



## The Annual Group Meeting: March 2018

### TED style presentations

The Moshe Mirilashvili Institute for Applied Water Studies

### Program

Names	Topics
<b>Aviv Kaplan:</b> Senior analytical chemistry technician & M.Sc. student	AOPs for Trace Organic Compounds (TrOCs) in effluent reverse osmosis concentrate  Ascidians – bio-indicators for contamination of the marine environment  Development of analytical method to differ Arsen(V) from Arsen(III) to study bacterias bioremediation potential
<b>Dr. Lakshmi Parasanna:</b> Postdoc	Drugs recovery from Wastewater
<b>Dr. Vinod Kumar:</b> Postdoc	Process stability of visible light driven self-cleaning photocatalysts and pilot-scale validation for trace organic chemical removal from wastewater treatment plant effluents
<b>D. Gokul:</b> Visitor Ph.D. students	Treatment of DEP from municipal leachate by ozone based AOP
<b>Adi Zilberman:</b> M.Sc. student	Hospital wastewater treatment- the pilot
<b>Dr. Gefen Ronen-Eliraz</b>	Ozone based AOP Kinetic
<b>Daniel Zachor:</b> M.Sc student	Method development for analysis of chemotherapy drugs
<b>Yan Rosen:</b> Ph.D. student	Enhancing the feasibility of ozonation pretreatment of lignocellulosic waste by reducing ozonation time

<b>Roi Peretz:</b> Ph.D. student	Co-conversion of Recycled Paper Sludge to bioethanol and Cellulose Nano Crystals via ozone based processes
<b>Liza Sterenzon:</b> M.Sc. student	Production of Crystalline Nanocellulose (CNC) and its application for water treatment membranes
<b>Patricia Akao:</b> Ph.D. student	Microalgae utilization for plasticizers degradation and biofuel production, the circular economy concept
<b>Dr. Yifaat Betzaleal</b>	The use of biosensors to determine bacterial intracellular damages that are attributed to UV stress
<b>Dana Pousty:</b> M.Sc. student	Comparison of UV-LEDs and low-pressure UV lamp for effect of Irradiation parameters (Average intensity, irradiation time etc.) on log inactivation of bacteria and virus

## Abstracts

### Aviv Kaplan

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*Ongoing studies at the Hydrochemistry laboratory*

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This presentation will include several ongoing studies at the Hydrochemistry laboratory:

- AOPs for Trace Organic Compounds (TrOCs) in effluent reverse osmosis concentrate. This study test the efficiency of AOP treatment on TrOCs in WWRO concentrate and asses the matrix scavenging potential.
- Ascidians – bio-indicators for contamination of the marine environment. Development of analytical methods to determine phthalates and drugs in organisms body.
- Development of analytical method to differ Arsen(V) from Arsen(III) to study bacterias bioremediation potential.

Adi Zilberman

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*Hospital wastewater treatment- the pilot*

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With the growth of the Israeli population in the last decades, the need for good and clean water is imperative. The care towards the health and environmental impact caused by the chemicals used by men, such as chemicals for agriculture, industry, medicine and home demand is growing. With the reuse of 84% of the wastewater in Israel for agriculture, the need for high-quality wastewater treatment is very important. That's why we are focusing on wastewater originated from the hospital. The hospital effluent contains highly toxic and persistent chemicals but are not required treatment in-situ worldwide (as industrial wastewater do), the wastewater reaches the municipality treatment center with no further treatment, which results in high quality effluent that contains pharmaceutical residues. Our solution is an in-situ ozone-based AOP for breaking down drugs. First, the wastewater undergoes a biological treatment that breaks some of the molecules, then the ozone treatment chops the MP (aromatic rings and double bonds) by that increases the biodegradability to a point that the molecules are much easier to degrade by bacteria.

Gefen Ronen-Eliraz

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*Ozone based AOP Kinetic*

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An attractive technology for the treatment of pharmaceuticals in water is the advanced oxidation process (AOP), where pollutants are chemically oxidized. The oxidation can be direct process or indirect, by a process that produces hydroxyl ( $\bullet\text{OH}$ ) free radicals. This section of study, aims to determine the potential of the UV/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> process for the degradation of the research target chemotherapy drugs.

Laboratory batch scale ozonation kinetics experiment of the research target TrOCs, were carried in order to evaluate the efficiency of each of the sub-processes composing the UV/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> process, on the degradation of the selected pharmaceutical. Experiment solutions were adjusted to pH 8, which is similar to the expected pH of the pilot system treated wastewater. A preliminary experiment of exposure to ozone, low and high doses (0.3 and 1 mg/L: DOC mg/L, respectively) was conducted to a mixture solution of the target TrOCs, and

specific experiment method, for resist- or competitive- compounds was fitted. The  $kO_3$  constants for each of the target TrOCs was calculated according to the specific results.

Daniel Zachor

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*Identification and Examination of removal efficiency of Six Anti-Cancer  
Drugs and medicine derived from the Oncology Building at Tel  
'Ha'Shomer' Hospital*

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Gemcitabine, 5-Fluorouracil, Cyclophosphamide, Doxorubicin, Paclitaxel and Dexamethasone are six anti-cancer and anti-inflammatory pharmaceuticals used extensively in hospitals worldwide, one of which is “Sheva ‘Tel Ha’Shomer” hospital, located the center of in Israel. These chemotherapy drugs are the most toxic chemical the human ever developed, they aim to destroy human cells. The method of operation of these anti-cancer drugs is by interacting with the DNA strands and thus remain unchanged and active even after they exit the human body. They are resistant to wastewater treatment plant secondary biological treatment and may spread around various water environments thus, require an aggressive and effective advanced treatment. Due to hospitals, worldwide, are not required for wastewater pre-treatment, these compound discharge to the nearby domestic wastewater treatment plant (WWTP), that already demonstrated insufficient removal of these toxic chemicals. Consequently, the chemotherapy drugs were detected in wastewater, WWTP effluents and surface water bodies. A specific and complicated analytical method using HPLC-UV-MS/MS and SPE sample preparation method was developed to detect these compounds in the aquatic environment. Cyclophosphamide, 5-Fluorouracil, Paclitaxel were found in “Sheva ‘Tel Ha’Shomer” hospital waste water.

Lakshmi Parasanna

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*Drugs recovery from Wastewater*

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Recovery and purification of lifesaving pharmaceutical from patient’s urine is a breakthrough innovative idea, standing in the main objective of this research. Resource recovery from wastewater is gaining momentum these days shifting the paradigm from “treatment and disposal” to “reuse, recycle and resource recovery”. Increasing demand for drugs, lack of raw materials and delay in manufacturing are some of the reasons for the drugs prices increase and

worldwide shortages. Patients pay thousands of dollars per 1 dose of an essential lifesaving drugs. Sometimes a lifesaving treatment reject because of drugs shortage. Depending on the rate of metabolism and adsorption, 30–90 % of drugs are excreted in urine as inactive unchanged drug and constitutes a worldwide problem. Since the drugs residuals excreted in patient's urine flushes to the regular municipal wastewater and are resistance to the customary treatment, they reach back our waterways and food, and threatening on the public health.

Our goal is to reuse the purified drugs as reference standards. Further, the highest purity recycled drugs, will be allowed for reuse as an Active Pharmaceutical Ingredient (API), which may decrease dramatically the price of the recycled drugs. Implementing appropriate methods and technology for pharmaceuticals recovery will gain in both aspects: drugs shortage and cost increase concerns as well as reducing negative environmental impact and threat on public health.

Vinod Kumar

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*Process stability of visible light driven self-cleaning photocatalysts and pilot-scale validation for trace organic chemical removal from wastewater treatment plant effluents*

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Our study examine scientifically the removal of trace organic chemicals (TOrcs) occurring at ambient concentrations from wastewater treatment plant effluents by advanced oxidation using visible light driven self-cleaning photocatalysis at pilot-scale. Pseudo first-order rate constants (kobs) for photolytic as well as combined oxidative and photolytic degradation observed at pilot-scale will be validated with results from a lab-scale performance. During continuous lab-scale operation at constant solar irradiation and catalyst dosage of 50 mg/L, the removal of various TOrcs was investigated. We are also interested to observe removal of photo-susceptible ( $k_{UV} > 10^{-3}$  cm<sup>2</sup>/mJ; like diclofenac, iopromide and sulfamethoxazole), moderately photo-susceptible ( $10^{-4} < k_{UV} < 10^{-3}$  cm<sup>2</sup>/mJ; like climbazole, tramadol, sotalol, citalopram, benzotriazole, venlafaxine and metoprolol), and most photo-resistant ( $k_{UV} < 10^{-4}$  cm<sup>2</sup>/mJ; like primidone, carbamazepine and gabapentin) compounds.

Additionally, based on removal kinetics of photo-resistant TOrcs, continuous lab-scale operation revealed high variations of OH-radical generated from different photocatalyst based on particle size, surface morphology, doping cation/anions and catalyst loading. Furthermore, a correlation between OH-radical generation and scavenging capacity could be determined and

proved by mechanistic modelling using photon influence, catalyst dosage, and standard water quality parameters (i.e., DOC, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup> and HCO<sub>3</sub><sup>-</sup>) as model input data. The nanocomposites have shown more significant visible light self-cleaning activity than that of commercial TiO<sub>2</sub> materials and represent an unusual step forward in visible-light driven self-cleaning treatment for flexible materials with a high potential for commercialization.

D. Gokul

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*Treatment of DEP from municipal leachate by ozone based AOP*

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In many developing countries like India, most of the solid waste generated is being sent to the open dumpsite for its final disposal. The urbanization has a major impact on municipal solid waste generation rate and further increasing in solid waste generation is a great burden for the dumpsite as well as to environment. One of the main problems in solid waste management is generation of leachate from the dumpsite. The interaction of waste with water that percolates through the landfill produces highly polluted wastewater termed as landfill leachate.

Leachate contains large amount of organic matter of which Humic substances are the major group along with ammonia nitrogen, toxic metals, chlorinated organic, phenolic compounds, pesticide residues and endocrine disruptors like phthalates which are considered as priority pollutant by US EPA. Biological process has very less efficiency in removing the phthalates due to its toxic characteristics. Physicochemical processes have been successfully applied for the removal of recalcitrant substances from stabilized leachate and refining the biologically pre-treated leachate. Among various physicochemical processes, Advanced Oxidation Processes (AOPs) have been widely applied to complete removal of phthalates in leachate that are non-biodegradable and/or toxic to microorganisms.

Presently, AOP treatment of phthalates is carried out by considering Diethyl phthalate (DEP) as a model compound due to its high solubility and toxic in nature by Ozonation (O<sub>3</sub>) and Ozone in combination with Hydrogen peroxide (O<sub>3</sub>/ H<sub>2</sub>O<sub>2</sub>) for complete degradation of phthalates and its transformation products. Our main focus will be of complete treatment process which degrades DEP and other organic contaminants from the leachate.

Yifaat Betzaleal

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*The use of biosensors to determine bacterial intracellular damages that are attributed to UV stress*

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Irradiation with ultraviolet (UV) is a common practice in water treatment and disinfection. Conventional UV light source are low pressure (LP) and Medium pressure (MP). Recently, light emitting diodes (LEDs) have become an alternative UV light source due to their many advantages such as wavelength diversity, longer life time and applicability for numerous design options. The objective of this research is to understand bacteria intracellular damage as a result of UV-LEDs exposure for further optimization of UV-based disinfection technologies. Biosensors provide an inner insight to the defense mechanisms that bacteria utilize once exposed to UV. In addition to viable cell counting (bacterial inactivation), a real time induction of selected genes was monitored by measuring the bioluminescence emitted by the biosensors using a multi-well plate reader (Tecan Spark10). Our results show that in response to UVC- and UVB-LED, genes that are related to DNA repair and oxidative stress are induced, indicating that bacterial inactivation maybe attributed to versatile damages and not only a direct DNA damage.

Roi Peretz

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*Co-conversion of Recycled Paper Sludge to bioethanol and Cellulose Nano Crystals via ozone based processes*

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To-date ethanol is produced mainly by fermentation of various sugars found in especially grown agricultural crops such as corn (USA), sugar beet (Europe), and sugar cane (Brazil). Nevertheless, the use of potential food crops for ethanol production has been blamed for rise in food prices and increased competition for land and water sources with other food crops, raising serious political, environmental and social issues. Furthermore, in the specific context of Israel there is simply not enough open land for growth of crops especially for biofuels. As paper is made from wood material it is very rich in cellulose, although exact numbers can vary, depending on the specific wood used and the pulping method used. This composition implies that paper sludge could be a good feedstock for ethanol production. Previous work found that short-term ozonation can be used for the ethanol industry as a pretreatment step in

production of ethanol from lignocellulosic wastes, as it is most likely that lignin will be oxidized rather than cellulose or hemicellulose.

To reduce the process costs and make the process even more economically feasible, another desired product of Cellulose Nano Crystals (CNC's) are investigated as an added value. These are rod-like cellulose whiskers and vary from 100-250 nm in length and 5 to 70 nm in width. CNC's serves today as a key component in many industrial applications as building blocks for developing materials including thin films, nanocomposites, biomedicines and smart materials. CNC's demonstrate low density ( $1.6 \text{ gr cm}^{-3}$ ) and reactive surface of hydroxyl groups that enable grafting chemical species for achieving different properties. These chemical functionalizations can introduce electrostatic charges on the CNC surface, which ultimately provide better dispersion in any solvent/polymer. Due to its' high oxidative properties, ozone can be used for surface modification of the CNC's thus allow a better dispersion of the crystals. Eventually, ozonation process may promote the utilization of two valuable products from RPS: bioethanol from the amorphous region and CNC's from the crystalline region of the cellulosic matrix.

The goal of this study is to examine the recovery of the RPS for the utilization of ethanol and CNC's. The specific objectives are:

- A. Design and optimize ozonation pretreatment process and studying the mechanical and biochemical processes involved.
- B. Increase ethanol production by finding and implementing the most suitable hydrolysis and fermentation. conditions.
- C. Production of CNC's as an added high value product to improve process economics.

Yan Rosen

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*Enhancing the feasibility of ozonation pretreatment of lignocellulosic waste by reducing ozonation time*

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Lignocellulosic waste (in this study municipal trimming) is a promising sustainable feedstock for ethanol production, but require costly and polluting pretreatment, that often result in toxic byproducts. Ozonation is a nonpolluting, effective pretreatment method, but is not used commercially due to the high energy requirements of the assumingly high ozone doses needed. Results demonstrated that both ozonation time and enzyme dose (at optimal pH) impact conversion efficiency to glucose. Ozonation (15 and 90 min, accumulated TOD=318 and 1114



mgO<sub>3</sub>/L) of water-submerged waste (at pH=5.5) prior to enzyme addition at (×1.5 industrial enzyme dose) enabled high conversion of the cellulose fraction of the waste to glucose (31% and 42% respectively) compared to non-ozonated sample (with enzyme, 12%), suggesting ozonation could offer an effective and feasible pretreatment method. In these ozone doses, only 20% and 40% of the lignin was degraded showing that there is no need for delignification (as opposed to the common hypothesis) to obtain high sugar conversion. In addition, ozone process can be easily monitored by change in absorbance at 230, 280 and 436 nm, making it useful to use spectral scan in the field. Moreover, reduction in net calculated energy balance was obtained at higher ozone dose (90 min compared to 15 or 30 min), demonstrating increased process efficiency at lower ozone doses. Consequently, ozonation can be generated on-site and on demand, enabling decentralized pretreatment operated near the feed source thus overcoming transportation costs.

Patricia Akao

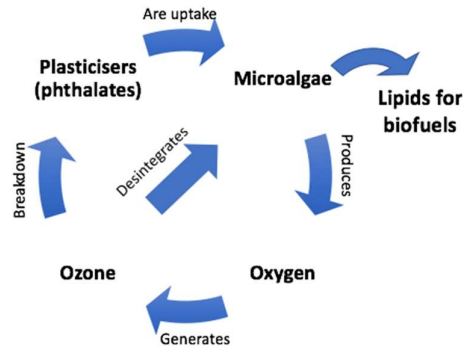
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*Microalgae utilization for plasticizers degradation and biofuel production,  
the circular economy concept*

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Microalgae have received greater attention lately, not just due their potential for wastewater treatment but also they are a promising alternative source to the conventional feedstocks for third generation biofuel production. In this field, microalgae can be regarded as the best source of feed-stocks in terms of high photosynthetic activity, reducing food insecurity and the harmful impacts on the environment. Another field of research is the effect of advances oxidation process on microalgae. The direct effects are disinfecting and oxidizing benefits of ozone, and several secondary benefits including: micro flocculation, reduction in coagulant dosages, improve water quality, reduction in the filter bed heads loss gradient.

Regarding this growing field of research, the goal of this proposal is to study the circular economy concept of utilize microalgae for oxygen generation and later on ozone production, that will be utilized for sanitization and plasticizers breakdown, the plasticizers and their sub products will be uptake by the microalgae, which will be ozonate to release lipids for biofuels. The remain wastewater is used for agricultural irrigation.



**Figure 1.** Scheme of circular economy concept for microalgae.

Preliminary data show the effect of different concentrations of ozone on microalgae, *Arthrospira platensis*. A concentration of 16 mg of ozone cause shortening and death of the microalgae. After ozonation the particles become transparent, their content is release from the cells, and what remains is just the sheath of the microalgae that is completely degraded with more ozone concentration.

**Table 1.** Micro flow imaging images elucidating the effect of ozone under spirulina particles.

No ozonation Mean Intensity - 370	16 mg ozone Mean Intensity - 758

Dana Pousty

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*Comparison of UV-LEDs and low-pressure UV lamp for effect of Irradiation*

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UV disinfection is one of the effective treatment for drinking water and wastewater. Differs from other typical forms of disinfection, as it does not require the addition chemicals, requires less space and does not leave a residual that can be harmful to humans or aquatic life.

The mechanism for UV disinfection transfers electromagnetic energy, from UV source to the genetic material (DNA and RNA) present in pathogens (bacteria, viruses, etc.). The nucleic acid absorbs UV light at wavelengths from 200 to 300 nm, the peak near 260 nm. The UV light damage is resulting in an injury and retarding the cell's ability to reproduce.

Common UV sources are low-pressure (LP) mercury vapor lamp that produces monochromatic (single wavelength) UV light at 253.7 nm, and medium pressure (MP) mercury vapor lamp that emits UV light over polychromatic spectrum throughout wavelengths 220-300 nm.

UV disinfection efficacy depends on the dose, which is defined as the product of average incident irradiance (intensity) and exposure time corrected for water absorbance. It has been proven that the same time does reciprocity may not lead to the same reduction of microorganisms, at different intensities. Sommer et al., (1996) reported that in several eukaryotic yeast strains, low intensity over long exposure times is more effective in inactivating cells. In contrast, *E.coli* showed higher UV inactivation when applying a high UV intensity over short exposure times (Sommer et al., 1998).

A dose-response curve for *E coli* in synthetic surface water, subjected to monochromatic low-pressure (LP) ultraviolet (UV) radiation was investigated using three different average intensities. When *E. coli* was exposed to a dose of 15 mJ/cm<sup>2</sup> at high intensity (0.774 mW/cm<sup>2</sup>sec) the log inactivation was 2.14 ( $\pm$  0.12) however for the same dose using low intensity (0.0174 mW/cm<sup>2</sup>sec) the log inactivation was 0.653 ( $\pm$ 0.06). Thus a difference of  $\sim$  1 log reduction was obtained at a dose of 15 mJ/cm<sup>2</sup>.

More recently, UV light-emitting diodes (LEDs) are emerging as a new UV source. Compared to mercury vapor lamp, the LEDs have some advantages: not contain mercury, compact and robust design, various wavelengths, longer lifetime, and faster start-up time.

LEDs have low electrical power requirements and need lower voltages than conventional mercury lamps, therefore, offering the option to be operated with solar cells or rechargeable batteries. In contrast, the low output power of UV- LEDs can decrease the intensity significantly that may lead to time does reciprocity effect described above.

The aim of this study is (a) to obtain a dose-response curve for *E. coli* in synthetic surface water, under monochromatic low-pressure (LP) UV vapor lamp and UV light-emitting diodes (LEDs). (b) to investigate the time-dose reciprocity using three different UV intensities under UV light-emitting diodes (LEDs) and monochromatic low-pressure (LP) UV vapor lamp.

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*Production of Crystalline Nanocellulose (CNC) and its application for water treatment membranes*

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Crystalline nanocellulose (CNC) is a natural, renewable polymer which is composed of rod-like nanocrystals of cellulose with average dimensions of 100 nm in length and 5 nm in diameter. CNC possesses unique optical and mechanical properties, such as high aspect ratio, low density, high tensile strength, etc. Such properties make CNC a highly useful material for the manufacturing of various bioproducts. In recent years, interest in CNC intensifies as the industry realizes its potential, especially with its production being cheap and based on extraction from plants.

There are, however, several problems that arise by the production of crystalline nanocellulose from plants, such as a waste of water and the occupation of agricultural lands. An even more environmental production of CNC might be achieved by using recycled paper sludge (RPS) instead of plants, as RPS consists mainly of wood – which is very rich in cellulose as well.

The goal of this study is to try and develop an environmental-friendly method of producing CNC from RPS, while examining two approaches:

- a. Chemical Hydrolysis: a hydrolysis using malic acid (di-carboxylic acid). Using such acid rather than the conventional use of phosphoric or sulfuric acid may add carboxylic groups to the cellulose, allowing higher electric charges and a better separation and recycling because it is a weak acid.
- b. Enzymatic Hydrolysis: incubation with enzymes may prove highly effective for crystal utilization.

The next step of the research will be manufacturing membranes that are made of CNC, which will be produced from the RPS, for various water treatments such as an adsorption of dyes from textile industry or heavy metal ions from wastewater.