water from the existing ozonation has been fed to the test rig to simulate the 2 stage process.

**Results and conclusions**

Figures 4 and 5 show the results of the different tests for color reduction. In a first test series ozone dosages up to 100 ppm led to a decrease in color from 400 to 100 degree. A later test series with ozone alone (Fig. 5) showed similar results, reducing an original color of 450 to 150 degree. Tests with a combination of ozone followed by O₃/H₂O₂ with a 20 ppm O₃ initial dose and a secondary ozone dose of 40 ppm and 18 ppm H₂O₂ (Fig.4) could overall reduce the color to less than 50 degree. Applying an initial ozone dose of 40 ppm (Fig. 5) reduced the color from 450 to 200, a consequent dosing of O₃/H₂O₂ of only 10 ppm O₃ and 10 ppm H₂O₂ reduced the color to less than 50 ppm.

The latter operational regime reduced the COD from initially 50...80 mg/l to less than 40 at constant pH of 7.2.

**Note:** Applied ozone dose equals total combined ozone dose (stage 1+2).

Molecular electrophile reactions contribute efficiently to the initial reduction in color reflected in a rather high initial ozone dose. Radical reactions brake down remaining refractory color compounds. The results show that an intelligent design of a reaction regime allowing molecular and radical reactions provide overall operational and investment cost savings in the range of 20%.

This case study demonstrates the application of AOP’s as polishing step in combination with ozone significantly increasing the overall treatment performances. Investment and operational cost are reduced providing promising treatment options for the future as alternative to classical designs with e.g. ozone or AOP alone.

**Key literature**


Mémento technique de l'eau, 10ème édition, edited by Degrémont, Lavoisier, Cachan, France, 2005.

NOTES
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