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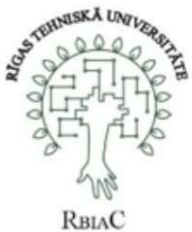
European Union  
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Development Fund

# Hi-Water project Closing Week

24-28 May, 2021 | Online

«Efficient and Affordable Water  
Treatment Technologies to  
Minimize Waterborne Diseases»

## Book of Abstracts



RIGA TECHNICAL  
UNIVERSITY



# Hi-Water project Closing Week

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## «Efficient and Affordable Water Treatment Technologies to Minimize Waterborne Diseases»

24-28 May, 2021 Online

Book of Abstracts



# Editors:

Linda Mezule

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## VIS-light Active BiOX Nanoparticles: Functionalisation of Carboxylated PES Membranes for the Application in a Photocatalytic Membrane Reactor

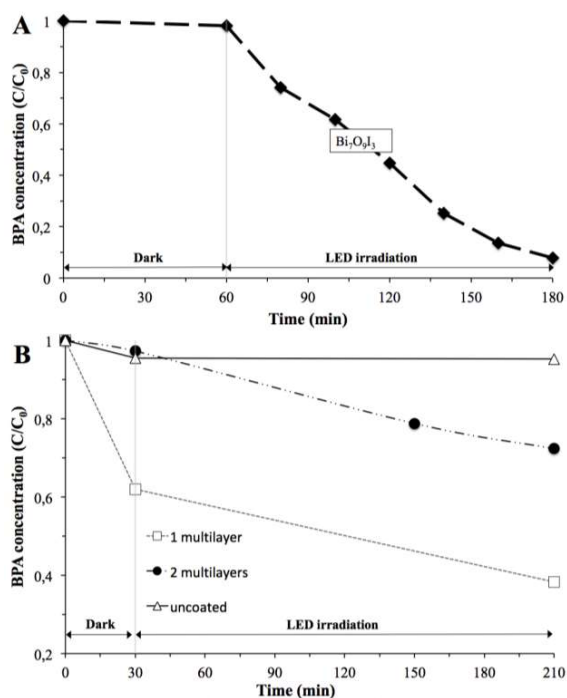
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**INTRODUCTION:** Coupling visible light active semiconductor photocatalysis with membrane processes are a promising technology for advanced water treatment [1]. Among these photocatalysts bismuth oxyhalide (BiOX) nanoparticles are known for excellent electrical and optical properties with respect to efficient photocatalytic activity under visible light irradiation [2]. Contaminants of emerging concern (CECs) in the aquatic environment continue to be a major challenge for nature and human health. Most frequently detected endocrine disrupter bisphenol A (BPA) is known to trigger carcinogenic and epigenetic effects [3]. Thus, in this work Bi<sub>7</sub>O<sub>9</sub>I<sub>3</sub>-nanoparticles were synthesized followed by characterisation. Photocatalytic efficiency was evaluated in a batch test, using BPA as a model pollutant. Furthermore, the as-synthesized nanoparticles were immobilized on carboxylated polyethersulfone (cPES) membranes in order to estimate photocatalytic BPA removal capability in a hybrid membrane process.

**METHODS:** Bi<sub>7</sub>O<sub>9</sub>I<sub>3</sub>-nanoparticles were synthesized using an oil bath and reflux system, according to the method of Xiao & Zhang [4]. Bismuth(III)-nitrate-pentahydrate served as the bismuth source and potassium iodide was used as the halogen supply. Ethylene glycol functioned as the solvent for the synthesis. XRD, SEM, EDX, and zeta-potential analysis provided knowledge about structure, morphology, composition, and surface charge of the as-synthesized nanoparticles. Layer-by-Layer (LbL) self-assembly technique was used to immobilize the photocatalyst on the permeate-site of the membrane. Poly(diallyldimethylammonium chloride) (PDADMAC) and polyacrylic acid (PAA) were selected for multilayer build-up as double-layer bases for Bi<sub>7</sub>O<sub>9</sub>I<sub>3</sub>-nanoparticle adhesion on the membranes surface. The photocatalytic activity experiments were conducted in a photoreactor equipped with a 50 W conventional white LED lamp (Ledvance Endura<sup>®</sup> Flood, T<sub>colour</sub> = 3000 K).



**Fig. 1. A:** Photocatalytic degradation of BPA ( $c_{BPA} = 20 \text{ mg/l}$ ) in a batch experiment with Bi<sub>7</sub>O<sub>9</sub>I<sub>3</sub>-nanoparticles as photocatalyst ( $c_{BiOX} = 1 \text{ g/l}$ ); **B:** Photocatalytic BPA ( $c_{BPA} = 10 \text{ mg/l}$ ) degradation in a membrane reactor. Comparison of four different membranes: one Bi<sub>7</sub>O<sub>9</sub>I<sub>3</sub>-multilayer, two Bi<sub>7</sub>O<sub>9</sub>I<sub>3</sub>-multilayers, uncoated.

**RESULTS:** Initially, photocatalytic degradation experiments were carried out in a batch reactor to assess both the photoreactor and the synthesized nanoparticles in terms of their efficiency in degrading model pollutants like BPA. Figure 1.A shows BPA concentration as a function of irradiation time in the presence of Bi<sub>7</sub>O<sub>9</sub>I<sub>3</sub>-photocatalyst ( $c_{Bi7O9I3} = 1 \text{ g/l}$ ). BPA ( $c_{BPA} = 20 \text{ mg/l}$ ) concentration decreased significantly by 93 % after two hours of LED-irradiation time. The investigation of the photocatalytic efficiency of



functionalised membranes was carried using a transparent membrane module operated in cross-flow mode placed inside the photoreactor for the degradation of BPA in the feed solution. The results demonstrated in Figure 1.B show a comparison of three membranes (uncoated; one multilayer PDADMAC/PAA/Bi<sub>7</sub>O<sub>9</sub>I<sub>3</sub>; two multilayers (PDADMAC/PAA/Bi<sub>7</sub>O<sub>9</sub>I<sub>3</sub>)<sub>2</sub>). It can be seen that photocatalytic degradation of BPA occurred in the filtration process of the two functionalized membranes. The membrane with just one multilayer has the highest BPA removal efficiency. The initial concentration (10 mg/l) could be reduced by 62 % after three and a half hours. Nevertheless, 38 % of the degradation can be attributed to the high adsorption of the pollutant on the surface of the membrane and 24 % was provided by photocatalytic degradation. The second membrane functionalised with a total of two Bi<sub>7</sub>O<sub>9</sub>I<sub>3</sub>-multilayers initially exhibits lower photocatalytic efficiency. However, only 3 % of BPA reduction resulted from the contaminant adsorption on the functionalised membrane. In this specific case, doubling the Bi<sub>7</sub>O<sub>9</sub>I<sub>3</sub> concentration on the membrane surface led to a photocatalytic degradation of 25 %.

**DISCUSSION & CONCLUSIONS:** The main focus of this work was on the development of a visible light active photocatalytic membrane reactor (PMR). Due to the high photocatalytic efficiency of the Bi<sub>7</sub>O<sub>9</sub>I<sub>3</sub>-nanoparticles demonstrated in the batch test, it was possible to develop a photocatalytic membrane process. The batch test guaranteed almost complete degradation (93 %) of BPA during a two hour LED-irradiation period. The three and a half hour PMR filtration with two Bi<sub>7</sub>O<sub>9</sub>I<sub>3</sub> functionalised membranes showed significant photocatalytic degradation abilities of BPA as model pollutant under LED-light irradiation (up to 25 %). Nevertheless, questions such as the right coating method, layer configuration, photocatalytic efficiency enhancement, neglecting high adsorption equilibrium and process stability need to be addressed. However, it was proven that bismuth-based photocatalyst possess a high potential for the use in energy-efficient water purification and wastewater treatment. Due to their excellent photocatalytic activity under low power LED-irradiation. It opens up further opportunities for the advancement of future advanced oxidation processes (AOPs) to remove CECs from polluted waters and make them harmless to humans and

nature. In order to make water treatment technologies more efficient, environmentally friendly and cost-effective in the future, new materials and processes need to be developed.

**ACKNOWLEDGEMENTS:** This work is part of the “Hi-Water-Project: Efficient and affordable water treatment technologies to minimise waterborne diseases”. It was funded by EU CELAC R6I funding agencies (EULACH16/T02-0143) (<http://eulachealth.eu/>). In addition, we would like to thank all the laboratory technicians who supported this work technically at Ikiam University and Leibniz-Institut für Polymerforschung Dresden e.V.



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## Application of BiOX Photocatalysts in the Degradation of Organic Pollutants

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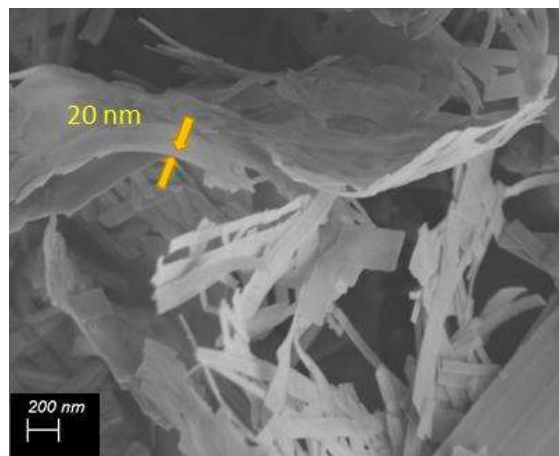
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**INTRODUCTION:** Bismuth oxyhalides (BiOX) are characterized by their open two-dimensional layered crystalline structures. The layered materials generally, have high specific surface area, larger proportion of surface exposed atoms, excellent physical and mechanical properties [3]. Majority of these compounds are functional in the visible light region along with band gap < 3.0 eV. In addition, BiOX based photocatalyst are chemically inert, non-hazardous and corrosion resistant in an aqueous medium [6]. Due these properties are envisioned as potential photocatalysts for degradation of organic pollutants.

**METHODS:** At least, there are three strategies used to study photo-degradation as a method of water purification: (1) The first is driven to increase photo-catalyst efficiency by improving the solar light absorption, promoting photoexcited charge carrier separation/transportation or modifying the band alignment of semiconductor photo-catalysts. The aforementioned aspects can be achieved, through the structural modification of BiOX. (2) The second one is driven to the degradation of one specific organic pollutant, where the conditions optimization and characterization of by-products plays an important role. (3) The third one is driven to use new or alternative sources of visible-light. In this work, representative examples of these strategies will be shown and analyzed.

**RESULTS:** The photo-catalyst  $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$  in the form of nano-sheets has a narrow band gap of 2.22 eV. However, due to the quick charge recombination rate it has poor properties of degradation. For example, methylene orange (MO) dye was degraded by 32%, under simulated solar irradiation. An efficient separation and transfer efficiency between photo-generated electrons and holes was possible, when homogeneous phase junction of  $\text{BiOCl}/\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$  was designed and prepared. A 60% degradation yield was obtained [1]. In addition, for the degradation of the endocrine disruptor Bisphenol A (BPA) mediated by phasejunction of  $\text{BiOCl}/\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$  a 73.32% yield was obtained. When the architecture of

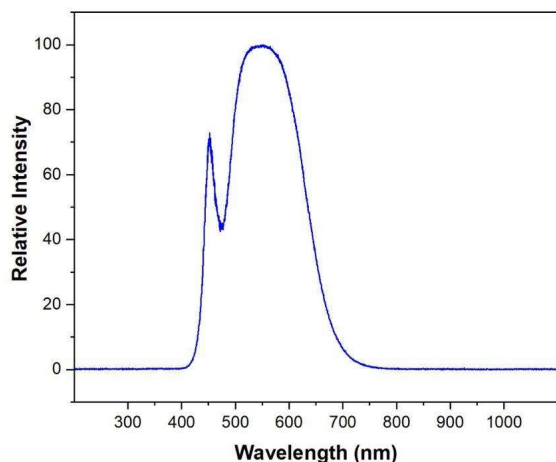
photo-catalyst  $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$  changed to nano-belts (Figure 1) in the degradation of BPA an increased 95% yield was obtained. Besides that, a decreased band gap of 2.07 eV was observed [5]. Likewise, the conversion of phenolic compounds to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  mediated by the photo-catalyst  $\text{Bi}_4\text{O}_5\text{Br}_{0.6}\text{I}_{1.4}$  (prepared at room temperature) was achieved between 72-79%. Trapping experiments indicate the generation of  $\cdot\text{O}_2^-$  and  $\text{h}^+$  played the chief role in decomposing phenolic pollutants [2]. Finally, the degradation of RhB over the photocatalyst BiOCl under white LED irradiation (Figure 2) was achieved with 96% yield after 25 min light irradiation the mechanism of RhB degradation over BiOCl is attributed to the dye photosensitization process [4].



**Figure 1.** SEM image of  $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$  nano-belts obtained according to the procedure reported by Wang's group [5].

**DISCUSSION & CONCLUSIONS:** The example of photo-catalyst  $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$  shows that the electronic properties of BiOX can be modulated to achieve a better performance in the degradation of organic pollutants. The second example evidences the significance of determining the degradation intermediaries by LC-MS, which led to the proposal of a degradation mechanism. This can be interpreted in terms of electronic phenomena occurring in the photo-catalyst. The third example

shows that BiOX technology is compatible with available visible light sources as LED. These studies demonstrate that bismuth oxyhalides have a high potential for the removal of organic pollutants under visible light.



**Figure 2.** Emission spectra of a similar LED lamp used by Tahmasebi's group [4].

**ACKNOWLEDGEMENTS:** To the members of #BiOX team at Ikiam.

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## Microalgae Harvesting After Tertiary Wastewater Treatment

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**INTRODUCTION:** Anthropogenic activities are increasing the input of nutrients, especially nitrogen and phosphorus, into water bodies, leading to eutrophication (Mennaa et al., 2015). Microalgae have demonstrated great potential as an alternative to advanced biological nutrient removal in tertiary wastewater treatment due to the phototrophic properties of these microorganisms to use solar energy and reduce inorganic nutrients to organic substances. By using microalgae in wastewater treatment, it is also possible to recover and reuse algal biomass. However, a critical step in every microalgae-based process is the harvesting. The process of microalgae harvesting is complicated as a result of the size of the microalgal cells (2-20  $\mu\text{m}$ ) and their colloidal stability in suspension (Richmond et al., 2013). Separation of the biomass from microalgae cultures can have up to 30% of the total biomass production costs (Grima et al., 2005). The aim of the study was to evaluate the available biomass recovery techniques that are suitable for both wastewater treatment and biomass production.

**METHODS:** Literature studies have been performed to collect and analyse available data and technologies for the characteristics, advantages and disadvantages of the microalgae harvesting methods.

**RESULTS:** Chemical coagulation or flocculation is one of the most common methods of harvesting algal biomass, which is mainly used to harvest large volumes of microalgae cultures and is suitable for a variety of microalgae species (Pandey et al., 2014). Biomass cellular concentration and surface properties, namely net charge and hydrophobicity, concentration of the coagulant/flocculant, as well as pH and ionic strength of the broth are key factors influencing this process. Several coagulants, such as  $\text{FeCl}_3$ ,  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{Fe}_2(\text{SO}_4)_3$ , can be used in microalgae harvesting. Although flocculation is easily induced by metal coagulants, large amounts of these salts are required (Vandamme et al., 2012). In addition, the treatment of microalgal biomass with these chemicals leads to risks of biomass contamination with used metals, which negatively affects the biomass reuse potential (Lee et al. 2010).

Alternatively, autoflocculation is performed by raising the pH level. It is an alternative method to classical flocculation, which is characterized by lower costs because no chemical addition is required. This process can occur naturally in microalgae culture. During the process of photosynthesis, microalgae absorb the dissolved  $\text{CO}_2$  in the culture medium, increasing the pH level, thereby causing cell flocculation (Larsdotter 2006). The second alternative method of flocculation is bioflocculation. It is a method of harvesting microalgae biomass based on the use of biopolymers released by microorganisms. Bioflocculation eliminates the need for chemical flocculants. However, the presence of other microorganisms in the microalgal culture means microbiological contamination which affects the further use of microalgal biomass (Christenson et al., 2011).

Another microalgal harvesting method is gravity sedimentation, which is suitable for different microalgae species and can be very energy efficient. The use of sedimentation tanks is simple and inexpensive, but the achieved sedimented biomass concentration is very low without prior coagulation/flocculation (Pandey et al. 2014).

Methods that are not widely used in microalgae harvesting are electrical based methods. These methods are applicable to several species of microalgae, while being environmentally friendly because they do not require the addition of chemicals. Due to the fact the microalgae cells are negatively charged when an electric field is applied to the culture suspension, the cells can be separated. They can form sediments on the electrodes (in the case of using the electrophoresis method) as well as accumulate at the bottom of the vessel if the electroflocculation method is used (Pandey et al. 2014). However, electricity requirements and equipment costs for this method are too high to use these methods on a large scale.

After thickening, the next step in harvesting microalgae is biomass dewatering. Dewatering is achieved by various mechanical methods. Filtration is a dewatering method, that is commonly used after coagulation/flocculation to improve biomass harvesting efficiency and reduce biomass water

content. To use this method, it is necessary to maintain a pressure drop throughout the system to expel the flow of fluid through the membrane (Christenson et al., 2011). In this process, the algal sediments on the filtration membrane can become thicker during the process, thereby increasing the resistance and reducing the filtration flow with a constant decrease in pressure (Shao et al., 2015). The second dewatering method is centrifugation. It is the fastest method of harvesting and dewatering microalgae biomass, but also the most expensive due to its high energy consumption (Pandey et al. 2014).

After harvest, the dehydrated biomass is dried to improve the efficiency of further biomass treatment processes.

**DISCUSSION & CONCLUSIONS:** There is no single best technology of harvesting microalgae. The choice of the most appropriate harvesting method depends on the microalgae species and its characteristics. Each method has its own advantages and disadvantages. Thus, to achieve the highest harvesting efficiency, it is often necessary to combine the above methods, such as the flocculation method with sedimentation. Normally, a two-stage separation, composed of thickening and dewatering processes, is required.

A low-cost reliable method for harvesting microalgal cultures is yet to be developed.

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## Theory of Constant Pressure Filtration and the Structure of Membrane Deposits

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**INTRODUCTION:** Surface water from three sections of Tena river (rural, suburban and urban), were monitored and ultrafiltered at constant-pressure at bench scale, Figure 1.

Commercial ultrafiltration (UF) membranes with 10, 30 and 100 kDa were used during experiments focused on membrane biofouling development. In this manuscript, a set of analyses on microstructural features of growing deposits is presented.

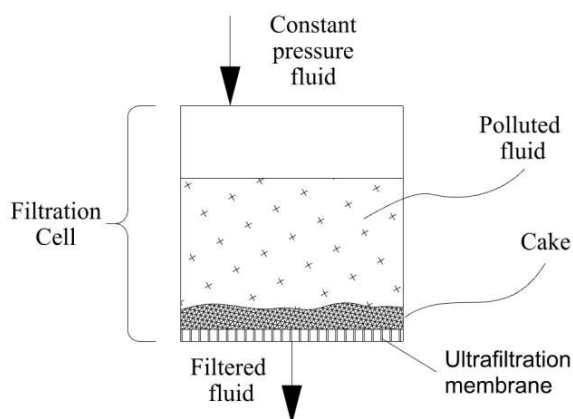


Figure 1. Constant pressure Transmembrane Ultrafiltration (CPTU) using an Amicon filtration Cell, [1].

The experimental results obtained allow us to analyze the structure of the capping of the membrane produced by the accumulation of separated substances during the filtration process, called cake, whose geometric complexity can be analyzed using the Fractal Dimension value (FD) of the structure that composes it, [2], where values of  $FD \approx 2$  and  $FD \approx 3$  correspond to a 2D and 3D type structure respectively, which could allow characterizing it.

**METHODS:** The UF process was applied to four water samples with different pollutant loadings. During this process, due to the filtration of the suspended solids in the sample fluid, the formation of the capping cake occurs due to the accumulation of material on the surface of the membrane ( $A_M$ ).

By using Darcy's law, [1], it is possible to estimate the effect of the cake on the membrane, thus obtaining the variation of the permeate flux as a function of the transmembrane pressure ( $\Delta P$ ), as shown in Figure 2 A.

This process allows to identify the value of the total resistance produced in the membrane, since  $J$ ,  $\mu$ ,  $\Delta P$  are known experimental values and correspond to the permeate flow, the viscosity of the sample and the induced transmembrane pressure, respectively. With these values, the specific resistance of the cake can be determined as shown in Figure 2 B.

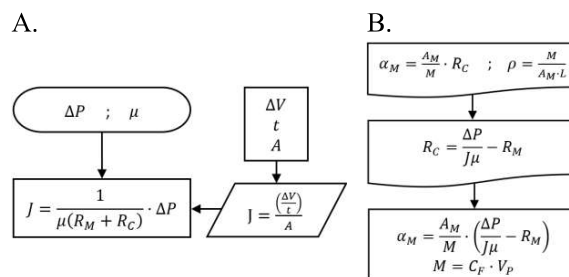


Figure 2. **A.** Darcy's Law. **B.** Specific Resistance of the membrane cake.

By analyzing the specific hydraulic resistance of the cake generated according to its thickness ( $L$ ), a model can be found to determine the porosity of the cake ( $\epsilon$ ), as shown in Figure 3, this value being defined as the relationship between the value of the empty volume with respect to the total volume, [3].

The porosity of the cake, combined with the characteristics of the UF process, allows the  $L$  to be determined. With this the value of the exponential coefficient ( $\phi$ ) that corresponds to the slope of the graph “ $\log L$  vs  $\log M$ ”, where  $M$  is the mass of the cake, is obtained. The value ( $\phi$ ) allows determining the FD of structure of the cake, whose value is proposed to be used as a reference to characterize the CPTU process, Figure 4.

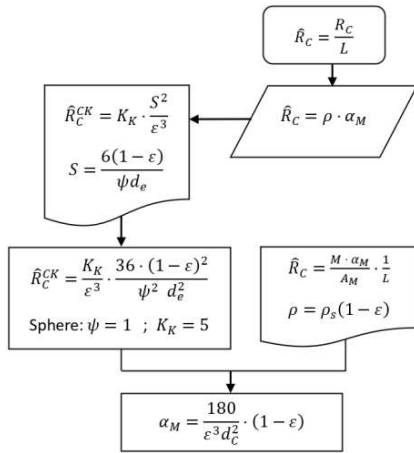


Figure 3. Model for measuring the porosity of the cake.

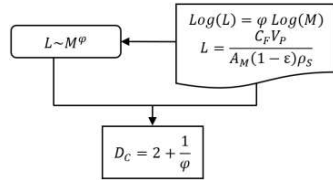
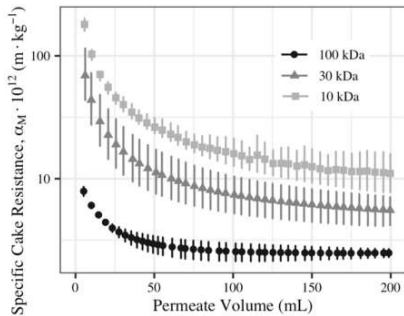


Figure 4. “L vs M” and calculation of FD, [1].

**RESULTS:** The specific resistance of the four water samples were measured using the UF process with membranes of three different Molecular Weight Cut-Off (MWCO): 100, 30, 10 KDa. In Figure 5 a direct relationship between the pore size and the specific resistance of the cake is observed, what means, the smaller the pore size the greater the specific resistance generated.


 Figure 5. Resistance ( $\alpha$ ) of the cake for different MWCO.

The behavior of the porosity of the cake ( $\epsilon$ ) was calculated by applying the process described in Figure 3, considering that the particles that form it are spheres ( $d_c \approx 400 \text{ nm}$  ;  $\rho_s = 1060 \frac{\text{kg}}{\text{m}^3}$ ), and results at each MWCO are shown in Figure 6. Finally, the FD value of the cake in the experimental samples is reported in Table 1. Comparing the experimental FD values with data obtained from references, it is observed that the calculated values are within the previously reported intervals for the CPTU.

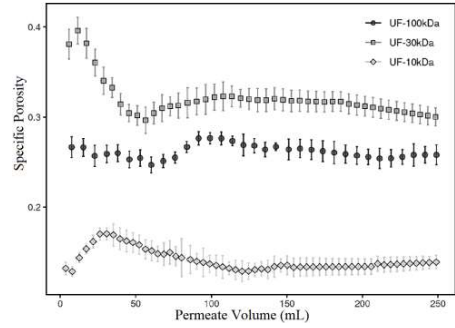

 Figure 6. Porosity ( $\epsilon$ ) for membranes with different MWCO.

Table 1. Fractal Dimension of samples

KDa	Experimental				*Theoretical		
	T <sub>A</sub>	T <sub>B</sub>	T <sub>C</sub>	P <sub>A</sub>	Ref <sub>1</sub> *	Ref <sub>2</sub> *	Ref <sub>3</sub> *
10	2.952	2.976	2.998	2.989		1.4	2.45
30	2.960	2.979	2.998	2.984	2.93	a	a
100	2.951	2.994	2.989	2.954		2.3	2.94

**DISCUSSION & CONCLUSIONS:** The results obtained show the structural behavior of the cake that is formed as a product of the UF process. It is observed that there is a direct relationship between the values of MWCO and  $\alpha$ , with the latter increasing with a lower value of membrane MWCO. In addition,  $\epsilon$  values in the cakes maintain a transient behavior, with periods of increased porosity and subsequent collapse, causing this value to remain metastable during the filtering process. Finally, it was determined that the filter cake has a complex 3D structure due to for all the cases analyzed the value of DF was greater than 2.95, being the value of  $DF = 3.0$  considered for cubic-type tridimensional structures.

**ACKNOWLEDGEMENTS:** Thanks to the HiWater-EULAC Research Consortium and the Geosciences Laboratory at Ikiam University.

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## Hi-Water is a Landmark in the Strategy of Internationalization of Research and Education at Ikiam University

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**INTRODUCTION:** Hi-Water research project is a landmark in the strategy of internationalization of research and education at Ikiam University. This project managed to create an exciting network of collaborative relationships between researchers and institutions, academic mobility, that later allowed the formulation of other international projects during its short period of execution.

**INTERNATIONALIZATION:** Ikiam University is a Public Higher Education Institution founded in 2013 and located in the Ecuadorian Amazon Region. Ikiam focuses on the developing knowledge, science, and high-quality education for the conservation and sustainability of natural resources.

The university is committed to providing solutions to Ecuador's current social and environmental challenges, the region, and the world. Ikiam aims to be a regional referent for training and research in sustainability, generating a meaningful environmental and social impact.

From the beginning, Ikiam has been working on developing solid national and international strategic relationships to expand the impact of its knowledge and research production. In this framework, the university had a collaborative relationship with Riga Technical University, which facilitated the configuration of a consortium including *Leibniz-Institut für Polymerforschung* Dresden and SENAGUA for the application under the project "Hi-Water: Efficient and affordable water treatment technologies to minimize waterborne diseases" to the 2017 EULAC Health call.

A long time ago, we received an email from Linda Mezule, letting us know that Riga Technical University was interested in incorporating a Latin-American partner for a European Union call. From the Inter-Institutional Office, we sent an email to some researchers asking them if they were interested in participating, and Miguel Herrera

Robledo quickly replied, expressing his interest. Even though there was little time for proposing, he did it at the time. Some months later, we received the good news that the proposal was approved and funded. Then the Hi -Water adventure started.

On October 30th, 2017, the General Undersecretary of Science, Technology and Innovation, Ximena Ponce, and the Rector of Ikiam, Jesús Ramos, signed a specific agreement to finance the Hi-Water project. Since then, this collaboration has proved that Latin America has a vital role in developing sustainable and efficient technologies to reduce the bacterial, viral, and protozoan load in rural communities' water supply and storage systems.

In February 2018, during the Hi-Water Consortium kickoff meeting in Riga (Latvia) a roadmap for the development of hybrid technologies to meet the consortium's goals in Ecuador was defined. For this purpose, two lines of undergraduate research programs were developed. The first, called BiOX. It is geared toward developing reactive membranes with the function of water disinfection. The other research line, called #VirEzone, is linked to the identification of the virome of river systems in the Tena metropolitan area.

In 2018 a Cooperation Agreement between Universidad Regional Amazónica Ikiam and Ernst-Abbe University of Applied Sciences-Jena (Germany) was signed.

In December 2018, Ikiam participated in the Stockholm Junior Water Prize competition and launched the first competition for water-related projects.

Poojesh Bertram-Mohammadi, our first undergraduate international student from Jena University, was involved in the Hi-Water project. After a year, when he left, he indicated that it was the best professional experience he had ever had.



The execution of the project has had an important impact on the student community, allowing the participation of four undergraduate students and the mobility of one student from Ernst- Abbe University of Applied Sciences-Jena (Germany).

Ikiam has been working to disseminate the valuable work made by all the consortium members and to expand the benefits to Amazon citizens through capacity building with high school students in Napo, preparing them to participate in the Stockholm Junior Water Prize organized by SR3INVENT. This project has contributed to the sustainable development goals regarding clean water and sanitation (SDG 6), good health and well-being (SDG 3), and partnership goals (SDG 17).

In 2019, students affiliated with VirEzone began to take samples from the Tena river and those affiliated with BiOX to synthesize photocatalytic nanoparticles by solvothermal methods. In addition to the participation in the association with SR3INVENT the training of the students took part in the Stockholm Junior Water Prize competition. In April 2019, the participatory science program called citizenship\_hw was launched during the conference "Meeting of technological research and musical arts," sponsored by the Secretary of Higher Education, Science, Technology, and Innovation (SENESCYT) of Ecuador. In October 2019, the BiOX team presented research at the Innovation Conference organized by the International Water Association (IWA) and the Inter-American Development Bank (IDB) in Guayaquil. Students Damian Tuba and Poojesh Bertram-Mohammadi were selected to be part of the Ecuadorian chapter of the IWA Young Water Professionals initiative.

Likewise, the VirEzone team attended the IV Latin American Virology Congress, held at El Bosque University, in Bogotá, Colombia. There, the team, under the coordination of Mrs. Carolina Bolaños presented a technical work that dealt with the concentration of virus in river systems through ultrafiltration and negotiated a collaboration agreement with the Virology group of said university.

**CONCLUSIONS:** The project constitutes a significant contribution and reference for the Latin America region and the achievement of the Sustainable Development Goals, thanks to the collaboration among the consortium members. It has enabled capacity building, allowing young leaders to appeal for safe water conditions for communities in the Amazon.



*Fig. 1. Ikiam at the 2019 Virology Symposium at Bogotá.*

PERSPECTIVES. Hi Water will continue its trend at Ikiam University because its research lines are also part of an Erasmus+ consortium denominated NB-Lab\* that will run during the next 36 months. Last november 15<sup>th</sup>the NB-LAB project started to contribute to the modernization and internationalization of higher education structures of the partner universities in Peru, Ecuador, Spain and Germany by setting up capacities for user-driven applied research and innovation through an interdisciplinary research group of Latin American and European universities, that will contribute to sustainable rural community development under preservation and responsible use of the natural resources in the Amazonian Region.

\* NB-LAB project "Nature-based living-lab for interdisciplinary practice and research semester on sustainable development and environmental protection in the Amazon Rainforest." EPPKA2 - Cooperation for innovation and the exchange of good practices.Code: 619346 - EPP - 1 - 2020 - 1 - DE - EPPKA2 - CBHE - JP.

**ACKNOWLEDGEMENTS:** A special acknowledgment to national and international partners that have contributed to this project's execution, to the Coordinator, Miguel Herrera, for his global vision, and also to the students that were the engine of this project.

## Application of Chitosan Nanoparticles in Drinking Water Disinfection

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**INTRODUCTION:** The access to clean, microbiologically safe and good quality drinking water is the essential requirement to maintain healthy life for human. However, according to the WHO, by 2025, nearly half of the world's population will live in regions affected by water scarcity. Waterborne diseases are mainly associated with drinking of unsafe water, lack of protection of water sources and poor hygiene (WHO, 2019).

The most often applied technique to prevent these problems is the disinfection of drinking water. Chlorination is the most common technique to keep the consumers away from infectious diseases by pathogenic microorganisms in developed countries (Howe et al., 2012). However, the crucial problem associated with the chlorination process is related to the formation of harmful disinfection by-products (DBS) like trihalomethanes and haloacetic acids, which are formed due to reactions between chlorine ions and organic/inorganic matters present in water (Srivastav et al., 2020), making the applicability of this process limited. Therefore, the development of highly efficient and innovative disinfection techniques with zero DBPs generation has been of strong interest.

The rapid growth of nanotechnology has introduced the use nanoparticles in water disinfection processes as an innovative approach with low or no toxicity to the consumers and environment. From these, chitosan nanoparticles (CNs) have been received growing interest as chitosan is a naturally occurring polysaccharide with well-known antimicrobial properties against bacteria, viruses and fungi (Raafat and Sahl, 2009).

Chitosan is produced by deacetylation of the chitin, which is obtained from the exoskeleton of shellfish and crustaceans, as well as from the cell-walls of insects, yeasts and fungi (Shukla et al., 2013). Chitosan is a biocompatible and environmentally green polymer, which is widely used in food, cosmetic, biomedical and agricultural areas due to its low toxicity and high biodegradability (Rizeq et al., 2019).

In this context, we propose that CNs might be used as antimicrobial agent for drinking water

disinfection. Consequently, the objective of this study was to demonstrate the effective antimicrobial activity of CNs on the survival of faecal indicator *Escherichia coli*.

**METHODS:** Chitosan with medium molecular weight chitosan (MMWC, 190,000-310,000 Da with 75-85% degree of deacetylation) was used for CNs preparation by an ionic gelation method (Yang et al., 2015). Briefly, CNs were generated using the following protocol: a 0.25% (w/v) chitosan solution was prepared with 2% acetic acid (v/v) and 1% (w/v) Tween®80. The solution was stirred overnight with a constant shaking at 200 rpm until no particles were observed. For cross-linking of chitosan, 10% of Na<sub>2</sub>SO<sub>4</sub> (w/v) was added to chitosan solution until the solution became cloudy. Then, the solution was sonicated at 60 W for 20 min to decrease its viscosity. After that, the newly formed CNs were collected by centrifugation for 25 min at 7220 rpm, and washed with sterile water three times before freeze-drying of the pellets.

*Escherichia coli* (*E. coli*) ATCC®25922 was used as an indicator microorganism for faecal contamination and microbial standard to evaluate the inactivation performance and disinfection efficiency. Experiments were performed in Luria-Bertani (LB) medium: approximately 5 x 10<sup>4</sup> CFU/mL of *E. coli* were incubated with 0.2% CNs for 24 hours at 37°C with shaking at 200 rpm. Antibacterial activity of CNs against *E. coli* was evaluated with plate count technique and calculated as reduction in the number of CFU represented the antimicrobial activity.

**RESULTS:** The antimicrobial activity of CNs were evaluated by measuring the log reduction in cultivable *E. coli* after 6 h and 24 h of incubation. The results showed that after 6 h incubation in tap water sample, 0.2% of CNs could reduce of cultivable *E. coli* to 2.8-log (99.8% inactivation). When the contact time was prolonged to 24 hours of treatment a 3.3-log reductions (99.9% inactivation) in cultivable *E. coli* were obtained. The results showed that 0.2% of CN were able to inhibit the

growth of cultivable *E. coli* in tap water significantly during 6 h of incubation.

**DISCUSSION & CONCLUSIONS:** The results indicated that CNs were able to inhibit the growth of cultivable *E. coli* and demonstrated the potential use of CNs in drinking water disinfection. Nevertheless, further studies are necessary in order to investigate the optimal treatment conditions (CNs concentration, time, etc.) to effectively and more rapidly treat pathogens in drinking water.

**ACKNOWLEDGEMENTS:** This research work was supported by ERA-NET EU-LAC Health project Efficient and affordable water treatment technologies to minimize waterborne diseases, Hi-Water (No. ES RTD/2018/26); and Riga Technical University's Doctoral Grant programme (DOK.BIF/20).

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## Membrane Fouling During Ultrafiltration of Surface Water – Pore-blocking Evolution

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**INTRODUCTION:** Ultrafiltration (UF) is considered to be an effective alternative to produce high purity water, however, the UF membrane is prone to loss of permeability due to fouling. Fouling is a complex phenomenon that begins in the early stages of filtration, when interactions between charged ions and the membrane surface promote the development of layers of contaminants on the membrane. Multiple charges along these layers promote the deposition of natural organic matter, extracellular polymeric substances (EPS), genetic material, and cell debris on the membrane. These organic compounds adhere to the surfaces of the membranes, causing partial or total clogging of the pores [1]; [2]. Currently, there are some mathematical models related to pore blocking mechanisms, and descriptions of the role of colloidal particles and polymers [3]; [4]. These models allow to identify if the fouling of the membrane is related to the pore blocking or associated to the surface deposition. The aim of this research was to describe the evolution of pore blocking during surface water UF using available mathematical models related to EPS and inorganic colloids.

**METHODS:** The study area is located in the metropolitan area of Tena, Ecuador, within the micro-watershed of the Tena river. Three sampling sites (A, B and C) were established. Site A was a pristine area of the Tena river, located in the Atacapi community (1500 P.E). Site B was located in the Muyuna community (5000 P.E), in the peri urban region of Tena. Site C was located within the urban area of Tena, apparently affected with a high pollution load (25 000 P.E). A water quality analysis was performed in the three sampling points from March 2019 to February 2020. Prior to filtration experiments, total and suspended solids, as well as a complete set of physicochemical measurements were performed. The filtration system consisted of a 5L of stainless-steel feed tank, connected to an unstirred 400 ml commercial UF cell, loaded with an UF polyethersulfone membrane with molecular

weight cut-off (MWCO) ranging from 10 to 100 kDa). To determine the hydraulic resistance of each pristine membrane, 5 L of distilled water was filtered making pressure variations between 69 and 275 kPa. Finally, surface water from the Tena river was used as the feed stream, filtering about 20 L of the sample with a constant transmembrane pressure of 207 kPa. Pore blocking models described the filtration performed at constant transmembrane pressure with the feed flow normal to the membrane surface and with retained fouling [3]; [4]. In addition, correlations between total permeate volume, volumetric permeate flux, initial flux and filtration time were used for each of the pore blocking mechanisms. Finally, the behavior of the pore blocking mechanisms was obtained after a linear least square fit and the error corresponding to a 95% confidence interval was calculated for the beginning and end of each experiment where the given blocking mechanism dominates.

**RESULTS:** *Analysis of solids.* Summary of solids content in the sampling points is detailed in Table 1. There was an increasing amount of total solids (TTS) as the river reached the city (Sampling point C). This fact must be related to the releasing of sewage into the river. Suspended solids (TSS) are related with EPS, bacteria and other pathogens. So, an indirect reading of the TSS content could indicate a higher concentration of EPS and pathogens in the urban zone of the river. Total dissolved solids (TDS) also increased as the river reached the city. TDS are composed mostly of organic and inorganic colloids and constitute a significant percentage of the total solids in all the A, B and C sampling points (79, 84 and 67% respectively).

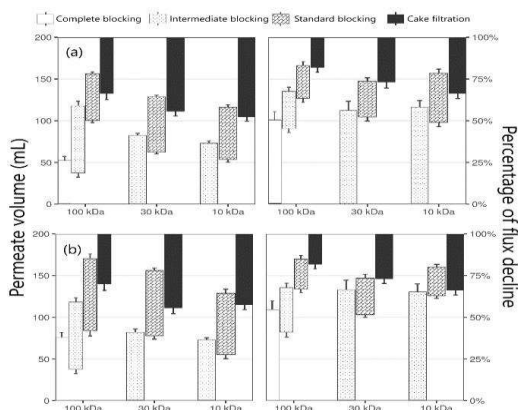
*Pore-blocking analysis.* The evolution of pore blocking versus permeate volume during UF of surface water is depicted in Fig. 1 (site A), Fig. 2 (site B) and Fig. 3 (site C). These figures are also showing the results for colloidal and polymeric models. The identified blocking mechanism that occurs during a particular filtration stage is the one

that dominates the fouling process during the referred period.

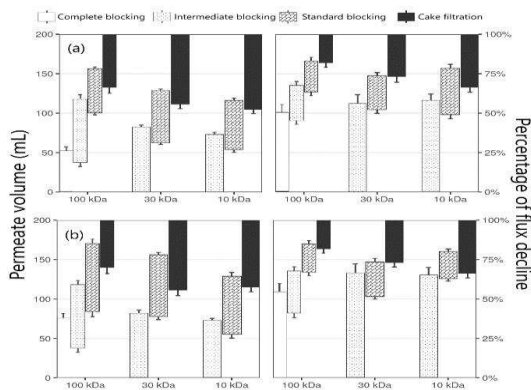
*Table 1:* Concentration of solids present in surface water of the Tena river.

PARAMETERS		Sampling sites			
		A	B	C	
TTS	mg/L	$\bar{x} \pm \sigma$	60 ± 10	71 ± 19	97 ± 14
		min - max	46 - 72	52 - 99	80 - 117
TSS	mg/L	$\bar{x} \pm \sigma$	11 ± 6	11 ± 4	32 ± 4
		min - max	5 - 22	4 - 14	27 - 36
TDS	mg/L	$\bar{x} \pm \sigma$	49	60	65
		min - max	37 - 61	40 - 85	49 - 90

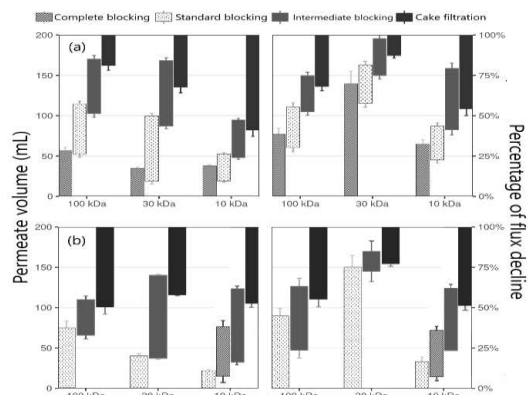
**Pore-blocking analysis.** The evolution of pore blocking versus permeate volume during UF of surface water is depicted in Fig. 1 (site A), Fig. 2 (site B) and Fig. 3 (site C). These figures are also showing the results for colloidal and polymeric models. The identified blocking mechanism that occurs during a particular filtration stage is the one that dominates the fouling process during the referred period.



*Figure 1:* Distribution and contribution of pore blocking mechanisms for (a) colloids and (b) polymers from sampling site A.



*Figure 2:* Distribution and contribution of pore blocking mechanisms for (a) colloids and (b) polymers from sampling site B.



*Figure 3:* Distribution and contribution of pore blocking mechanisms (a) colloids and (b) polymers from the sampling site C.

Although only one mechanism is assigned for a specific filtration section in the initial stage, it is observed that more than one of these blocking mechanisms occurs simultaneously, resulting in an “overlap”. Because models with linear equations were used in this study, the data were fitted to more than one linear equation. Therefore, this “overlap” was established as a transition stage in which two blocking mechanisms act simultaneously and the decrease in flow was proportional. The main difference between the models lies in the amount of volume and decrease in the permeate flux that characterized each mechanism (secondary Y axis in Fig. 1, 2 and 3).

**DISCUSSION & CONCLUSIONS:** Evolution of pore blocking involves several transitions. For sampling site A (low pollution), both models presented similar behaviors with the same pore blocking mechanisms in fouling formation due to the similarity in the parameters of their equations. On the other hand, in the application of the polymeric model to filtration of sampling point B datasets (suburban), the 10 kDa membrane did not show complete blocking, but this mechanism was predominant in the 100 and 30 kDa membranes. Surface water from sampling site C (highest solid content), exhibited a behavior contrary to the observed in the suburban and pristine sampling points. Despite that complete blocking (a total pore occlusion) was computed in several UF trials, there was no evidence of a total decrease in permeate flux. Pore-blocking by colloids took place in the early stages of filtration, mainly dominated by intermediate blocking with a high percentage of flux decline (Figures 1-3). Causes of the standard blocking are related to dissolved solids (metallic ions, nutrients, soluble organic compounds) and colloidal particles (arrangements of silicon, viruses

and other nanoscale components) [2]; [4]. The formation of fouling depends directly on the composition and load of contaminants in the feed stream, which can describe different blocking mechanisms depending on the nature of the foulant particles. Therefore, the outcomes from pore-blocking modelling will provide physical information about the zones in which foulant accumulate and also can allow the improvement of cleaning procedures and pretreatment alternatives before implementing the process in the field or on an industrial scale.

**ACKNOWLEDGEMENTS:** This research was founded by SENESCyT (EULACH T02). We also thank Ikiam University and the staff of the Ikiam's Geosciences Laboratories and National Water Reference Laboratory for their participation in the design of the research and laboratory work.

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## TiO<sub>2</sub> Photodoping, its Modification and Uses

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**INTRODUCTION:** Photochromic materials have been proposed for the development of novel light base technologies such as smart windows, displays, optical storage media, optical signal processing as well as chemical sensors. These materials can be either organic or inorganic, as well as hybrid materials, with each having their own strengths and weaknesses. Out of these, transition metal oxide materials offer increased stability and light transmittance modulation in the range from near UV all the way into infrared light.

One such material is TiO<sub>2</sub>, which is an earth-abundant, nontoxic and chemically stable wide band gap semiconductor. This semiconductor, when irradiated with light with a photon energy higher than its band gap, will, under anaerobic conditions, undergo photodoping. This expresses itself as photochromism and has been described in literature.<sup>1,2</sup> That being said, not much has been done in order to study and modify the photochromic properties of TiO<sub>2</sub>, with the exclusion of theoretical studies.<sup>3</sup> In this work, we've studied a few ways in which to modify the photochromic properties of TiO<sub>2</sub>, such as media modification as well as doping. A possible use in both photochromic and UV-assisted gas sensing applications was also studied.

**METHODS:** The particles used in the studies were synthesized using a simple hydrolysis method. For doping purposes, the synthesis method was coupled with solvothermal treatment. Thin films of the particles for gas sensing were made by using spin-coating. To analyse the synthesized nanoparticles XRD and Raman spectroscopy was used to study the chemical structure, while particle size was determined via Rietveld refinement and TEM. Optical properties (including photochromic properties) were determined via DRS and UV-vis spectroscopy. In particular, to determine the photochromic properties, the particle colloids were transferred into UV-quartz cuvettes with inlet and outlet ports for gas exchange and pressure equilibrium. These samples were irradiated using a UV-LED setup with a wavelength of 365 nm. For recovery of the transmittance, both dynamic (with

continuous air injection) and static (with a set amount air injected at the start of the experiment) experiments were done. Finally, for electrical measurements, a Keysight B2987A at a bias voltage of 15 V was used to measure resistance. UV irradiation was done with the same UV-LED.

**RESULTS:** Firstly, all the synthesized nanoparticles were anatase TiO<sub>2</sub> as indicated by both XRD and Raman. Doping with Nb<sup>5+</sup> resulted in a slight increase in nanoparticle size, from 3.6 nm to 6.7 nm depending on the content of Nb<sup>5+</sup>, as was observed via TEM and Rietveld refinement. Furthermore, the doping lead to distortions in the crystalline lattice indicated by shifts in both Raman and XRD peaks. Optical properties studied by DRS showed a decrease in the optical band gap of TiO<sub>2</sub> via doping.

Photochromism was studied by both using the doped particles. In the case of un-doped TiO<sub>2</sub> the solvent was also changed to change the photochromic response. All the colloids were highly transparent both before and after the experiments.

For un-doped TiO<sub>2</sub> the solvents used were ethanol, *n*- and *i*- propanol as well as *n*-butanol, *n*-pentanol and *n*-hexanol. For further evaluation, ethanol/ethanolamine (MEA, DEA and TEA) mixtures were also used. The highest photochromic response, in terms of transmittance change rate, was recorded for colloids in ethanol and the ethanol/ethanolamine mixtures, with the lowest response being for both propanol colloids. The recovery rate, studied with the injection of air, showed a slightly different picture. Here, the fastest recovery speed was recorded for the ethanol/ethanolamine mixture colloids, with the *n*-butanol colloid being the fastest pure solvent used. The ethanol colloid was one of the slowest.

Nb-doping had a very strong influence on the photochromic properties of the colloids (that were made using *n*-butanol as a solvent), resulting in a dramatic increase in the photochromic response. This allowed the photochromic colloids to go from transparent to a deep blue almost black state in a matter of minutes (see Fig. 1.A) This increase was visible across the measured spectral range of

400-1000 nm, with a linear correlation in the visible range (see Fig. 1.B), but an exponential one in the near infrared. On the flip-side, Nb-doping also had a detrimental effect on the recovery time, which now ranged from a few hours to several days, for the TiO<sub>2</sub> colloids with the highest amount of Nb-doping.

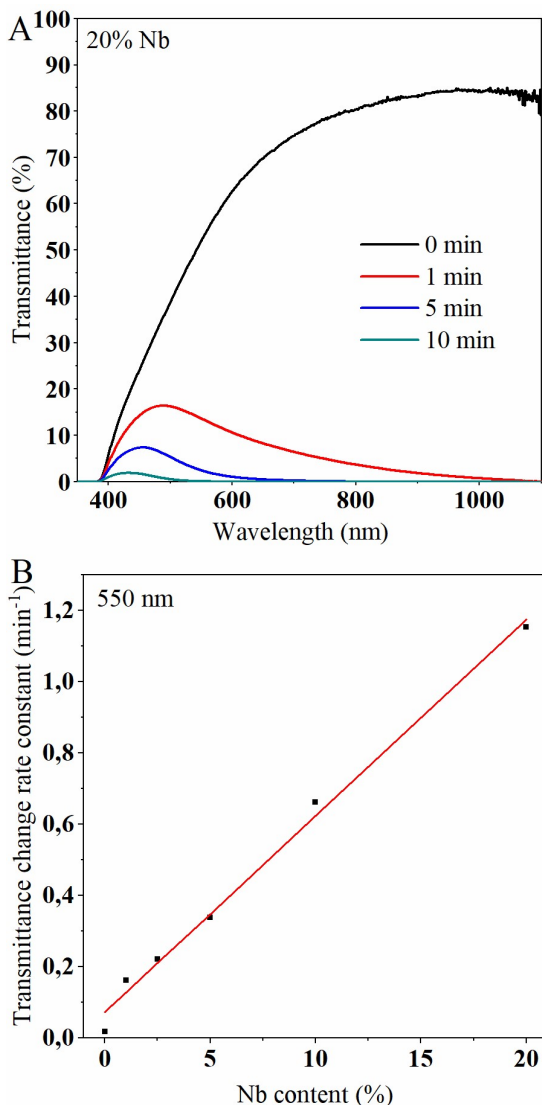


Fig. 1. A) Transmittance spectra of Nb-doped TiO<sub>2</sub> with a 20% Nb content during UV irradiation; B) Transmittance change rate constant at 550 nm for Nb-doped TiO<sub>2</sub> samples with different Nb content.

As a possible use case, the UV-assisted gas sensing application was looked at, revealing the material as being a good candidate for alcohol vapour sensing applications, especially ethanol or *n*-butanol. Furthermore, this was possible at a relative humidity range of 10-40%

**DISCUSSION & CONCLUSIONS:** Un-doped TiO<sub>2</sub> when experiencing photodoping, can be made photochromic, if a hole scavenger is present, adsorbed on the surface of the particle. What this allows is for the electrons to accumulate, if no electron scavengers are present. This allows for a part of the electrons to be trapped on Ti<sup>4+</sup> sites, producing Ti<sup>3+</sup>, while a small portion of the electrons are left to populate the conduction band. How fast the electrons can accumulate is dependent on how fast holes can be scavenged. Hence the solvent effect observed in the study.

If doping is implemented, in our case Nb-doping, the added cations act as additional trap sites, speeding up the accumulation process. Furthermore, the excess positive charge of the Nb<sup>5+</sup> ions allows for a greater accumulation of delocalised electrons, which explains the dramatic increase in infrared light absorption after UV irradiation.

UV-assisted gas sensing was allowed by the aforementioned photodoping, as the alcohol vapour acted as hole scavengers and permitted electron accumulation to take place, thus increasing the conductivity of the material in relation to the amount of hole scavenger present in the surrounding air. For the recovery, the oxygen present in air acted as an electron scavenger.

**ACKNOWLEDGEMENTS:** This research was supported by the Latvian Council of Science in the framework of FLPP (Plasmonic oxide quantum dots for energy saving smart windows, lzp-2018/1-0187) as well as RTU doctoral student grant.

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## Dairy Wastewater Treatment by Using Coupled Coagulation-Adsorption Technologies

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**INTRODUCTION:** The dairy industry processes raw milk into different products by using several techniques like heating, chilling, pasteurization, centrifugation, and filtration and generates huge amount of wastewater containing different organic and in-organic contaminants <sup>1,2</sup>. Present work focuses on the removal of dissolve and suspended solids from the dairy wastewater by using natural coagulant (chitosan) and nontoxic adsorbent (powdered activated carbon i.e., PAC). A hybrid system of chitosan-PAC was used for a combined coagulation-adsorption process for the treatment of dairy wastewater. A batch adsorption, coagulation and coupled adsorption-coagulation experiments were done with varying parameters like adsorbent/coagulant loading, temperature and stirring speed.

**METHODS:** All experiments were carried out in a 1 L jar tester (Phipps and Bird PB-700, USA) at room temperature by following standard procedure<sup>3</sup>.

**RESULTS:** Experiments were performed to investigate the effect of adsorbent-coagulant dose on the removal of COD, and TN from the dairy wastewater (Figure 1).

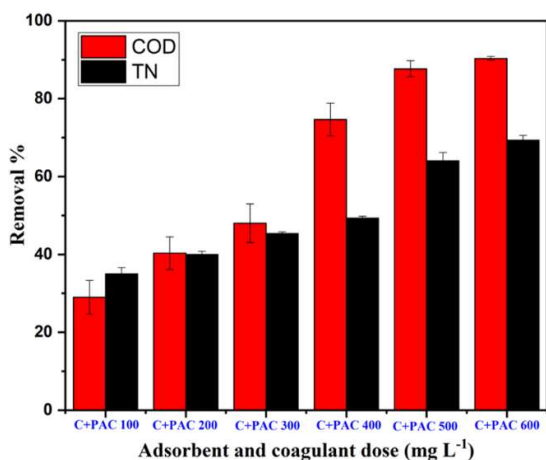


Fig. 1. Effect of adsorbent-coagulant dose on removal of organic contaminants.

**DISCUSSION & CONCLUSIONS:** The current study aimed to reduce the organic and inorganic contaminants load on dairy wastewater. In this direction, natural coagulant and a nontoxic adsorbent was chosen. However, to get the higher removal ability, a hybrid system of coupled adsorption-coagulation process was implemented and the results showed that the hybrid process could provide higher rate of contaminants removal as compared to the individual processes. The higher removal capacity for chitosan-PAC maybe attributed to physical or chemical interaction i.e. electrostatic attraction, surface complexation, hydrogen bonding etc. Chitosan and powdered activated carbon represent eco-friendly materials, which could be used in dairy wastewater treatment. This study demonstrated the impact of adsorbent addition on coagulation system. The removal of contaminants changed drastically by adding the powdered activated carbon which is a non-toxic adsorbent.

**ACKNOWLEDGEMENTS:** This work was supported by the European Regional Development Fund within the Activity 1.1.1.2 “Post-doctoral Research Aid” of the Specific Aid Objective 1.1.1 “To increase the research and innovative capacity of scientific institutions of Latvia and the ability to attract external financing, investing in human resources and infrastructure” of the Operational Programme “Growth and Employment” (No.1.1.1.2/VIAA/2/18/325).

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## Precipitation Process of Hydrophilic Polymers

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**INTRODUCTION:** Polyether sulfones are often used for ultrafiltration processes because of their good mechanical, chemical and thermal properties. However, these polymers are also highly hydrophobic, which has a negative effect on the fouling behaviour of the membrane. Therefore, two sulfonated PES with different amount of sulfonic acid groups were prepared to increase hydrophilicity and decrease the fouling behaviour. The sulfonation causes a different precipitation behaviour, so that it is not possible to cast membranes from standard casting solutions mixture. Therefore, the effect of LiCl addition to the casting solution on the precipitation behaviour of sPES and the properties of the resulting membranes is investigated [1].

**METHODS:** The porous membranes are fabricated using the phase inversion process. Viscosity measurements, scanning electron microscope (SEM) images, filtration data, protein retention and cut-off limits are used to characterize the membranes. Contact angle measurements are performed to verify hydrophilicity. The inversion speed of the polymer solutions is determined using transmission measurements.

**RESULTS:** The viscosities of the polymer solutions increase with increasing LiCl content and sulfonic acids groups. The SEM images clearly show the asymmetry of the membranes and characteristic features. With the help of transmission measurements, the different precipitation rates in the phase inversion process of the investigated polymers can be seen. From the filtration data obtained, the reversible part of fouling on the sPES membrane has been reduced. The contact angles of the membranes also decrease, indicating increased hydrophilicity.

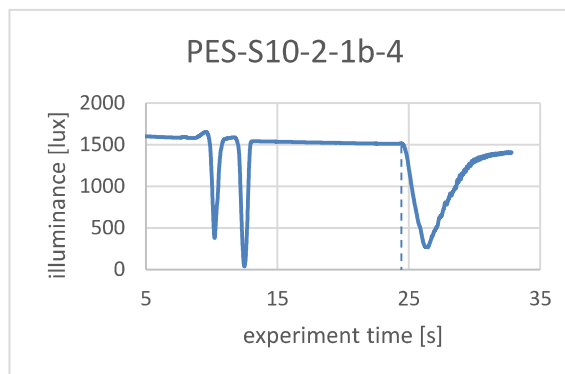


Figure 1. Precipitation speed with 1:1 LiCl content; start precipitation at 24 s

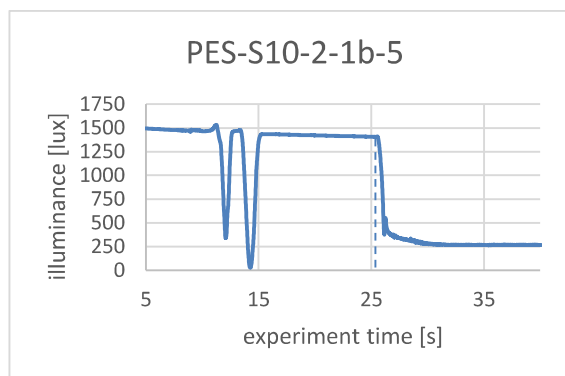


Figure 2. Precipitation speed with 1:2 LiCl content; start precipitation at 26 s.

**DISCUSSION & CONCLUSIONS:** Contrary to PES, the prepared sPES, having a DS of 10%, do precipitate in water very slow. The addition of LiCl to the casting solution has two main effects. (a) The viscosity of the casting solution increases with increasing LiCl content, which can be attributed to ion-dipole interactions between the carbonyl group of NMP and the Li-ion as well as ion-dipole interactions between the proton of sulfonic acid group and the chloride [2]. (b) The addition of LiCl makes it possible to precipitate the sPES in water and thus allows for the preparation of membranes. Furthermore, the precipitation speed can be controlled by the amount of LiCl added to the polymer solution as outlined in Fig. 1 and Fig. 2. The observed effect is explained by ionic and dipolar interactions between LiCl and solvent and the sulfonic acid groups of the polymer,

respectively. The changes in the precipitation speed and solution viscosity also lead to changes in membrane morphology. Furthermore, by the sulfonation of PES a negative surface charge is introduced and makes the membrane more hydrophilic as verified by  $\zeta$ -potential measurements and contact angle measurements. Hence, the fouling behaviour of the membrane is improved by two effects; (a) repulsive electrostatic interactions between the negatively charge surface and negatively charged protein molecules and (b) the increased hydrophilicity (decreased contact angle).

**ACKNOWLEDGEMENTS:** I would like to thank my supervisors Mr. J. Meier-Haack and Mr. T. Oddoy as well as all staff members of the Leibniz-Institut für Polymerforschung Dresden.

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## Structural Characteristics for Membrane Fouling during Ultrafiltration of Pisciculture Ponds

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**INTRODUCTION:** Ultrafiltration is a process that has gained great importance in water treatment in recent years. One of the challenges that this technology faces is membrane fouling. Fouling is a phenomenon that depends on membrane and feed effluent characteristics<sup>1</sup>. Some constituents that contribute significantly to the formation of membrane fouling have been previously identified, such as extracellular polymeric substances, natural organic matter, ions and dissolved solids<sup>2</sup>. Despite this previous knowledge, there are some unsolved questions around membrane fouling and exploring this process using effluents from environmental sources could provide important information. In this study, the structural characteristics of the fouling caused by the fish tributary were explored using membranes with different molecular weight cut-off sizes (MWCO).

**METHODS:** Natural water samples used for fish farming in the Ecuadorian Amazon (0° 52'22"S - 77° 49'50"W) were collected and transported to the laboratory for further analysis. Using an end-point ultrafiltration module (Fig. 1), the collected samples were processed using polyethersulfone membranes with different MWCOs, the details of each of the membranes are detailed in Table 1.

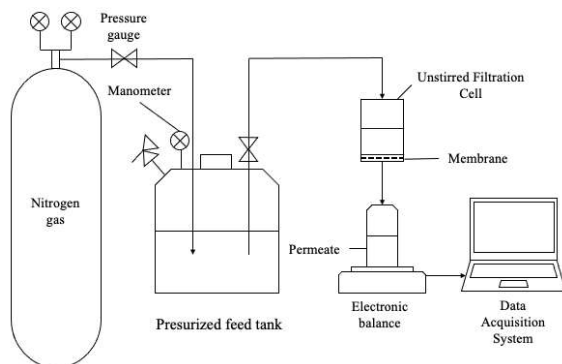


Figure 1: Experimental setup.

Equations 1-3 were used to explore the structural characteristics of the plugging process, which model parameters such as permeate flux, specific

cake resistance, and effective porosity, respectively<sup>3</sup>.

$$J = \frac{P}{\mu \cdot (R_m + R_c)} \quad (1)$$

$$R_c = \alpha_c \cdot \frac{C_f \cdot V}{A} \quad (2)$$

$$\alpha_c = \frac{180(1-\varepsilon)}{\rho_c \cdot d_p^2 \cdot \varepsilon^3} \quad (3)$$

Table 1. Membrane properties

Membrane	MWCO (kDa)	Hydraulic Resistance (m <sup>-1</sup> )
PBHK	100	3.29x10 <sup>11</sup> ± 5.88x10 <sup>10</sup>
PBTK	30	8.59x10 <sup>11</sup> ± 2.48x10 <sup>11</sup>
PBGC	10	1.70x10 <sup>12</sup> ± 9.68x10 <sup>10</sup>

**RESULTS:** Figure 2 shows the normalized flux for the 3 different MWCOs. Reductions in flux of 43, 59 and 64% are observed for 10, 30 and 100 kDa at a volume of 200 ml.

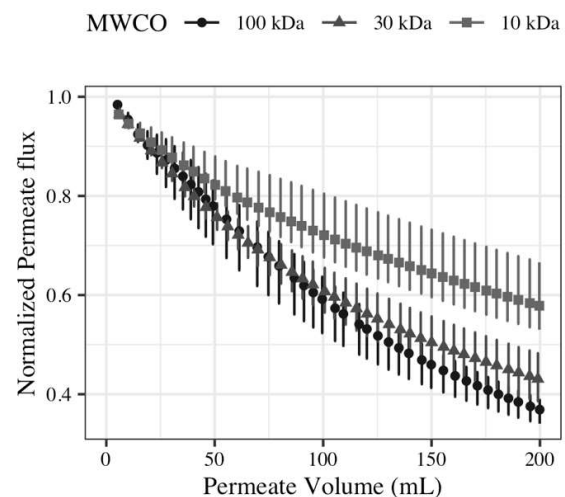


Figure 2: Normalized permeate flux obtained from different MWCO membranes.

Figure 3 shows the variation of the specific membrane resistance for different MWCOs. It is

observed that at smaller MWCOs the resistance tends to increase. A reduction in the specific resistance of the cake is also shown when permeate volume increases, this reduction in the specific resistance is more pronounced at initial stages of filtration.

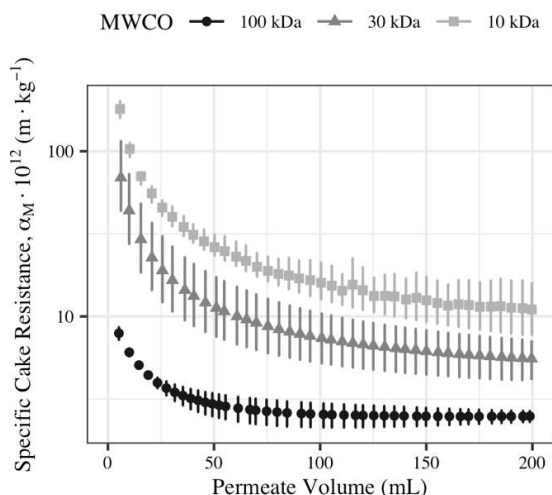


Figure 3: Specific Cake Resistance behavior for membranes with different MWCO.

Figure 4 shows the specific porosity of the cake obtained for the experiments at different MWCO. The results show an increase in porosity in the initial stages for all experiments, reaching stabilization in later stages. An increase in porosity is also observed in membranes with a higher MWCO.

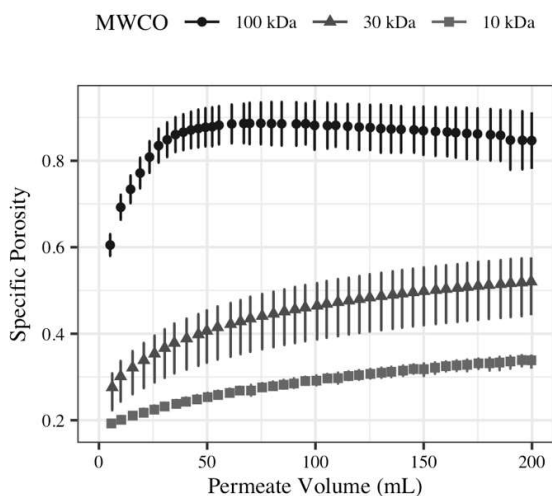


Figure 4: Specific Porosity for membranes with different MWCO.

**DISCUSSION & CONCLUSIONS:** The results described indicate a change in the structural characteristics of cake structure during ultrafiltration process. The trend of the results

obtained has been previously reported in experiments that use water with synthetic pollutants at known concentrations<sup>3</sup>. The fouling phenomenon in complex samples such as natural water will have the presence of multiple contaminants, several of them interact to form organic-inorganic hybrids that contribute to a rapid formation of the plugging cake<sup>4</sup>. Colloid formation processes have also been identified with feed streams with natural organic matter<sup>5</sup>. The results in the increase in porosity are attributed to a random packing of the particles during their deposition in early stages on the surface of the membrane<sup>1</sup>.

**ACKNOWLEDGEMENTS:** This work was supported by the HI Water-EULAC Research Consortium and the Geosciences laboratory of the Ikiam Amazon Regional University.

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#### SYMBOL LIST:

A	Membrane area
$\alpha_c$	Specific cake resistance
$C_f$	Feed concentration
$\Delta P$	Transmembrane pressure
$d_c$	Particle diameter
$\rho_c$	Particle density
$\varepsilon$	Effective porosity
J	Permeate flux
$R_c$	Cake resistance
$R_m$	Membrane Resistance
$\mu$	Water viscosity
V	Permeate Volume

## Photocatalytic Oxidation of Ammonia

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**INTRODUCTION:** High concentration of ammonia in surface waters causes eutrophication of water bodies and toxicity to aquatic life [1]. In addition, it decreases the efficiency of water treatment plants, causes corrosion and a higher demand for oxidants, and finally, unpleasant taste in processed water [2].

The processes used to remove ammonia are mainly biological (nitrification-denitrification, anammox [3]), but there are also physical or chemical methods such as microwave radiation, ion exchange, chlorination, ozonation and others [4]. Photocatalytic oxidation is a general method to eliminate organic pollutants. Photocatalysts able to oxidize ammonia are less general, however they would be of interest when the oxidation proceeds with visible light as energy source [5].

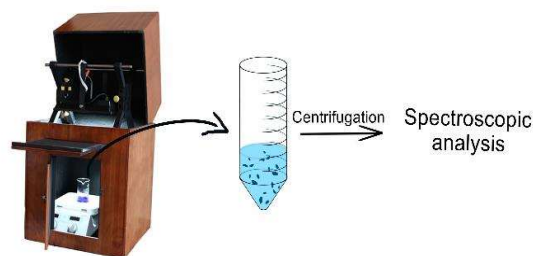
**METHODS:** For our ongoing research, Bismuth oxyiodide (BiOI) was chosen as model compound [6]. It will be studied if it oxidizes ammonia under visible light irradiation in a slurry reactor. Our hypothesis is that ammonia will be oxidized by direct gap oxidation or via reactive oxygen species [7].

The hydrothermal synthesis of BiOI nanostructures is straightforward and simple as mixing of the reactants and heating of the mixture in a Teflon-sealed autoclave. Filtration, and drying will yield the desired product. Parameters that influence the shape and therefore, catalytic properties, are the pH, additives, temperature and time.

The synthesized photocatalysts will be characterized by X-ray diffraction (XRD) patterns for purity and crystallinity. The morphologies will be analyzed using scanning electron microscopy (SEM) and transmission electron microscopy. UV-vis diffuse reflectance spectra (DRS) measurements can provide the band gap energy of the photocatalyst.

The evaluation of the photocatalytic efficiency of BiOI will be performed in a photoreactor equipped with a 50W visible-light LED lamp (Fig.1). A solution with a known ammonia concentration is stirred with the photocatalyst at different pH.

A sample will be taken in fixed intervals and filtered in order to remove the suspended catalyst. Ion exchange chromatography allows for the direct measurement of nitrate concentration. There are also photometric methods available for determination of ammonia concentration.



*Figure 1. Photocatalytic activity in a photoreactor and concentration measurement during activity.*

**DISCUSSION & CONCLUSION:** A decreasing ammonia concentration after irradiation in presence of the photocatalyst has to be investigated further in order to know the final product, and to exclude the possibility of absorption or evaporation. Among possible oxidation products, nitrate and nitrite can be detected by ion chromatography, but others, like hydroxyl amine, will be required more special methods for detection. However, a confirmation that the final product is molecular nitrogen would require for a change in the experimental design. The presented research project will help to identify possible candidates for the photocatalytic oxidation of ammonia with visible light, a first step to develop an efficient photocatalytically oxidation process.

**ACKNOWLEDGEMENTS:** Thanks to the Hi-Water project, Inedita (Senescyt, Ecuador) PIC-18-INE-IKIAM-001, Laboratorio de Referencia Nacional del Agua, and Ikiam University technicians and facility manager.

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## Biomaterials for Waste-water Treatment

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**INTRODUCTION:** Water is an essential commodity which was once available for free. Out of total water available on earth, only 1% is available for human consumption. Increase in demand and pollution has intensified the pressure on this precious resource. Due to rapid industrialisation, water pollution has become a global problem. Industrial waste-water treatment is a multi-step process that requires sophisticated instrumentation, land, labour, electricity etc. All these parameters increase the overall cost of the project. In the industrial sector, chemical, dyes, fertilizers, paper, food processing and leather industries are the major contributors for water pollution. Among these majority are small scale industries, for which wastewater treatment becomes expensive. Furthermore, the dye industry releases numerous dyes into the water bodies that are difficult to remove even with sophisticated techniques. Hence, we have formulated a composition containing a natural and cost-effective biomaterial for removal of dyes from water. The use of this composition is simple, and the operation does not require any external energy which makes the process economical.

**METHODS:** The composition consists of a blend of different biopolymers and clays. The formulations were casted into a mould and then lyophilised. The structural integrity of the lyophilised product was maintained by cross-linking it. The dye removal capacity was analysed by treating the dye solutions with the prepared composition. Spectrophotometric analysis was performed at different time points to monitor the dye removal. Dye removal efficiency (%) was calculated by the following equation,

$$\% = [(C_i - C_f) / C_i] * 100$$

$C_i$  - Initial concentration of dye

$C_f$  - Concentration of dye after treatment

**RESULTS:** The prepared composition has been shown in Fig 1a. Scanning electron microscopy, micro-CT and BET analysis revealed that the tablets of polymer composition were highly porous, having the surface area of 160.80 m<sup>2</sup>/g. The dye removal efficiency of the tablet was found to be 99%, as shown in Fig 1b. The dye recovery from the tablet was 80%.

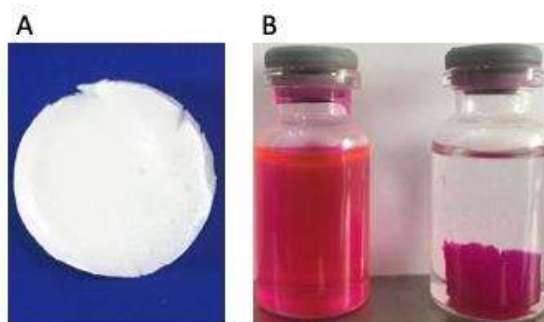


Fig. 1. (a) Fabricated tablet from biomaterials  
(b) The dye removal efficiency of the tablet.

**DISCUSSION & CONCLUSIONS:** The prepared composition exhibited 99% efficiency in dye removal process. The tablets were mechanically robust; hence its addition and removal are easy. In addition to this the dye adsorbed on the tablet could be recovered using different solvents. This provided advantage to retain expensive dyes from the wastewater. Biomaterials used in the table could be recycled by heat treatment, making entire process eco-friendly. The fabricated tablets could also be used as a pre-filter in the large-scale industries, which may reduce pressure on advanced techniques like reverse osmosis. Additionally, this will increase the life of the membranes used in tertiary process.

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## Coating Feed-side of Membranes with BiOX Particles and Antifouling Testing

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**INTRODUCTION:** Fouling is one of the most challenging issue in the development of membrane technology. It is a phenomenon which refers the obstruction of flow through membrane pores during the filtration over the time caused by deposition of particulates on the membrane surface or within the membrane pores. Fouling leads to adverse effects on performance of the membrane. Bisphenol A is one of the representatives of pollutant in the surface water. Smaller molecular size of Bisphenol A makes it difficult to remove from water by membrane filtration. Degradation of Bisphenol A can be done using Titanium dioxide ( $\text{TiO}_2$ ).  $\text{TiO}_2$  shows photocatalytic activity under UV irradiation which makes the degradation process risky to carry out. Bismuth Oxy-Halide Nano particles degrade Bisphenol A under the visible spectrum of light which gives them upper hand over  $\text{TiO}_2$ . In this experiment, the effectivity of BiOX particles, in particular  $\text{Bi}_7\text{O}_9\text{I}_3$  for degradation of BPA under the visible spectrum of light was checked and different possibilities of coating BiOX particles on the Carboxylated Polyethersulphone membrane were analyzed.

**METHODS:** Photo-catalytic batch experiment was conducted to check the degradation of BPA using BiOX particles. Equal amounts of BiOX and BPA solution mixed in a beaker with the concentration of 1g/l and 20mg/l respectively. The mixture was placed under darkness for 1 hr and then under visible light LED lamp for two hrs. Samples were taken at regular interval and analyzed using uv/vis spectroscopy.

Layer by Layer technique was employed to coat the BiOX particles on the surface of the membrane. Different layering schemes of polyelectrolytes like PDADMAC (positively charged) and PAA (negatively charged) along with BiOX particles were tested in the following way.

- 1) Vacuum Filtration Method: coating of polyelectrolyte/BiOX on the feed side by applying vacuum in the permeate side (Fig. 1).
- 2) Coating on the feed side using spray gun.

- 3) BiOX embedded membranes by incorporating BiOX particles in the polymer solution.

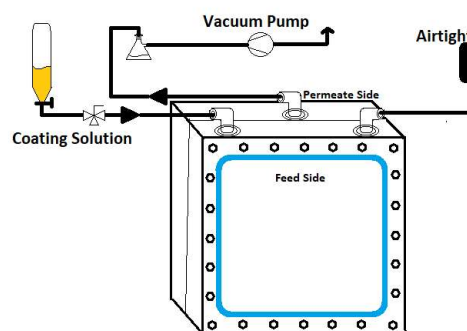


Figure 1: Schematic of Vacuum Filtration Method

**RESULTS:** More than 70% degradation of bisphenol A was observed for 1:50 concentration ratio of BPA/BiOX solution. PDADMAC – BiOX (in  $10^{-6}$  M NaOH Solution) – PAA as a LBL scheme was successful to coat the BiOX particles on the feed side of Carboxylated PES membrane. Agglomeration and settling tendency of BiOX particles in the liquid limits the use of spray gun for coating. BiOX embedded membranes showed around 15-20% degradation of bisphenol A.



Fig. 2. Feed side of BiOX coated membrane.

**DISCUSSION & CONCLUSIONS:** Removal of Bisphenol A from surface water can be achieved in presence of BiOX particles under irradiation which makes surface water safe to use. BiOX coating is also an effective way to increase the lifetime of the membrane by degrading foulants on it. LBL technique using vacuum filtration method is useful for coating BiOX particles on carboxylated membranes. Uniform distribution of BiOX particles in a coating is however difficult to achieve for large membrane area and while casting BiOX embedded membranes is much simpler. Amount and strength of the coating need to be determined for the optimal results.

**ACKNOWLEDGEMENTS:** I would like to show my gratitude towards Dr. Jochen Meier-Haack and Mr. Tim Oddoy from IPF Dresden for giving me this opportunity and guiding me throughout the project.

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## Removal of Phosphorus from Wastewater by Microalgae

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**INTRODUCTION:** Wastewaters from various sources contain high amounts of nutrients, including phosphorus. Wastewater discharge into aquatic ecosystems leads to deterioration of their ecological status. Various innovations are introduced in the conventional wastewater treatment process to improve the process. Methods for targeted phosphorus removal are well established in large wastewater treatment systems. However, scaling their operation to small WWTPs results in high capital and operational costs. Moreover, the phosphorus reduction rates are often insufficient and fail to meet environmental safety standards (Bunce et al., 2018).

Many studies have shown that microalgae are good candidates for wastewater post treatment as they can reduce the phosphorus concentrations in wastewaters to ultra-low levels (Cai et al., 2013). At certain conditions microalgae can consume more phosphorus than their production requires. Enhanced algal phosphorus uptake (EAPU) and storage of excess phosphorus in algal cells can be achieved by manipulation with external phosphorus availability (Lavrinovičs et al., 2020). The two approaches known to cause this phenomenon are the luxury P uptake mechanism and phosphorus starvation (Solovchenko et al., 2019), which are initiated by excess phosphorus availability and phosphorus limited conditions, respectively. In addition to more efficient phosphorus uptake, biomass exposure to nutrient stress is known to promote valuable substance production by algal cells (Levasseur et al., 2020), thus adding value to the produced biomass.

The existing knowledge on enhanced phosphorus uptake induced by algal biomass starvation shows it as a promising feature for algae-based wastewater post-treatment technologies. Though, there are many details that needs to be specified in a lab-scale before proceeding with EAPU implementation into large scale systems. This study demonstrates the effect of biomass manipulation with phosphorus availability on microalgal strain that is widely used for wastewater phytoremediation.

**METHODS:** Microalgae strain *Chlorella vulgaris* was used for the experiment. It was exposed to P-deficit conditions (BG-11 medium without P source) for 3 and 5 days. The experiment was run for 10 days in a batch regime at a room temperature (23 – 27 °C) and under a fluorescent light with PAR of 150  $\mu\text{mol m}^{-2} \text{s}^{-1}$  and 16:8-hour lighting regime. The batch was constantly aerated (10 l min<sup>-1</sup>) and supplied with 1% (v/v) CO<sub>2</sub>. An effluent from a small municipal WWTP were used as a medium. The wastewater was double filtered through membrane filters with pore sizes of 0.45 and 0.2  $\mu\text{m}$ . The change in concentrations of algal biomass (mg DW L<sup>-1</sup>), DIN and DIP (mg L<sup>-1</sup>) and biomass polyphosphate ( $\mu\text{g mg}^{-1}$ ) concentrations were measured to assess the efficiency of the starvation period on nutrient removal and biomass quality.

**RESULTS:** *C. vulgaris* showed higher  $\mu$  after its biomass exposure to P-deficiency (Table 1). The biomass growth rate after 3- and 5-day starvation was 49.7 and 30.3% higher than at the reference conditions, respectively.

Table 1. Growth parameters of *C. vulgaris* biomass.

Starv. period	Growth rate, $\mu$ , d <sup>-1</sup>	Productivity, g DW L <sup>-1</sup> d <sup>-1</sup>	Biomass increase, g DW L <sup>-1</sup>
0 days	0.276	0.069	0.712
3 days	0.413	0.141	1.037
5 days	0.360	0.115	1.097

A 73.0 % increase in biomass productivity was observed after 3-day P-starvation. The overall biomass increase was 45.5 and 55.0 % higher after 3- and 5-day starvation, respectively, than observed in the reference batch.

After 3 days of P-starvation *C. vulgaris* showed higher PO<sub>4</sub> removal rate than the reference and 5-day starved biomass. However, it required 5 – 6 days for >90% PO<sub>4</sub> reduction. Nearly complete (>99%) nitrate removal was reached within 5 days. No significant impact on NO<sub>3</sub> removal by biomass P-starvation was observed (Fig. 1).

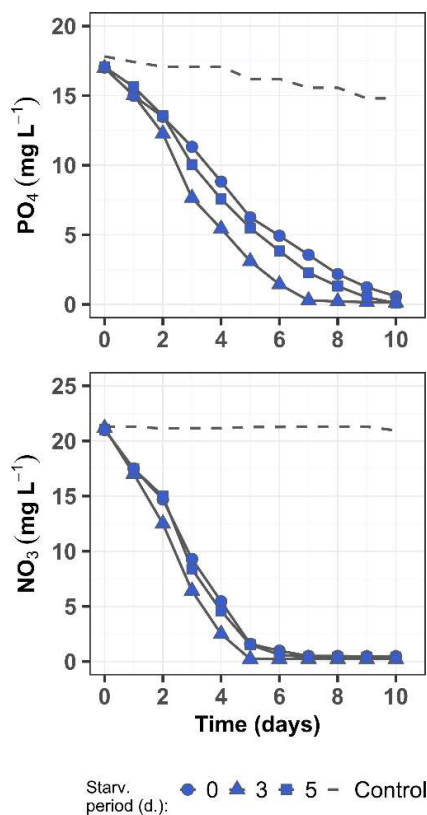


Fig. 1. Phosphate (top) and nitrate (bottom) reduction by *C. vulgaris* biomass after different P-starvation periods.

Biomass polyphosphate content shows a declining dynamic indicating to a constant consumption of internal P reserves. Only 5-day starved *C. vulgaris* biomass showed 4.4% accumulation during first two days, followed by poly-P content reduction until the end of experiment period (Fig. 2).

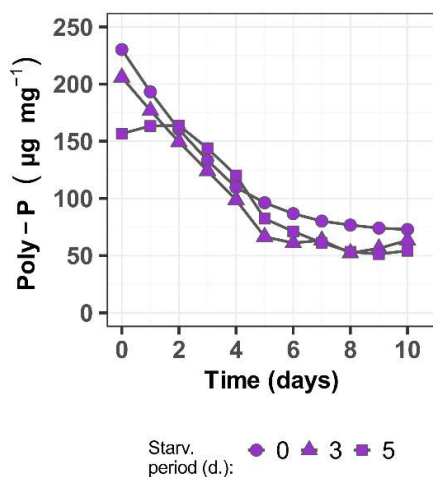


Fig. 2. Polyphosphate content change of *C. vulgaris* biomass after different P-starvation periods.

**DISCUSSION & CONCLUSIONS:** Increased biomass growth for P-starved biomass is likely related to replete  $\text{PO}_4$  conditions during phosphorus refeeding. Abundance of phosphate from different sources ensures enhanced metabolism and production of new cells.

The obtained  $\text{PO}_4$  reduction rates after biomass P-starvation were not significantly enhanced mainly due to very low N:P ratio (2:1) in the wastewater. Such a condition made nitrogen the limiting nutrient and the first preference for algal consumption. Another reason for a relatively slow  $\text{PO}_4$  uptake is the initial biomass polyphosphate content. During the P-starvation the previously accumulated poly-P reserves provided biomass with energy for its metabolic processes. Therefore, it did not experience strong P-deficiency conditions.

Successful use of biomass P-starvation for enhanced phosphorus uptake in engineered algae-based wastewater treatment systems require strict control over the N:P ratio. Also, a clear indicator for biomass P-deficiency should be identified.

**ACKNOWLEDGEMENTS:** This research was financially supported by the Latvian Council of Science, project „Post-treatment of municipal wastewater using sequenced-batch photobioreactor technology” (Project No. LZP-2019/1-0271).

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## Membrane Preparation Processes

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**INTRODUCTION:** Synthetic polymer membranes are often used for separation processes in medical and technical applications. Main areas of application are e. g. hemodialysis, drinking water and wastewater treatment, beverage and food industry (clarification filtration, sterile filtration) or pharmaceutical industry (sterile filtration), gas separation and desalination. Micro-, ultra- and nanofiltration as well as reverse osmosis have established themselves as energy-efficient separation techniques. The market share of the different membrane types and membrane separation technology market by application are shown in Figure 1.

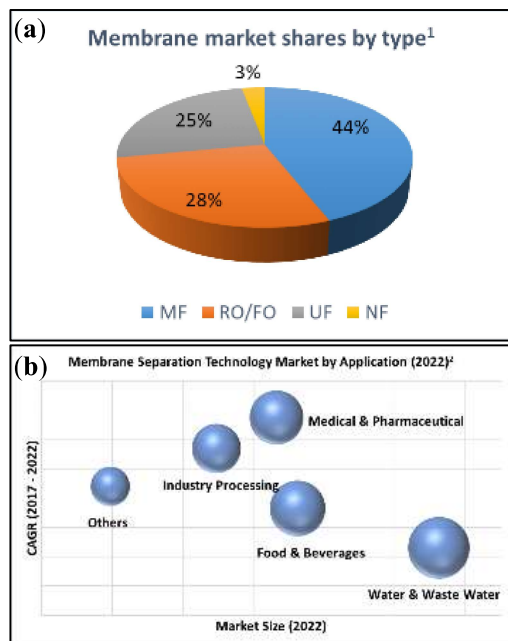


Fig. 1 (a): Membrane market shares by membrane type<sup>1</sup>; (b): Membrane market by application<sup>2</sup>

Furthermore, the demand for sustainable energy supply and the advantages over conventional energy generation systems have brought fuel cells and Li-ion batteries into the focus of numerous applications (e.g. e-mobility). In the course of the expansion of regenerative energy generation systems (wind energy and photovoltaics), the development of systems for the efficient storage of excess energy

(Li-ion batteries, redox flow batteries, electrolysis) is seen as essential.

Depending on the type of membrane to be produced, different processes have been established to prepare porous and dense membranes for applications mentioned above. These processes will be introduced and discussed in detail. Examples for membranes prepared by (a) the non-solvent induced phase separation process (NIPS; ultrafiltration), (b) extrusion-stretching process (microfiltration) and (c) interfacial polymerization process (reverse osmosis membrane) are shown in Figure 2.

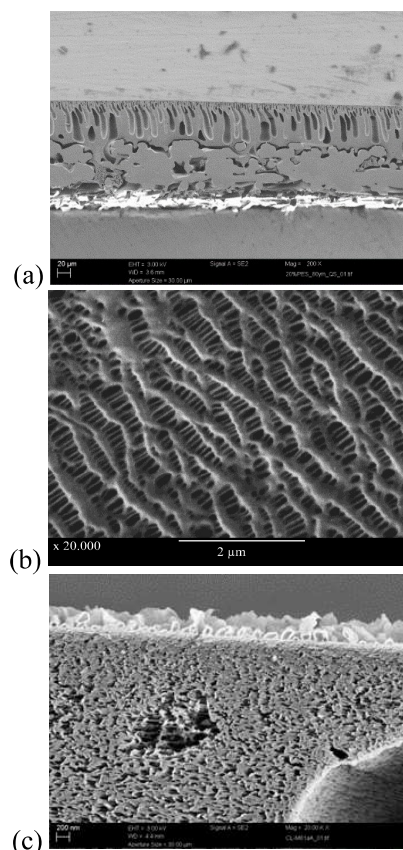


Fig. 2 SEM micrographs of membranes prepared by different processes (see text)

### References:

- <sup>1</sup> Adopted from Market and Market Report CH 2635 (2020)
- <sup>2</sup> Adopted from Market and Market Report CH 5250 (2017)

## Biotechnologies in Engineering Systems

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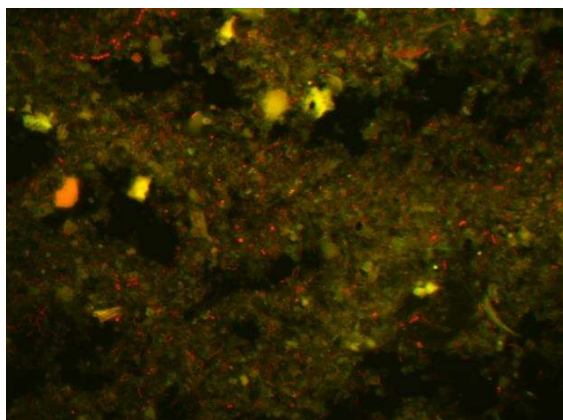
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**INTRODUCTION:** The complexity and imminent presence of living organisms in engineered systems highlight the importance to understand these life forms to control man-made systems. Some of the examples include activated sludge processes in wastewater treatment, microbial communities in biofilms of drinking water supply, anaerobic digestion, fermentation to produce high value products, use of algae or fungi for wastewater treatment and production of biomolecules for subsequent treatment of waste or energy production. The general aim of the research is to facilitate the efficiency of the biological processes to reduce anthropogenic impact.

**METHODS:** The research methodology is based on the principles of process validation in batch and laboratory pilot scale, then full scale. Often the assessment of the system performance and adjustment is performed directly in full scale, e.g., activated sludge of anaerobic digestion processes. This is linked to the impossibility to transfer laboratory scale studies to full scale. Alternatively, laboratory scale pilot systems can be used to mimic microbial processes.

### RESULTS:

*In situ* characterization of microorganisms: traditionally microbial viability is estimated with culture-based assays that rely on their ability to grow in artificial media. As recognized (Matsubayashi et al., 2017) in numerous engineered systems direct cultivation is not sufficient to characterize and understand the communities. Alternative technologies, e.g., fluorescent *in situ* hybridization, epifluorescent staining or genome sequencing can be used to explain the processes (Fig. 1).



*Fig. 1. Archaeal (green) and Eubacterial (red) communities in anaerobic digestate visualized with fluorescent in situ hybridization.*

Lignocellulose degrading fungal enzymes: Hydrolytic enzymes for lignocellulose degradation together with constant and sufficient supply of defined quality biomass resources are currently the most important factors for efficient production of intermediates and subsequent alcohols or fine chemicals. To develop an efficient and friendly zero-to-low waste technological concept for lignocellulosic biomass conversion, novel enzyme products are essential. White rot fungus *Irpex lacteus* (Mezule and Civzele, 2020) was selected as the optimal species and growth conditions have been scaled-up to bioreactor volume (Fig. 2).



*Fig. 2. Fungal enzyme production in batch and reactor scale.*

Biobutanol production from carbohydrates obtained from lignocellulose: Some of genus *Clostridium* bacteria are naturally able to produce butanol via acetone-ethanol-butanol (ABE) fermentation. Replacement of food-crop carbohydrates with carbohydrates from lignocellulosic waste aid to reduce the costs of the process and support the introduction of European Green Deal targets.

**DISCUSSION & CONCLUSIONS:** Enzyme cocktails from white-rot fungi can be produced in less than 5 days of cultivation and used to release carbohydrates from lignocellulosic biomass. This material can be further used in fermentation to produce liquid biofuels or fine chemicals.

**ACKNOWLEDGEMENTS:** The work has been funded by ERDF Project “Zero-to-low-waste technology for simultaneous production of liquid biofuel and biogas from biomass”, No. 1.1.1.1/18/A075 and National Research Programme “Energetics” Project “Innovative solutions and recommendations for increasing the acquisition of local and renewable energy resources in Latvia”. Anna Civzele, Alise Anna Stipniece is acknowledged for technical support.

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## Analysis of Soluble Microbial Products in the Effluent of Membrane Bioreactor Wastewater Treatment Plant

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**INTRODUCTION:** The main cities in the world that have cutting-edge technology for the treatment of their wastewater use the MBR bioreactors with membranes, and the city of Tena-Napo in the Ecuadorian Amazon, is no exception. Additionally, innovative processes that combine photocatalysis as disinfection treatment have been integrated in a dual process (MBR + Photocatalysis), guaranteeing high quality treated water [1].

However, the MBR has operational limitations due to the membrane fouling result of Soluble Microbial Products (SMP: carbohydrates and proteins). These are derived from the biomass generated by microorganisms cell lysis present in the mixed liquor. In recent years, SMPs has been an object of study due to the attenuation screen effect in the signal (quenching) by absorption or scattering of UV-visible light during the photocatalytic disinfection of the effluent of a membrane bioreactor [2,3,4].

The relationship between carbohydrate-protein concentrations (C/P) is a key indicator for understanding the phenomenon of signal attenuation. Because, the fraction of SMP to absorb light destined for photocatalysis is not clear yet. This joint effect of light scattering and absorption by organic matter, significantly reduces the efficiency of dual treatment (MBR + Photocatalysis) [3]. Several authors identify the SMP as the main responsible for membrane fouling in addition to the attenuation of the signal by competitive adsorption of light that occurs by dissolved organic matter (DOM) and other colloidal compounds that can deflect the light signal. In this sense, this work tries to affirm or refute the following hypothesis.

**Hypothesis:** Proteins usually have more tridimensional structural complexity (e. g: fractal dimension, roughness) and greater average surface area than typical planar carbohydrates. Low values

of the index in the C/P ratio (more proteins) in the MBR effluent, would attenuate a greater measure of the light signal (UV-visible) than the observed for high C/P ratios (more carbohydrates) causing the catalytic inactivation process to be less effective. General objective. To identify the role of SMPs in light signal attenuation during experiments of photocatalysis mediated by semiconductors. Specific objectives. (a) To analyze the soluble microbial products from the effluent of a membrane bioreactor. (b) To design a series of light adsorption experiments using solutions with different carbohydrate / protein (C / P) ratios. (c) To identify the effect of light adsorption in each (C / P) condition and (d) To propose improvements to optimize protein degradation during the activated sludge process.

**METHODS:** Daily samples will be collected from the effluents of two MBR full scale plants (*Tereré and Palandacocha*) in the city of Tena (Napo, Ecuador).

Water samples will be analyzed by using standard and nonstandard methods. To determine the total and suspended solids in the effluents, AWWA/APHA incineration methods will be followed. Proteins and carbohydrates will be quantified using adaptations of the classical methods of Lowry and Dubois [4]. After knowing the C/P ratio in the SMP, a set of synthetic wastewaters will be prepared at different C/P ratios using low molecular weight Chitosan (LWC) and bovine serum albumin (BSA) and their quenching effect measured. The light attenuation tests will be carried out in a commercial 96-well microplate placed inside a photoreactor (Fig. 1).



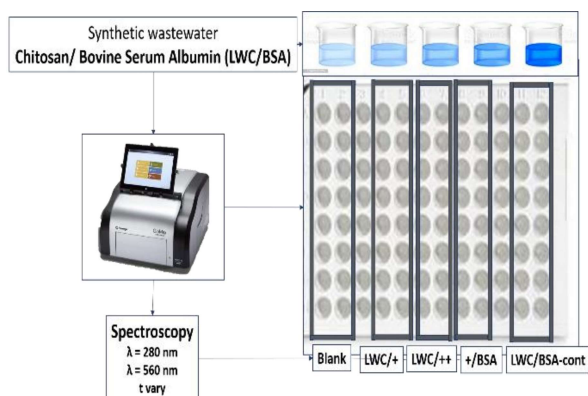


Fig. 1. Experimental design.

### SCHEDULE OF ACTIVITIES:

Description	May				June				July			
	1	2	3	4	5	6	7	8	9	10	11	12
Kick-off activities	1	2										
Sample collection		2	2	3								
Manuscript writing, final report.				4								
Molecular characterization of SMP			5	6								
Prepare synthetic wastewater solutions						6						
Assessment of quenching light by SMP							7	7				
Dissemination of findings											8	

\* To evaluate the progress of the project, the following milestones will be use as a landmark:

1. Enlist Ikiam undergraduate students in international research and collaboration.
2. Kick off meeting (organized by Prof. M.Herrera-Robledo).
3. The research plan and experimental design are reviewed by a tutor committee
4. First functional version for light attenuation tests.
5. Presentation proposed thesis closing week Hi-water program.
6. First manuscript version of light attenuation by organic matter (results preview).
7. Professor Orlando Ugalde joins the project.
8. Submitted final manuscript revisions, defending the thesis.

**ACKNOWLEDGEMENTS:** This undergraduate thesis proposal is supported by the Hi-Water international research consortium between Ikiam-Ecuador Amazon Regional University, Geosciences Laboratory, Riga Technical University-Latvia and the Leibniz Polymer Research Institute-Germany.

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## Photocatalytic Reduction of Nitrate

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**INTRODUCTION:** The nitrate concentration in groundwater of developed and developing countries has increased significantly mainly due to the use of nitrogen fertilizers in agriculture. It can have harmful effects on human health like cancer and diseases such as methemoglobinemia in infants. In addition, excessive nitrate is one of the main contributors to eutrophication and algae blooms [1]. Nitrate is removed from wastewater by biological denitrification in municipal wastewater treatment plants. Alternative technologies for the management of nitrate in water in order to maintain nitrate concentration below 50 mg/L (acceptable level WHO) can base either on physical (reverse osmosis), chemical (reduction, ion exchange) and electrochemical processes (reduction) [2].

Photocatalytic reduction of nitrate is a chemical process which uses UV light as an energy source and a catalytic material, mostly based on semiconductors [3]. Among the main challenges in photocatalytic reduction of nitrate as water treatment technology are low yield due to charge recombination (general for photocatalysis), the demand of high selectivity in the catalyzed reactions (nitrate may produce other pollutants) and the energy consumption (UV-light) [4]. Most desirable would be a highly effective, economic and non-toxic photocatalyst that works with light from the visible spectrum, at ambient conditions.

**METHODS:** Our ongoing research is devoted to the investigation of bismuth-based photocatalysts able to reduce nitrate under visible light irradiation. Bismuth oxybromide (BiOBr) was chosen as a model compound because it has a high chemical stability and a low charge recombination and photocatalytic activity under visible light irradiation [5]. The photocatalytic reduction process can be due to direct interaction with conduction band electrons ( $e^-_{cb}$ ) or induced by addition of “hole scavengers” such as formic acid, that produce  $CO_2$  reducing radicals on reaction with positively charged holes in valence band ( $h^+_{vb}$ ) (Fig.1).

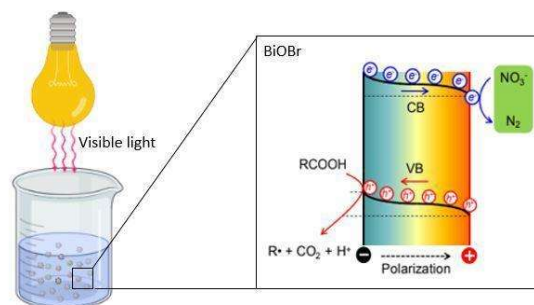


Fig. 1. Possible ways of photocatalytic nitrate reduction on BiOBr-nanosheets.

The synthesis of BiOBr nanosheets is a straightforward hydrothermal process, as simple as mixing of the reactants and heating of the mixture in a Teflon-sealed autoclave. Filtration, eventually calcination will yield the desired product. Parameters that influence the shape and therefore, catalytic properties are the pH, additives, temperature and time.

The synthesized photocatalysts will be characterized by X-ray diffraction (XRD) patterns for purity and crystallinity. The morphologies will be analyzed using scanning electron microscopy (SEM) and transmission electron microscopy. UV-vis diffuse reflectance spectra (DRS) measurements can provide the band gap energy of the photocatalyst.

The evaluation of the photocatalytic efficiency of BiOBr will be performed in a photoreactor with a 50W visible-light LED lamp (Fig.2). A solution with a certain nitrate concentration is stirred with the photocatalyst at different pH, with or without hole scavengers (formic acid).

A sample will be taken in fixed intervals and filtered in order to remove the suspended catalyst. Ion exchange chromatography allows for the direct measurement of nitrate concentration. There are also photometric methods available.

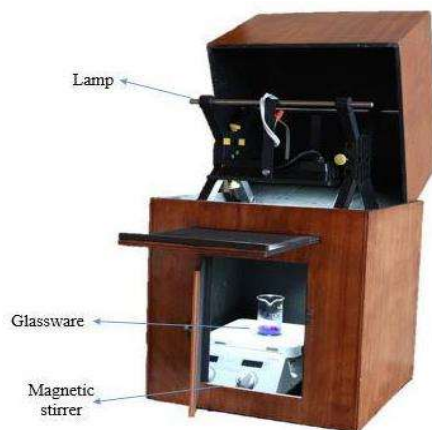


Fig. 2. Photoreactor for the photocatalytic reduction of nitrate.

**DISCUSSION & CONCLUSION:** Any observed decrease of the nitrate concentration on irradiation in presence of the photocatalyst has to be investigated further in order to know, what are the final products. Nitrite and ammonia are also detectable by ion chromatography. A confirmation that the final product is molecular nitrogen and not dinitrogen monoxide, would require for gas analysis, and therefore, for a change in the experimental design. However, the presented research project will help to identify possible candidates for the photocatalytic reduction of nitrate under visible light, a first step to develop efficient photocatalytically reduction processes.

**ACKNOWLEDGEMENTS:** Thanks to the Hi-Water project, Inedita (Senescyt, Ecuador) PIC-18-INE-IKIAM-001, Laboratorio de Referencia Nacional del Agua, and Ikiam University technicians and facility manager.

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## Hydrophilic Carboxylated PES Membranes Coated with Polyelectrolytes

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**INTRODUCTION:** Membranes made of polyether sulfone (PES) are widely used in water treatment due to its outstanding properties and durance [1]. Nevertheless, enhancing membrane lifetime and characteristics is easily achieved by coating with polyelectrolytes (PELs). PELs are known to minimize fouling and enhance hydrophilicity of a membrane [2]. The present study demonstrates the advantage of membranes made from hydrophilic functionalized polymers coated with an additional PEL layer.

**METHODS:** A carboxylate polymer was synthesized from difluoro diphenyl sulfone and the previously silylated monomers dihydroxy diphenyl sulfone and 3,5-dihydroxybenzoic acid. NMR spectroscopy was used to determine the polymer composition and the degree of polymerization. Membranes were prepared from NMP solutions by a machine assisted hand casting process and precipitation in water. A PET non-woven was used as support. Filtration of a BSA (Bovine serum albumin) solution (1 g/L at pH 7) was conducted to describe the fouling behaviour. The filtration of dextran was used to specify the MWCO and to evaluate the suitability of the membranes for drinking water treatment. Information on the surface properties and the morphology (cross-section) of the membranes was obtained from scanning electron microscopic examinations. Different techniques were applied for surface modification by layer-by-layer assembly of polyelectrolytes. Additional measurements of zeta potential, contact angle and Attenuated total reflectance Infrared spectroscopy accompanied the development.

**RESULTS:** Recording of NMR spectra has confirmed the successful and quantitative (10 mol-%) incorporation of the carboxylated monomer into the polymer backbone. During the filtration of deionized water over a period of 20 hours, the membrane is compacted, which is associated with a decrease in permeability to approx. 165 LMH. The subsequent loss of permeability during the filtration of a BSA solution can be reversed to 100% by a

washing step with deionized water in crossflow mode. (Fig.1).

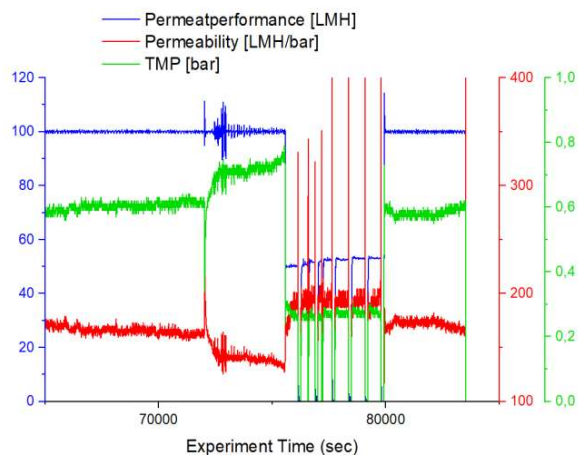
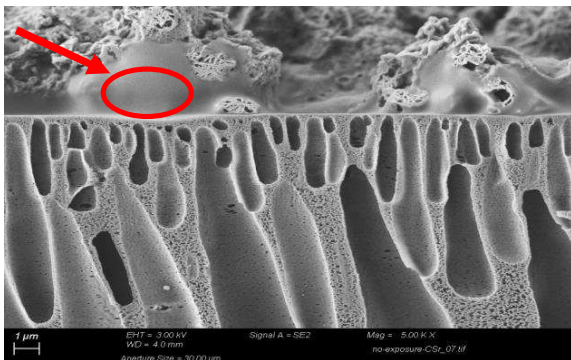


Fig. 1: BSA-Filtration over 23h, recipe 20PESC10-80NMP.

The permeability decreases stepwise on layer-by-layer deposition of PEL. Furthermore, the permeability decrease depends on the number of cycles, the coating method and PEL concentration. Zeta potential measurements demonstrated a clear difference between comm. PES, carboxylated PES and coated ones by a shift of the isoelectric point. SEM measurements have revealed the appearance of a single PEL-Layer on the membrane already after the very first coating cycle (Fig. 2). That single coating step significantly reduces the permeability by covering the membrane surface.



*Fig. 2: SEM picture of a membrane coated by LbL-Method with top layer of PAA (0,05M aqueous solution) on nanoparticles. Spot shows PAA-Layer.*

**DISCUSSION & CONCLUSIONS:** The introducing functional groups enables an improvement of permeability and fouling reduction of membranes [1].

As expected, the permeability of the membranes and the retention capacity for certain molecules can be adjusted by gradually coating with PEL. The extent of the changes is highly dependent on the chosen coating method and the concentration of the aqueous PEL solutions. The proper coating technology can be determined by the need for time and equipment as well as process targets. Zeta potential of the membranes surface can specify the pH of the isoelectric point and thus the pH of the polyelectrolyte solution to reach an enduring layer [3].

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## Capacity Building Associated to HiWater at Ikiam University

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**INTRODUCTION:** Science and technology are pillars for the development of the countries of Latin America and the Caribbean (CELAC). In this area, scientific progress is usually hampered by the lack of resources directed to the Ministries of Science and Technology. International collaboration and the constant search for funding are daily tasks of CELAC scientists and universities. This international cooperation, mainly with funds of European origin, has provided international funds to carry out joint projects with Universities and institutions in Europe. One of these projects, “Hi Water: efficient and affordable water technologies to minimize waterborne pathogens” was awarded by the Eu LAC Health 2017 call.

Hi Water involves the constant interaction of three institutions: two European (RTU, Riga and IPF, Dresden) and one from CELAC (Ikiam, Ecuador).

Ikiam University, which was then expanding a laboratory building, received \$ 226,000 to meet the following objectives: (1) Build institutional capacities to meet Hi Water commitments; (2) Create undergraduate research plans focused on the development of photocatalytic membranes [#BiOX] as well as the exploration of the viroma of river systems [#viEzone] and (3) Develop a participatory science program in the metropolitan area of La city of Tena [#citizenship\_hw].

During the seminar "Capacity building associated to Hi Water at Ikiam University" details will be provided about the footprint that Hi Water leaves, not only in Ikiam, but in the Tena metropolitan area.

**ACKNOWLEDGEMENTS:** To the inhabitants of the City of Tena. To Ikiam staff and to SENESCYT personnel.

**INTRODUCCIÓN.** La ciencia y la tecnología son pilares para el desarrollo de los países de América Latina y el Caribe (CELAC). En esta zona, el progreso científico se ve usualmente obstaculizado por la falta de recursos orientados a los Ministerios de Ciencia y Tecnología. La colaboración internacional y la búsqueda constante de financiamiento, son tareas cotidianas de los científicos y de las universidades de la CELAC. Esta cooperación internacional, principalmente con fondos de origen europeo, ha proveído de fondos internacionales para ejecutar proyectos conjuntos con Universidades e instituciones de Europa.

Uno de estos proyectos, “Hi Water: efficient and affordable water technologies to minimise waterborne pathogens” fue premiado por la convocatoria Eu LAC Health 2017. Hi Water involucra, desde Enero de 2018, la interacción constante de tres instituciones: dos europeas (RTU, Riga and IPF, Dresden) y una de CELAC (Ikiam, Ecuador). La universidad Ikiam, que entonces se encontraba expandiendo un edificio de laboratorios, recibió \$226 000 para cumplir con los siguientes objetivos: (1) Construir capacidades institucionales para cumplir los compromisos adquiridos mediante Hi Water; (2) Crear planes de investigación de pregrado con foco en desarrollo de membranas fotocatalíticas [#BiOX] así como en la exploración del viroma de sistemas fluviales [#viEzone] y (3) Desarrollar un programa de ciencia participativa en la zona metropolitana de la ciudad de Tena [#citizenship\_hw].

Durante el seminario “Capacity building associated to Hi Water at Ikiam University” se proporcionarán detalles acerca de la huella que deja Hi Water, no sólo en Ikiam, sino en la zona metropolitana de Tena.

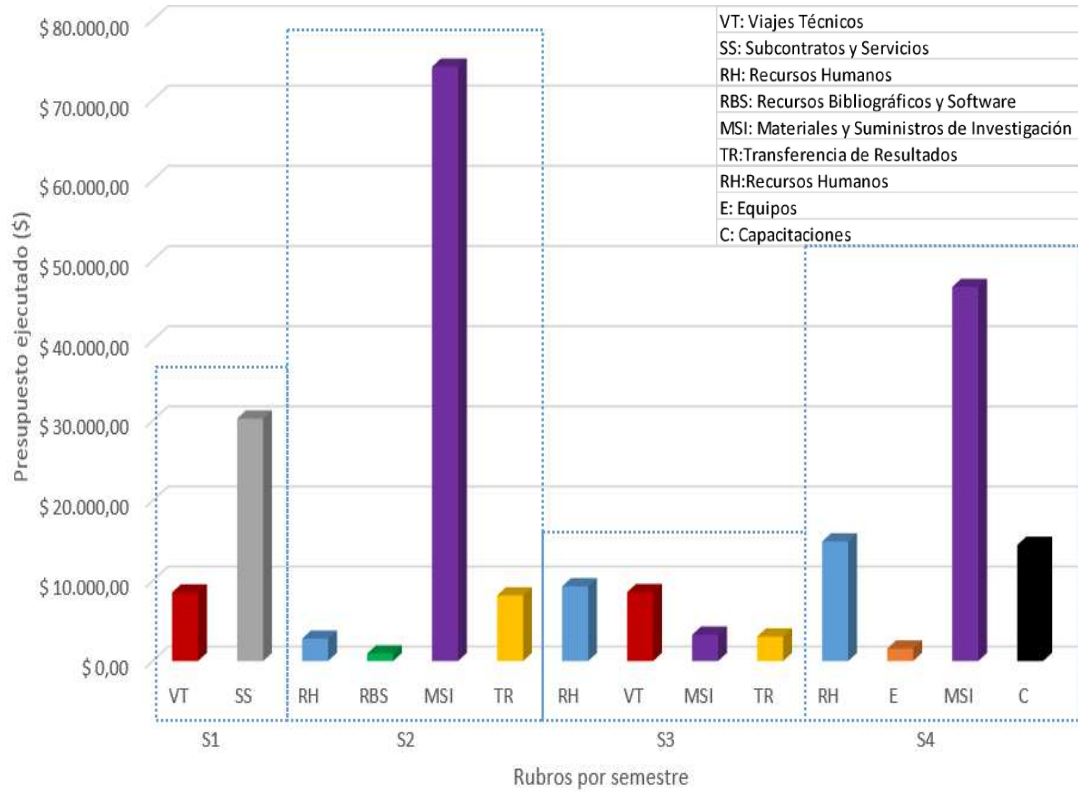


Fig 1. Distribution of HiWater budget.

## Inactivation of Microcystin-LR by a Photocatalytic Membrane Reactor

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**INTRODUCTION:** The frequent emergence of cyanobacteria blooms has gained global concern. Cyanobacteria are autotrophic microorganisms, capable of producing a wide variety of secondary metabolites such as cyanotoxins, that usually cause different degrees of toxicity on human and wildlife health [1, 2]. Cyanotoxins can be classified into three categories: neurotoxins -which act in the transmission of nerve impulse and can lead to death from respiratory paralysis-, hepatotoxins, -which cause liver damage and has carcinogenic effects-, and dermatotoxins, which cause irritations to any exposed tissue [2].

*Microcystis* is the main producer of cyanotoxins, including microcystins [3]. Microcystins are a group of toxic cyclic heptapeptides of low molecular weight and have in common an amino acid  $\alpha$  called ADDA, which is responsible for its toxic characteristics [4]. The most common microcystin has a leucine residue (L) at position 2, and an arginine (R) at position 4, [5], that is the reason that this microcystin is known as LR.

Conventional methods for surface water treatment such as coagulation/flocculation are not effective against colloidal microcystin LR and can trigger secondary contamination with an inevitable release of intracellular organic matter [6].

Inactivation of this kind of molecules requires advanced oxidation process (AOP), which is a very attractive alternative to complement the treatment of wastewater containing hard-to-degrade substances such as microcystin-LR and other compounds of emerging concern. Most of the studies conducted to inactivate microcystin-LR were performed using titania as photocatalyst. However, Bismuth oxyhalides (BiOX) have been used in AOP recently because of its ability to produce reactive oxygen species (ROS) when irradiated by visible light [7]. Although the inactivation with TiO<sub>2</sub> is robust and reliable, it is not guaranteed to be used by the rural communities because of its activation with UV light.

Information on the use of BiOX for microcystin-LR removal is limited, studies have been conducted varying the material of the photocatalizer but not its type, that is why in this research it is intended to study the change in the variation of the *BiOBr* nanostructure layers.

In line with the background outlined above, the following research question arises:

What is the direct relationship between the efficiency of a photocatalytic process with the variation in the number of layers of the *BiOBr* nanostructure used in microcystin-LR inactivation?

**Hypothesis:** An Increasing in the number of *BiOBr* layers will boost the efficiency of the photocatalytic method by inducing microcystin-LR inactivation in a shorter time.

To solve this hypothesis, the following objectives are proposed: (a) To develop and validate an analytical strategy to quantify microcystin-LR; (b) To inactivate microcystin-LR using ceramic membranes covered by different numbers of *BiOBr* nanocoatings using synthetic surface water and a visible-light photoreactor (Table 1).

### EXPERIMENTAL STRATEGY:

1. Estimation of the physical, human and financial resources of the project
2. Purchasing of the equipment and reactants
3. Develop and validate an analytical method to quantify microcystin-LR
4. Design a photoreactor (Note: a prototype is available for the research (Fig 1).
5. Coating of commercial membranes using layer by layer methods
6. Prepare synthetic solutions with microcystin-LR, KI and water
7. Complete the experimental design described in Table 1.



Table 1. Design scheme of 27 experiments on photocatalytic activity at constant LED light.

Number of layers of BiOBr deposits	Ionic strength (mM KCl)	Concentration of microcystin-LR (mg / L)
0 (Blank)	0 10 100	0,5
3	0 10 100	1
5	0 10 100	2

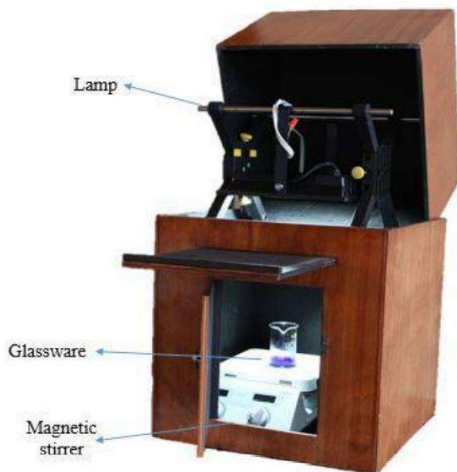


Figure 1. Photoreactor available for the experiments.

**FUTURE PERSPECTIVES:** From the studies and results compiled in the thesis, the importance of the study of cyanotoxins (microcystin-LR) will be discovered. Therefore, it is necessary to continue working in this research, fundamentally in the identification of microcystin-LR in natural samples of the rivers of the Napo and Pastaza province that present a higher degree of contamination as mentioned in the literature, which increases the probability of the presence of these cyanotoxins.

**ACKNOWLEDGEMENTS:** A special thanks to the Coordinator, Miguel Herrera, who has trusted in the potential of the students, thus giving an opportunity to the development of the future.

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## Microbiology and Water Quality of Tena River

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**INTRODUCTION:** The Rio Tena is located in the province of Napo and on its way it crosses two important municipalities, Muyuna and the city of Tena. This city was founded in 1560, but in 1970 oil reserves were discovered in this area, which led to improved access infrastructure to the city. As a result the trade increased significantly in this province [1].

These changes generated in the Napo province, have allowed favourable growth in logging activities, real estate projects, tourism, agriculture, livestock, etc. However, in this economic benefit, these changes also came along with the adverse effects of anthropogenic interventions over their natural resources and the disruption of river ecosystems. Concerns regarding the water quality of the Tena river have grown.

In view of the "One Health" concept, we know that the well-being of aquatic ecosystems is an important or indisputable health of humans and animals. For this reason, contaminated water is of important means of transmitting infectious diseases through bacteria (*Cholera*, *Salmonella*), viruses (*Norovirus*, *adenovirus*, *rotavirus*), and parasitic origin (*Tapeworm*, *Schistosomiasis*, *Cryptosporidiosis*).

Determining the microbial load on the Tena river at various points along its path gives us an insight into the importance of generating technological health strategies and to decrease the impact of anthropogenic interventions on the river and therefore to ensure the health of those who depend on its waters.

**METHOD:** In the present work, two microbiological indicators were used: Aerobic mesophilic bacteria (AMB) and total coliforms bacteria (TCB). The AMB allows us to determine the effectiveness of the water treatment towards the bacteria related to body temperature, and the TCB indicates the presence of matter from enteric origin in the water bodies.

**RESULTS AND CONCLUSION:** The results obtained in pristine areas were compared with those obtained in places of high anthropogenic impact. In the three points studied (see Figure 1), it was shown that there is a great variation in microbial load. Comparing the points much higher with less anthropogenic intervention on the Tena river (point A) to the points of greater disturbance of the ecosystem (Points B and C) [2]. All of the above described samples, were ultrafiltrated by commercial membranes to retain microorganisms that may have a high epidemiological impact on human health.

Among the alternatives for removing microorganisms ultrafiltration membranes, with pore size small enough to retain the viral particles and microorganisms. In order no plugging of membrane-pores arises it is necessary to stop the water filtering process after some time.

Evaluating the efficiency of the membranes during the purification of the water from the different sampling points, we observe that the 30 kDa and 10 kDa membranes are the most efficient in the removal of microorganisms and viral particles (Fig. 2). Nevertheless it is necessary to solve the inconveniences of membrane biofouling [3] [4].

Additionally, we established objectives to ensure the continuity of this research: (i) to implement a metagenomic analysis of the eDNA collected from the different sampling points. This should be established to detect bacteria of clinical importance such as *Legionella* and *Mycobacteria*, (ii) to characterize the fluvial virome and (iii) determine the presence of antibiotic resistant genes that increasingly threatens public health systems.

The ultrafiltration process, improves the quality of the water to the point that it can be reused or recycled, which is highly feasible due to its low cost compared to other techniques (nanofiltration and reverse osmosis). Easy automation and handling, and its proven ability to eliminate pathogenic microorganisms, are the advantages of this treatment method [5].

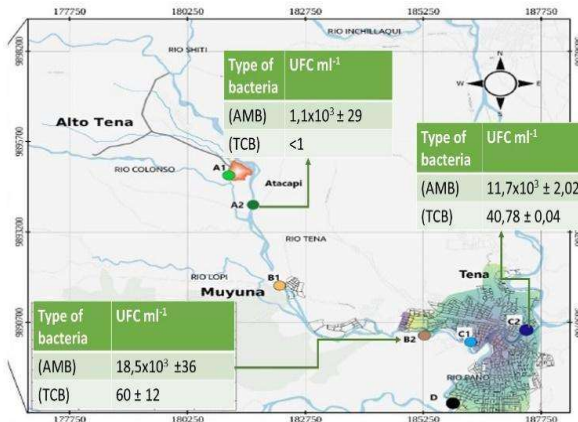


Figure. 1. Microbiological analysis of surface waters of the Tena river.

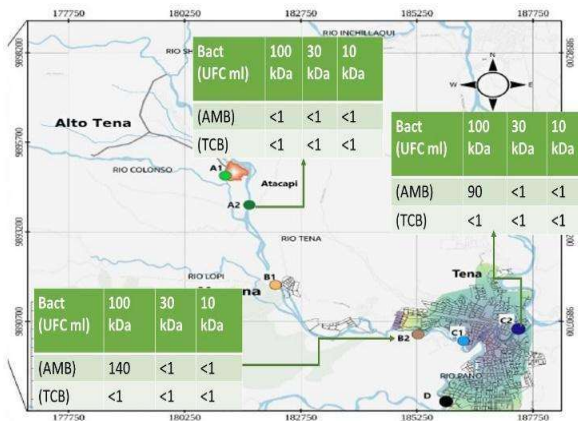


Figure. 2. Efficiency of ultrafiltration in the removal of microbiological contaminants with membranes of different pore sizes.

**ACKNOWLEDGEMENTS:** This work is part of the “Hi-Water-Project: Efficient and affordable water treatment technologies to minimise waterborne diseases”. It was funded by EU CELAC R6I funding agencies (EULACH16/T02-0143) (<http://eulachealth.eu/>).

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## Deposition of BiOX Nanoparticles over Ceramic Membranes

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**INTRODUCTION:** Catalyst deposition techniques are widely used in the field of energy production, chemical synthesis, wastewater treatment and functionalize substrates to degrade pollutants. Qing et al. describe the types of deposition (physical and chemical) and conclude that the use of these techniques is prominent but premature [1]. Currently, the most used methodologies to coat substrates are: dip coating, sol-gel method, chemical vapor deposition, grafting and layer-by-layer assembly. The latter stands out from the rest because it takes advantage of oppositely charged polymers to homogeneously deposit nanoparticles that generate catalytic activity on substrates. In the field of water treatment, several studies have been developed based on this principle, using TiO<sub>2</sub> in the presence of UV light, few of them use filter membranes as a substrate and perform under the visible spectrum. Taking this into account, this research aims to deposit a catalytic surface that reacts under visible light (Bi<sub>7</sub>O<sub>9</sub>I<sub>3</sub>) on a microfiltration membrane to degrade pollutants of emerging concern (BPA) since these processes: i) optimize the degradation of pollutants, ii) they recycle the catalyst through immobilization and iii) reduce energy consumption.

**METHODS:** Hierarchical microstructures of Bi<sub>7</sub>O<sub>9</sub>I<sub>3</sub> will be synthesized due to its photocatalytic activity under visible light [3]. To coat the ceramic membrane, the methodology of Starr et al. (Fig. 1) was used [2]. To ensure the aggregation of the catalyst on the surface, it must have a pH lower than its point of zero charge.

Similarly, it must be ensured that the pH of the terminating (anionic) polyelectrolyte and of the catalyst solution are the same. Along with this experiment, TiO<sub>2</sub> deposited on a ceramic membranes will be used in order to compare its photocatalytic activities.

The coated membranes will be inserted into a photocatalytic membrane reactor with 4 lights (1000 W LED). The white contaminant to be degraded will be Bisphenol A (BPA). Three experiments will be carried out for each catalyst, maintaining the

same pressure. A spectrophotometer will be used to measure the degradation of the contaminant.

SEM will be used to record the images of the photocatalytic membranes at different magnitudes. The XRD will be used to examine the crystalline structure of the catalysts. In addition, the use of numerical methods will be proposed as an important tool for the modeling of photochemical reactors, since it can integrate all the physical-chemical phenomena involved in the process, and they are not limited to the differences in the distribution of radiation [5].

**RESULTS:** It is expected to obtain a greater degradation of BPA, using Bi<sub>7</sub>O<sub>9</sub>I<sub>3</sub> since it reacts under visible light unlike TiO<sub>2</sub> nanoparticles, which develop their photocatalysis in the presence of UV light. As for the photocatalytic membranes, it is expected to have a dispersed coating in both the Bi<sub>7</sub>O<sub>9</sub>I<sub>3</sub> catalysts and the TiO<sub>2</sub> due to the use of the LbL methodology. In addition, the coatings of the membranes before and after deposition will be compared by SEM and the presence of the crystalline phase of the catalysts deposited on the membrane will be corroborated with the XRD.

**DISCUSSION & CONCLUSIONS:** Using Bi<sub>7</sub>O<sub>9</sub>I<sub>3</sub> in an aqueous solution exhibits a high degradation efficiency of BPA [6]. Therefore, it is essential to evaluate the removal of this contaminant in a photocatalytic membrane reactor, which recycles the catalyst through its immobilization. Different depositions of similar catalysts (BiOI) on glass fibers have been tested in a fixed bed reactor with thin film, obtaining a 98% degradation of BPA in 2 h [6] but there are no depositions on ceramic membranes, which present a synergistic effect when wastewater treatment is used. Although LbL is an extensive procedure. It should be noted that its use is cheap, simple, flexible and has satisfactory thickness control per layer [1].

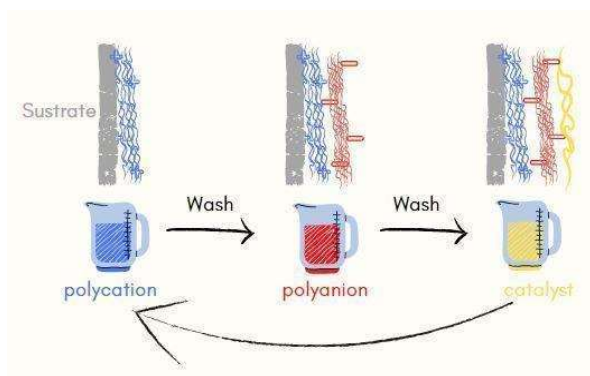


Fig. 1. LbL methodology for the deposition of catalysts on the ceramic membrane.

Which makes LbL suitable for making the coating. Additionally, similar methodologies such as spray LbL can be applied to reduce procedure time.

Developing this remediation methodology is essential, as it degrades pollutants under visible light and promotes the reuse of the catalyst on a ceramic substrate.

**ACKNOWLEDGEMENTS:** This work is part of the “Hi-Water-Project: Efficient and affordable water treatment technologies to minimize waterborne diseases”. It was funded by EU CELAC R6I funding agencies (EULACH16/T02-0143) (<http://eulachealth.eu/>).

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## SmartLIX project - Potential Use of Hybrid Membranes for Treating Landfill Leachates

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**INTRODUCTION:** To be sustainable, cities must reduce their negative environmental impact through the management of their municipal waste. In Ecuador, the treatment of leachate generated in sanitary landfills is almost non-existent even though guaranteeing the integral management of solid waste is the responsibility of the Municipal Governments.

Leachates are liquids formed by the mixture of rainwater infiltrated in the solid waste from sanitary landfills plus the products of its degradation. They contain high concentrations of organic matter, total suspended solids, nitrogen, phosphorus, and heavy metals. In the sanitary landfill of the Tena city, the leachates are stored in swimming pools, due to their physicochemical characteristics they have a high environmental impact on the receiving water bodies.

In response to this problem, the SmartLIX project proposes to develop a rotating biological contactor (RBC) controlled by instrumentation, control and automation (ICA).

The RBC is an aerobic treatment of fixed film and could allow the removal/degradation of the pollutants present in the leachate to the maximum permissible limits for its discharge, in compliance with the Ecuadorian environmental regulations.

RBCs are an economical alternative, with a 60 to 70% pollutant removal efficiency, a useful life of 7 to 10 years, and they easily adapt to variations in the physicochemical characteristics of the leachate and its flow rates.

With the control of the RBC main operating variables the aeration rate and the organic loading can be optimized. Implementation of ICA also offers tools for performance evaluation, reduction of operating costs, improvements in the robustness of the process, increases in the efficiency of pollutant removal, as well as the reduction of the use of resources and the increase of the useful lifetime.

**METHODS:** To develop the RBC/ICA prototype, the following stages are planned:

- (1) Design the RBC and stabilization of the sludge.
- (2) Develop the ICA protocol. Process variables such as flow, level, disc rotation speed, dissolved oxygen, temperature, pH, and the detachment of the biofilm will also be controlled.
- (3) Operation at lab-scale with dilute samples of landfill leachate to quantify the pollutant removal
- (4) Operation at lab-scale with real samples to identify pollutant removal

**RESULTS:** The RBC/ICA laboratory-scale prototype (Figure 2), will allow the members of the SmartLIX team to offer the consulting service for the design of public or private leachate treatment plants.

The use of the RBC reactor as the base technology to define the most suitable treatment train for the removal of the specific pollutants of each client will allow an experimental study of the process before the development of the full-scale designs of the treatment, depending on the requirements of each sanitary landfill. The treatment train will consist of:

1. Primary treatment.
2. RBC with four stages, includes settlers (Figure 1).
3. Tertiary treatment, microfiltration using ceramic membranes.

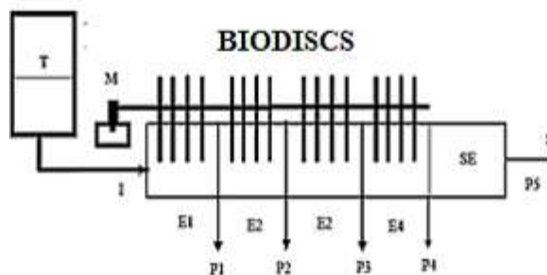


Fig. 1. Diagram of RBC, four stages (E1, E2, E3, E4). P1, P2, P3, P4, P5: Sampling points. SE: Sedimented. T: Storage tank. S: outlet of the treated effluent. I: Income from leachate. M: Disc rotation system.

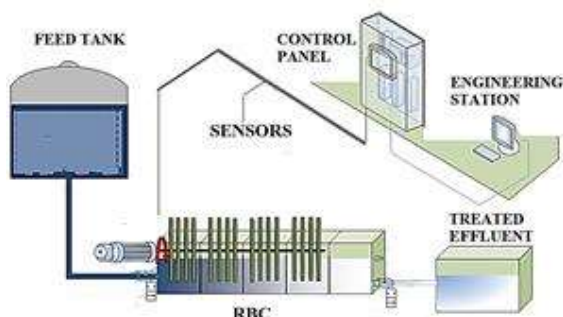


Fig. 2. Diagram of the RBC with ICA.

**DISCUSSION & CONCLUSIONS:** Currently in several Ecuadorian cities such as Loja, Ambato and Guaranda there are leachate treatment plants with anaerobic processes (UASB reactors), although studies show that RBC reactors achieve removal efficiencies higher than those achieved with UASB reactors, see Table 1 (Pérez, J., 2010). UASB reactors achieve BOD and COD removal percentages of 58% and 49% respectively, below the efficiencies achieved with an RBC reactor.

Equipping a rotating biological contactor (RBC) with ICA will allow the development of an economic, intelligent and efficient prototype for the treatment of leachates, a persistent problem due to the continuous increase in the population and the generation of solid waste in cities.

Table 1: Percentages of removal of physicochemical parameters in leachates with RBC reactors

Parameter	Removal percentage, %	Study
COD, mg/l	75 - 90	Borzacconi et al, 1996
BOD5, mg/l	75 - 98	Rivera et al, 1988; Metcalf & Eddy, 1996
Total Suspended Solids (TSS), mg/l	80 - 95	Metcalf y Eddy, 1996; RAS, 1998; Spellman, 2003
Total nitrogen Kqendal (NTK), mg/l	63,1 - 85	Behling et al, 2003; Moghabghab, 1997
Total phosphorus, mg/l	10 - 25	Metcalf & Eddy, 1996; RAS, 1998

Note. Adapted from Pérez, J. (2010).

**ACKNOWLEDGMENTS:** SmartLIX thanks the Hi Water Consortium that promoted the creation of this project and the Ikiam University Geosciences Laboratory.

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## Immobilisation of Photoactive Nanoparticles

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**INTRODUCTION:** Most applications of photocatalytically active nanoparticles require immobilisation of the photocatalyst on a solid support. Representative examples of immobilisation methods from different fields of applications are discussed. Special attention is devoted to the molecular basis of the coating and immobilisation strategies used so far.

**METHODS:** The presented data were taken from recent review articles and other relevant documents [1-3].

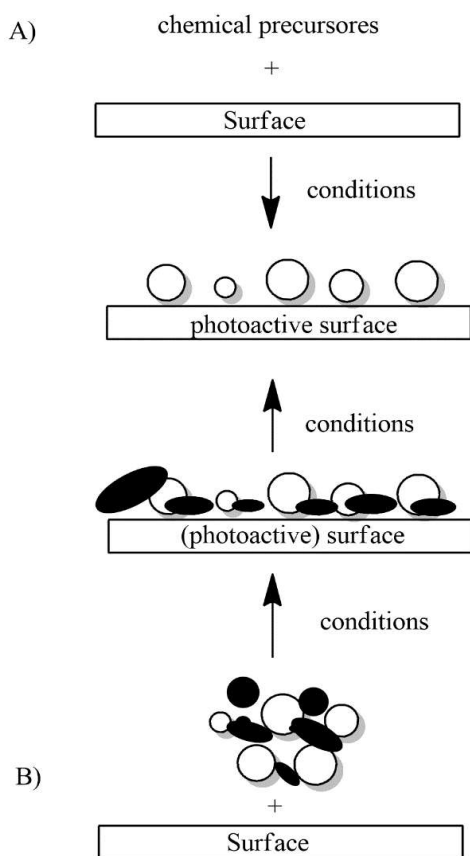


Fig. 1. Immobilization methods. A: Generation of nanoparticles on the surface; B: Application of preformed nanoparticles.

**DISCUSSION & CONCLUSIONS:** Titanium dioxide ( $\text{TiO}_2$ ) was chosen as the representative “photocatalyst”. It has been widely used in many applications, predominantly air purification and self-cleaning materials, but also in other fields, e.g., water treatment. Some of these immobilisation methods used for this material can be applied to other transition metal oxides.

General requirements for the immobilisation include acceptable cost, durability, and environmental impact (toxicity of leaching particles). It is also self-evident that the coating technique must produce a uniform and reproducible covering of the supporting material. There are also further requirements, more specific for photoactive materials.

The immobilization methods can be divided into two cases, which are depicted in Figure 1. The methods in which the catalyst is formed from precursors in reactions directly on a surface (above, A), cannot be changed easily in order to produce other photocatalysts than  $\text{TiO}_2$ . More general are the methods, in which the prior produced catalyst is fixed on a surface as a mixture with a support material, which is removed finally by thermolysis and sintering (B).

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## Theory of Biofouling Development during UF of Surface Water

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**INTRODUCTION:** Membrane biofouling is a complex phenomenon that depends on the properties of both the membrane and the inlet stream. Surface water is usually composed of living substances (bacteria, algae and viruses) and abiotic substances (inorganic colloids, natural organic matter and extracellular polymers). Due to the high retention of suspended pollutants, ultrafiltration (UF) is considered a robust technology for industrial solid-liquid separations and surface water potabilization. Little is known about the internal structure of biofouling during UF of surface water. A detailed description about the stages of development of biofouling could help in the design of novel strategies for its control. The present study aimed to set a theory to explain the roles that microorganisms could perform during biofouling development. The proposed theory is based on UF experiments performed in three different sections of Tena river: A: Rural [1500 PE], B: Suburban [5000 PE] and C: Urban [25 000 PE].

**METHODS: Water sampling:** A total of 50 surface water samples, with volumes of 20L were collected during the 2019/2020 hydrological cycle. A set of physicochemical analyses, including AWWA/APHA suspended and total solids, were performed on surface water samples and UF permeates (Table 1). Presence of aerobic mesophilic bacteria (AMB) and total coliforms (TC) also were measured on a bi-weekly basis [1]. **UF experiments:** Using a stainless-steel tank as a feeder tank, it was connected to an 400 ml AMICON ultrafiltration cell (millipore, MA). Twenty liters of each water sample was filtered at a constant transmembrane pressure (30 psi) and the biofouling development was recorded. Microstructural parameters of biofouling (specific cake resistance, % of porosity, fractal dimension of cakes) were evaluated using the mathematical approaches based on Kozeny-Carman equations [2,3].

**DNA isolation, biomass estimation and number of bacteria.** The number of bacteria in the biofouling was estimated after the isolation and quantification of the associated DNA as follows: (i) DNA isolation was performed once the biofouling was mechanically removed from fouled membranes using a commercial kit (DNeasy PowerSoil PRO kit, Qiagen, Germany). (ii) Concentration of DNA was obtained by using spectroscopy indexes (260/280, 260/230) in a NanoDrop 8000 (ThermoFisher, MA, USA). (iii) Cell mass was estimated considering the DNA/cell biomass ratio proposed by Fleming et al. (cell biomass = 16.6X DNA mass) [4,5] and (iv) Cell mass was used as the basis to compute the number of cells per cm<sup>2</sup> according to the fact that average dry weight of a prokaryotic cell is 2x10E-13 g [6].

**RESULTS:** *Table 1* contains a summary of the accumulation rates of constituents on membrane (in mg/h) during the UF of surface water from sampling points A, B and C. There was accumulation/assimilation of nutrients and inorganic materials at membrane level, so it was hypothesized that living bacteria were able to use them to grow. *Table 2* shows a summary of the results obtained from the estimations of number of cells per square centimeter of fouled membrane based on DNA isolations from biofouling developed during UF of surface water from sampling point C (urban). *Figure 3* depicts the microbiological loads of water from A, B and C sampling points. As expected, a total removal of microbiological indicators (AMB, TC) were assessed in all the experimental UF tests. In fact, all the AMB and TC were removed at membrane level.

**DISCUSSION & CONCLUSIONS: Theory for biofouling development during the UF of surface water:**

(a) *Membrane conditioning.* When the feed water comes into contact with the membrane, the filtering surface is conditioned, that is, it is surrounded by "clouds of electrical charge", scenarios that produce

a decrease in the filtration area. This membrane conditioning causes an electrostatic bilayer that leads to a significant decrease in the permeate flux. Although this decrease in filterability begins when the membrane resistance is measured with solids-free water, it is exacerbated when the membrane comes into contact with surface water, which contains a certain amount of solids and microorganisms. This membrane conditioning occurs in early stages of UF in the experiments described in this manuscript.

*(b) Restriction of flux by cooperative standard blocking.* The application of mathematical approaches to measure pore-blocking indicated that pore-blocking started with the accumulation of materials inside the membrane pores. This phenomenon is known as standard blocking (SB). According to the whole analysis of the results of pore-blocking during UF of surface water. The components of the SB can be both organic and inorganic, according to the results of the mathematical modeling of the block [7,8]. The causes of this phenomenon are undoubtedly related to dissolved solids (metal ions, nutrients, soluble organic compounds, natural organic matter) and colloidal materials such as nano-silica arrangements and viruses. Reduction of the rates of flow loss associated with SB is only possible using a pretreatment such as sand filtration.

*(c) Stochastic surface colonization.* The accumulation of material inside the membrane tends to increase the flow through each pore (local flow, JL) that is still open [9]. Increases in JL promote the accumulation of solids in such zones in the membrane. Because this accumulation is stochastic (and also because the feed stream is heterogeneous), a mixture of blockages at the surface level coexists (complete and incomplete). This coexistence of patterns of aggregation gradually translates into the formation of a glycocalyx because microorganisms already started to colonize the surface and cores of the membranes.

*(d) Surface cake development due to bacterial colonization.* During this stage there are no considerable changes in the permeate flux in the UF experiments conducted with water from A, B and C sampling points. It seems that a steady state was reached and could indicate that the biofouling is structurally stable. As the filtration time continues, the local flux-induced spots could serve as niches for bacterial colonization, maybe promoted by a massive secretion of quorum sensing signals (QS) released by specific pioneer bacteria [9]. According to the report by Lo [9], most of these pioneers

belong to different phyla, including the Firmicutes, Proteobacteria, Bacteroidetes and Planctomyces. According to Oh and Lee, massive QS secretion promoted EPS release and later exponential growth of colonizers.

*(e) Biomineralization of glycocalyx as the starting point of irreversible fouling.* Several authors consider that there is accumulation of minerals within the growing glycocalyx [11,12]. This mineralized, reinforced glycocalyx, allows the passage of nutrient-rich streams, and adapts its shape to create dynamic porosity (measured as % porosity). Such empty spaces can serve as compartments, in which microorganisms could be able to control the deposition of minerals in order to gain stiffness and substratum to attach [13]. As filtration evolves, maybe there is a massive biologically-induced mineralization within such holes, a scenario that could explain the development of irreversible fouling, a very hard to remove material composed by organic, inorganic and biotic constituents.

Although the quantity by mass, or the number of bacteria associated with the biofouling analyzed could seem negligible, their contribution to the development of cake should not be demerited. It is known that various microorganisms associated with biofouling are capable of secreting large amounts of QS/EPS and therefore their role in the “design and operation” of the steady-state glycocalyx should not be underestimated.

**ACKNOWLEDGEMENTS:** This research was founded by SENESCyT (EULACH T02). We also thank Ikiam University and the staff of the Ikiam Geosciences Laboratories and National Water Reference Laboratory for their participation in the design of the research and laboratory work.

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Table 1. Accumulation rate (mg/h) of physicochemical and microbiological contaminants on the UF membrane (MWCO = 10 kDa).

Type of water constituents	Rural (A)	Suburban (B)	Urban (C)
Nitrites	0.01 ± 0.02	0.47 ± 0.02	0.071 ± 0.05
Nitrates	1.63 ± 0.43	51.16 ± 0.43	5.51±0.22
Ammonia	0.42 ± 0.07	41.65 ± 0.07	10.18 ± 0.1
Phosphates	0.76 ± 0.07	33.21 ± 0.07	7.72± 0.08
Fe	0.39 ± 0.08	20.44 ± 0.08	4.97± 0.11
Mn	0.017 ± 0.01	3.07 ± 0.008	0.62±0.01
Ca (Hardness)	11.54 ± 0.84	110 ± 0.84	26.53 ± 1.3
Mg (hardness)	4.49 ± 1.02	116 ± 1.02	22.5 ± 0.64

Table 2. DNA isolation, biomass estimation and number of bacteria.

Biofouling sample	DNA isolation [ng/uL]	Abs 280/260	Biomass linked to cells [ug/cm <sup>2</sup> ]	Cell number [per cm <sup>2</sup> of membrane]
100 kDa membrane	155.1	1.88	71.52	3.57 x 10E07
30 kDa membrane	310.3	1.83	143.08	7.15 x 10E07
10 kDa membrane	236.8	1.78	109.19	5.46 x 10E07

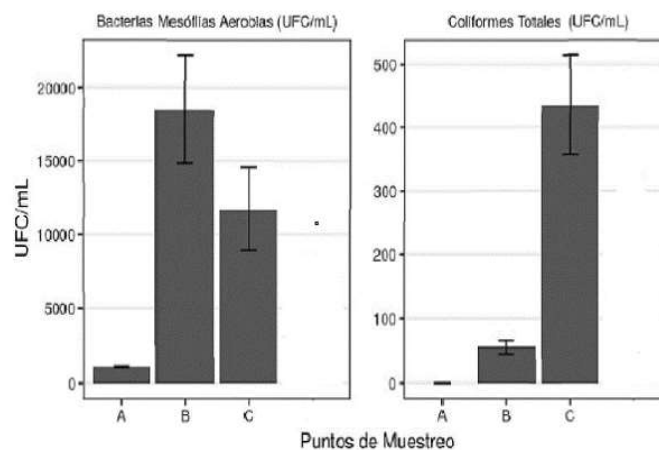


Figure 3. Results from culture-based microbiological test. Left side shows the amount of mesophilic aerobic bacteria and the right side shows the amount of Total coliforms [CFU/ml].

## Inactivation of Compounds of Emerging Concern by BiOX Nanoparticles

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**INTRODUCTION:** Contaminants of emerging concern (CEC) are compounds product of anthropogenic activities (i.e., drugs, pesticides, antibiotics) that are present in domestic and industrial wastewaters, which are treated by wastewater treatment plants. However, these plants do not remove them entirely. In fact, CECs have been detected in surface water, groundwater, lakes and drinking water sources, threatening human health and aquatic ecosystems [1]. Currently, 197 CECs have been reported, among these Bisphenol A (BPA). It is an organic compound employed to manufacture plastic bottles, baby bottles, medical equipment, lining of canned goods and others. However, its effect on human health are: endocrine disruptor, metabolic syndromes, alterations in thyroid function and vascular diseases.[2] Similarly, Rhodamine B (RhB) is an organic dye, used in the paper, paint, food and textile printing industries. When this compound is discharged into the environment, it obstructs the penetration of light and thus alters biological processes. Additionally, RhB is toxic, carcinogenic, irritating to the skin and causes respiratory and gastrointestinal disorders [3]. Therefore it is necessary to develop technologies to degrade CECs. Photocatalysis has emerged as a promising alternative for degradation of CEC in water. Bismuth oxyhalide photocatalysts (BiOX, X = F, Cl, Br, I) are potential candidates due to their structural characteristics and lower band gap energy (1.7 – 3.2 eV), allowing them to efficiently harvest light from the visible light spectrum. However, most of these studies (BiOXs) have been carried out using Xenon and halogen lamps, which are an excellent source of visible light, nevertheless they have high costs, heat generation, poor light penetration, need of cooling systems and short life time. Light-emitting diodes (LEDs) have been used in this study as an alternative, because they do not produce heat, thus making the use of cooling systems unnecessary, which results in lower economic costs [4]. For this reason, this study analyzes the

efficiency of CEC degradation by BiOX nanoparticles by visible light LED lamps.

**METHODS: Synthesis:** Hierarchical Bi<sub>7</sub>O<sub>9</sub>I<sub>3</sub> were synthesized using an oil bath and reflux system: 0.728 g Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was dissolved in 20 mL EG (Solution A) and 0.249 g KI in 10 mL EG (Solution B) by stirring at room temperature. Afterwards, 30 mL EG was poured in a 250 mL three-necked round-bottom flask and pre-heated at 160 °C by an oil bath with a refluxing system. Then B solution was added for 10 min. Subsequently, the solution A was added and was stirred continuously for three hours at 160 °C. The precipitates were collected by centrifugation. The samples were washed with distilled water and ethanol and dried in an oven at 60 °C for 12 h.

Bi<sub>12</sub>O<sub>17</sub>Cl<sub>2</sub> nanobelts were prepared via a hydrothermal method: 0.97 g Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was dissolved in 10 mL EG using an ultrasonic bath for 10 min and stirring. Simultaneously, 0.324 g NH<sub>4</sub>Cl and 0.8 g NaOH were dissolved in 60 mL distilled water under stirring for 10 min. These two solutions were mixed and placed into a 100 mL teflon-lined autoclave which was heated up to 140 °C for 12 h. The resulting precipitate was collected by centrifugation and washed with distilled water and absolute ethanol. The resulting powder was dried at 80 °C for 6 h.

**Characterization:** The X-ray diffraction patterns of the samples were obtained by using a X-ray diffractometer (XRD, SEIFERT 3003 T/T, GE Sensing & Inspection Technologies, USA), which is equipped with a Cu K $\alpha$  radiation source ( $\lambda = 0.1542$  nm,  $E \sim 8.04$  keV). Additionally, the average crystallite size was calculated using the Debye-Scherrer equation.

**Photocatalytic activity:** The photocatalytic activities were tested in a photoreactor equipped with LED lamp (50 W). Batch experiments were conducted as follows: 50 mL BPA solution (20 mg/L) and 50 mL RhB (10 mg/L) was mixed with 1g /L photocatalysts. Prior to irradiation the solutions were stirred for one hour in the dark, to

allow the system to reach adsorption/desorption equilibrium. BPA (276 nm) and RhB (554 nm) concentration were determined using a UV-Vis spectrophotometer. Additionally,  $\text{TiO}_2$  and photolysis (without photocatalyst) was evaluated in the same conditions.

## RESULTS:

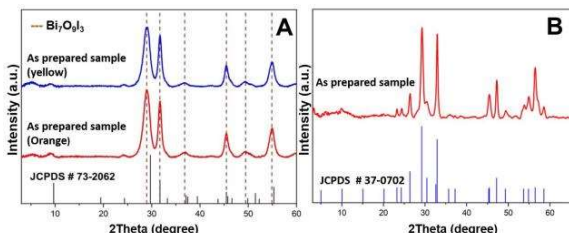


Fig. 1. XRD images of: (A)  $\text{Bi}_7\text{O}_9\text{I}_3$  catalyst (orange and yellow color). (B)  $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$  catalyst.

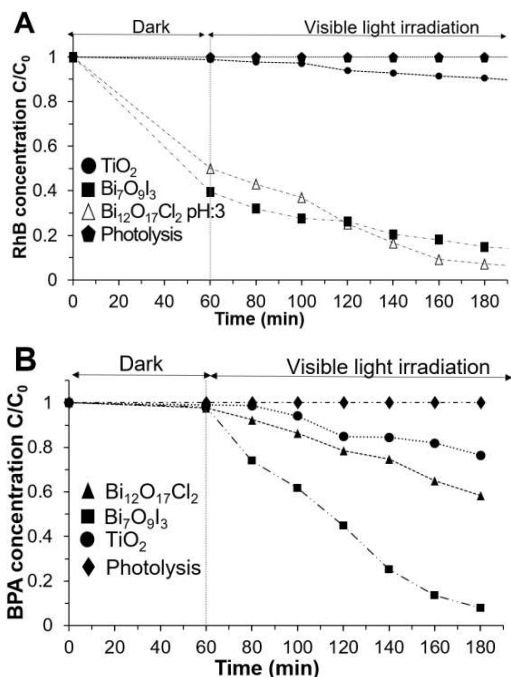


Fig.2. Photocatalytic evaluation of photocatalysts  $\text{TiO}_2$ ,  $\text{Bi}_7\text{O}_9\text{I}_3$ ,  $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$  and photolysis. (A) Degradation of BPA. (B) Degradation of RhB.

**DISCUSSION & CONCLUSIONS:** X-ray diffraction analysis for  $\text{Bi}_7\text{O}_9\text{I}_3$  showed peaks positioned match those reported for Xiao et al. [4]. Similarly,  $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$  reported diffraction peaks equal to Wang et al. [5]. Both catalysts present high purity of the crystal. The average crystal size for  $\text{Bi}_7\text{O}_9\text{I}_3$  and  $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$  was 8,5 nm and 240 nm respectively.

With respect to its morphology  $\text{Bi}_7\text{O}_9\text{I}_3$  reveals flower-like micro-rectangles, flower-like microspheres, and hexagonal microplates. While  $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$  shows belt-like nanostructures. On the other hand, the RhB percentage degradation with  $\text{Bi}_7\text{O}_9\text{I}_3$  and  $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$  photocatalysts was 85% and 80% respectively (Fig. 2A). Additionally, the percentage of absorption by  $\text{Bi}_7\text{O}_9\text{I}_3$  and  $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$  were 22% and 44% respectively. In the case of BPA the percentage degradation was 95% by  $\text{Bi}_7\text{O}_9\text{I}_3$  and 40% by  $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$  after 3 hours of irradiation. In comparison,  $\text{TiO}_2$  showed poor degradation for RhB and BPA. These results demonstrate that both photocatalysts have a high efficiency to degrade dyes and organic compounds under white LED light irradiation.

**ACKNOWLEDGEMENTS:** The *HiWater* consortium (SENESCyT: EULACHT02-0143) provided the resources to develop this research work. To the laboratory technicians of Ikiam University (RL, AS, MQ and from the *Leibniz-Institut für Polymerforschung* (IPF-Dresden), especially Mrs. Cornelia Schlendstedt.

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## Study of Bimetallic Pt-based Catalysts as Anodes for Low Temperature Fuel Cells and its Performance to CO Oxidation

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**INTRODUCTION:** The demand for highly efficient and environment friendly technologies for energy transformation has become an important driving force for research in fuel cells. In the field of energy related materials, such as Pt-based catalysts, it is often necessary to characterise and identify transfer processes as mass transport or charge transport on the electrode surface. Electrochemical Impedance Spectroscopy (EIS) is an important research tool for identifying these transfer processes [1].

**METHODS:** For this study, the bimetallic PtMo/C catalysts were synthesized by platinum (Pt) and molybdenum (Mo) phases with carbon Vulcan as an support. Electrochemical techniques such as Cyclic Voltammetry (CV) and EIS have been used for the diagnosis and the characterisation of electro-catalysts during the oxidation of organic species and their carbon monoxide (CO) poisoning. The strategy to use the EIS technique generally requires the formulation of an Equivalent Circuit (EqC) model to describe the experimental data [2]. One of the main drawbacks in the use of EqC to explain EIS is its non-uniqueness, the same EIS behaviour can be presented by very distinct circuits, because of this the EqC model has significant limitations and can be challenging [3].

To overcome the EIS limitations, the Distribution Function of Relaxation Times (DFRT) has recently attracted significant research attention. DFRT technique has shown better separation and visualization of the underlying electrochemical processes [4].

Hence, in this work the EIS technique through DFRT analysis was used to study the adsorption and electro-oxidation processes of CO species on PtMo/C catalysts surface. Two main potential ranges were characterised in order to reveal the

phenomena promoted by the molybdenum phase on the surface of PtMo/C catalysts.

**RESULTS:** Figures 1 and 2 (see next page).

**DISCUSSION & CONCLUSIONS:** Figure 1 shows the voltammetry results that are supported by DFRT data (figure 2), both graphical representations prove that the PtMo/C catalyst surface was not affected during the CO oxidation process, i.e. the PtMo/C catalyst surface was available even under the poisoned conditions, in contrast to a single Pt/C catalyst.

Therefore, the main conclusion is that the Mo layer could play an important role on catalyst stability and the CO-Pt interactions, increasing the surface area and offering auxiliary catalyst to leave Pt sites free for oxidizing other organic species.

**ACKNOWLEDGEMENTS:** This work was financially supported by the Conacyt Mexico through a graduate scholarship programme.

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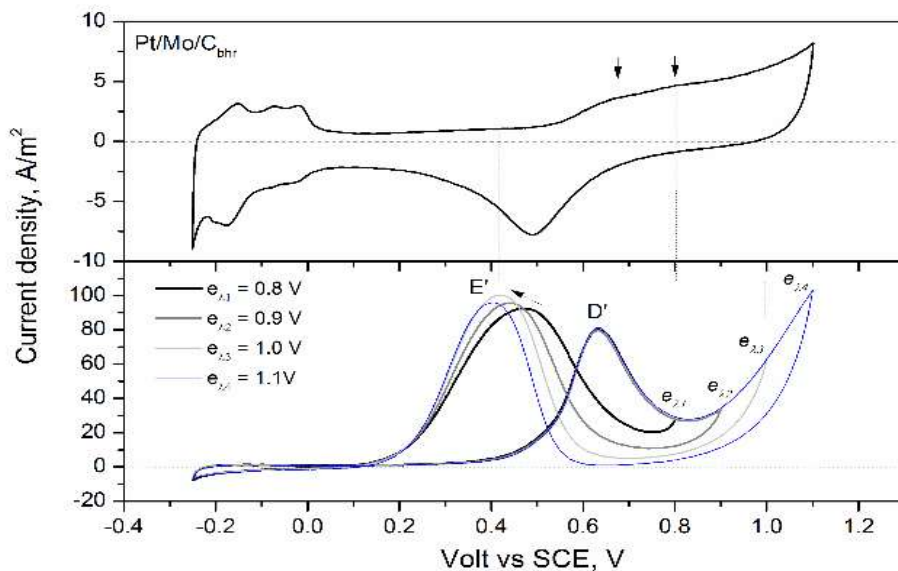


Figure 1. Methanol oxidation voltammetry on PtMo/C, in 1 M methanol, 0.5 M  $H_2SO_4$ , at 50 mV/s, with varying inversion potential  $e_i$  [5].

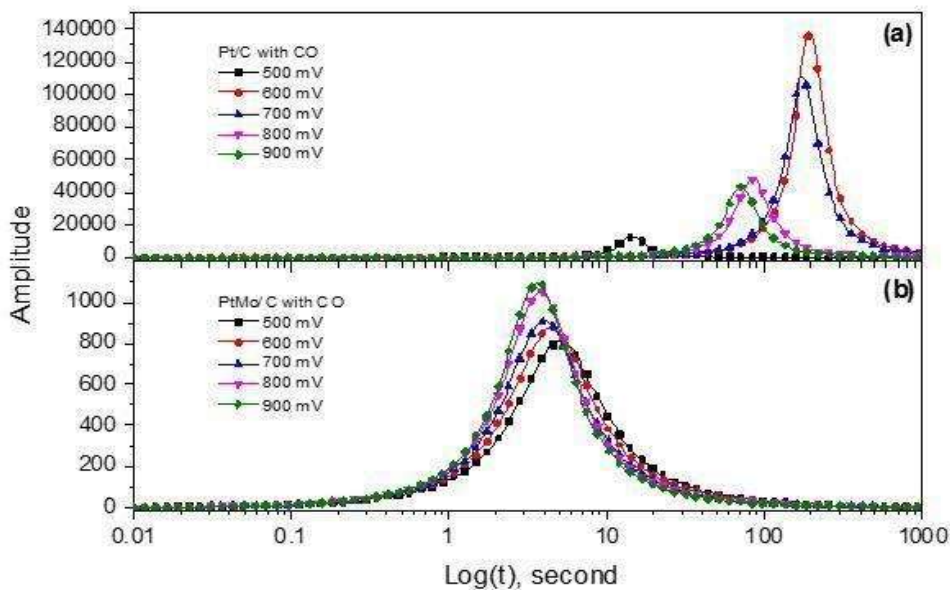


Figure 2. DFRT for Pt/C (a) and PtMo/C (b) with CO species adsorbed on catalyst surface at oxidation over-potentials region.

## Effect of Fouling Development on Key Operational Parameters during Ultrafiltration of Surface Water

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**INTRODUCTION:** Ultrafiltration is one of the low-pressure membrane filtration processes that has stood out as one of the most promising tools, in contrast to conventional techniques for treating wastewater and drinking water[1]. The effect of particle deposition on operational parameters such as decreased permeate flux and increased resistance to filtration, directly influence the structure of membrane fouling. The objective of the present study was to evaluate the effects on the fouling development over key operation parameters during ultrafiltration such as: initial permeate flux, rate of fouling, sustainable flux, specific cake resistance, permeability, % porosity and fractal dimension of cake deposits.

**METHODS:** The methodology described here was executed simultaneously in three different locations. Two of them along the Tena River (Napo, Ecuador), from the Ikiam Regional Amazon University (URAI) to the metropolitan area of Tena: A (pristine area = 1500 PE) and B (medium contamination = 5000 PE). In the Pano River and Tena River, within the metropolitan area of Tena: C (high contamination = 25 000 PE). The environmental water samples (approximately 10 L of fluvial water) were ultrafiltered in an AMICON 8400 cell with a polyethersulfone membrane (PES) of 100, 30 and 10 kDa Molecular Weight Cutoff (MWCO), respectively. The permeate volume was measured in real time, using an electronic scale and recorded through an information acquisition system. The operational parameters: membrane resistance, volumetric permeate flux, specific hydraulic resistance of the cake and porosity of the membrane cake were calculated according to the mathematical approach described by Amjad et al. [2].

**RESULTS:** The resistance of the membrane of 100 kDa, presented values of an order of magnitude lower than the membranes of 30 and 10 kDa

( $3,907 \times 10^{11} \text{ m}^{-1}$ ,  $1,00 \times 10^{12} \text{ m}^{-1}$  and  $1,14 \times 10^{12} \text{ m}^{-1}$  respectively). The transient behavior of the permeate flow shows that the initial permeate flow is significantly higher. Its decrease is more pronounced during the first volume, during the last volume the decrease in flow is less (Figure 1).

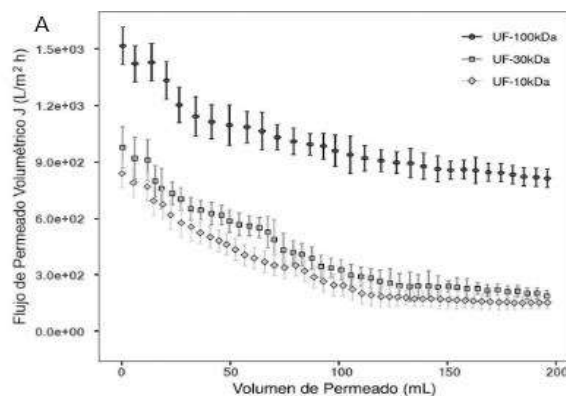


Fig. 1. Transient behavior of the permeate flux at point A.

The transitory behavior of the specific hydraulic resistance of the cake,  $\alpha M$  (Figure 2), shows that at points A and B during the first volumes of permeate  $\alpha M$  increases considerably. During the last volumes of permeate the values tend to remain in a narrower range and present small fluctuations with a slight inclination to decrease, thus  $\alpha M$  increases as the MWCO decreases.

During the first volumes, points A and C show that the porosity of the membrane cake decreases considerably, while in the later volumes it increases slightly. Abrupt changes that are related to re-organization and compaction of deposits are observed in the values of porosity along the UF trials conducted with 10, 30 and 100 kDa as MWCO membranes and surface waters with low and high solid content (Figure 3).



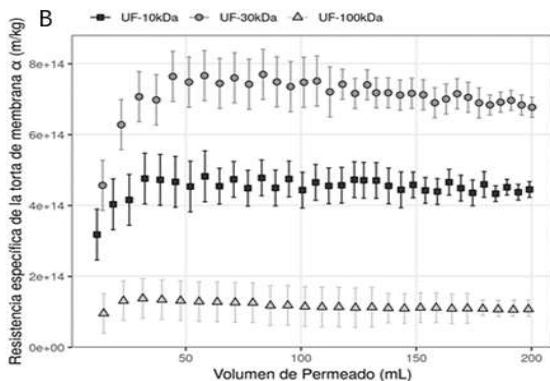


Fig. 2. Transient behavior of the specific hydraulic resistance of the cake ( $\alpha M$ ) of point B.

**DISCUSSION & CONCLUSIONS:** As expected, the 100 kDa MWCO membrane showed a higher initial flux than the 30 and 10 kDa membranes in all tested conditions (Fig. 1). Maximum values of initial flux were 1700, 1800 and 1500 L/m<sup>2</sup>h for the A, B and C sampling points. UF trials using membranes with MWCO of 30 and 10 produced lower permeate flux in the B and C sampling (600-800 and 400-700 L/m<sup>2</sup>h, respectively) than in the sampling site A, which produced between 1000 and 1100 L/m<sup>2</sup>h. This can be rationalized by taking into account the relatively lower amount of total solids, higher apparent surface porosity in the 100 kDa membrane which, in conjunction with its lower membrane resistance, makes it possible to pass a higher permeate flux.

Thus, membranes with a higher MWCO presented a higher permeate volume than membranes with a lower MWCO. In the case of sustainable fluxes (the value of flux at the plateau in Fig. 1), they reach acceptable values (1000- 1500 L/m<sup>2</sup>h) in the case of ultrafiltration using membranes with 100 kDa as MWCO, but limited values (400-600 L/m<sup>2</sup>h) in the trials that used membranes with 30 and 10 kDa as MWCO. During early stages of UF of surface water from sampling points A and B, an exponential increase in specific cake resistance ( $\alpha m$ ) was observed in most of the UF trials.

This behavior is probably caused by the continuous deposition and layering of foulants on the membrane. Water from sampling points B and C showed a decrease in porosity, Amjad et. al., established that the continuous collapse of the cake should lead to a decrease in the overall porosity of the cake [2]. Thus, the porosity of the plugging layer is reduced due to the continuous deposition of solids. From another point of view, in areas with

less contamination (point A), the transition from pore blockage to cake filtration involves the formation of irregular structures or layers of the cake with a certain porosity caused by the continuous deposition of particles

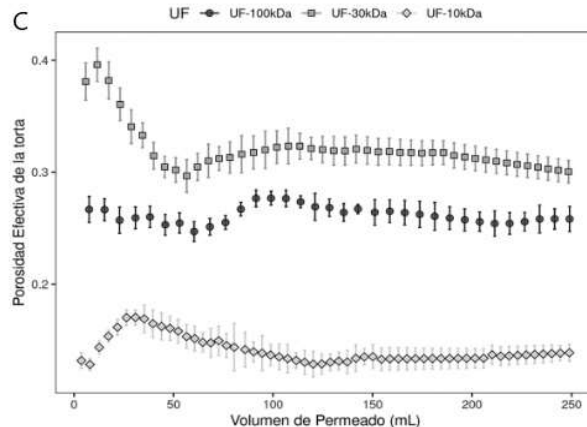


Fig. 3. Evolution of cake porosity as a function of permeate volume (mL) for points A, B and C.

**ACKNOWLEDGEMENTS:** This research was funded by SENESCyT (EULACH T02).

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## Assessment of Coated Membranes in Water Treatment

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**INTRODUCTION:** In today's modern world there still are large number of areas around the globe, where infections and diseases are caused by untreated drinking water. Usually, such problems occur in poor and developing countries or rural areas, where centralized treated tap water supply is not available [1]. One of the approaches for water treatment is membrane ultrafiltration (UF) that can filter most of microorganisms, but unlike reverse osmosis still preserve valuable minerals in drinking water. UF has several advantages over other filtration and pathogen reducing technologies, i.e., low energy consumption, low cost, compactness and possibility of installation on existing water supply infrastructure [2]. The objective of the present study was to investigate the efficacy of PES C10 PDADMAC Layer-by-Layer coated ultrafiltration membrane to remove microbial pollution.

**METHODS:** UF membranes were prepared from a PES having 10 mol-% carboxylic acid groups in the polymer backbone (PES-C10). These membranes were further coated with poly (diallyldimethylammonium chloride) (PDADMAC). The removal efficacy and the filtration performance of the coated UF membrane of PES C10-1-w% PDADMAC was evaluated and compared to the performance of non-coated UF membrane (PES C10).

A pilot-scale crossflow filtration system was used for experiments (Fig. 1). The system was equipped with three equal membrane crossflow cells (RTU Design Factory, Latvia), pump, control unit and data acquisition system. The membrane cell consisted of rectangular plate-and-frame unit, which contained flat sheet membranes placed in a rectangular channel with an active area of 76 cm<sup>2</sup>.



Fig. 1. The photo of experimental pilot-scale crossflow UF membrane filtration system.

The ultrafiltration experiment was conducted at room temperature ( $25 \pm 2$  °C) for 8 days, during which filtration capacities, fouling of membranes were tested, and chemical parameters were measured. The pilot-scale crossflow filtration membrane cells were connected to public drinking water distribution system in Riga (Latvia) and complying to EU regulations (Table 1) [3]. The feed water total flow rate was set at 20 l/h and monitored by a floating disc rotameter (Sho-Rate 1350G, Brooks Instrument, USA). The average operating pressure was  $3.4 \pm 0.1$  bar at the inflow of membrane cells. The retentate flow rate and permeate flux was recorded every day using a graduated cylinder (0.1 L) and timer. Both permeate and retentate were discharged directly to sewer.

Table 1. Permissible limits of drinking water parameters

Parameter	Value
Coliform bacteria	0 /100 mL
pH	$\geq 6.5$ and $\leq 9.5$
Conductivity	2 500 $\mu\text{S}/\text{cm}$
Permanganate index	5.0 mg/L O <sub>2</sub>

**RESULTS:** The total flow rate (retentate and permeate) decreased rapidly for each cell during every day of the experiment. The main reason for this was fouling of the feed side membrane spacers, which slowed retentate discharge for both coated and uncoated membranes. In order to provide some retentate outflow in cells and similar total flow rates each day, retentate discharge was increased to reach the total flow of 20 l/h every working day. The permeate flux of all membranes was calculated at known similar conditions and is shown in Fig. 2.

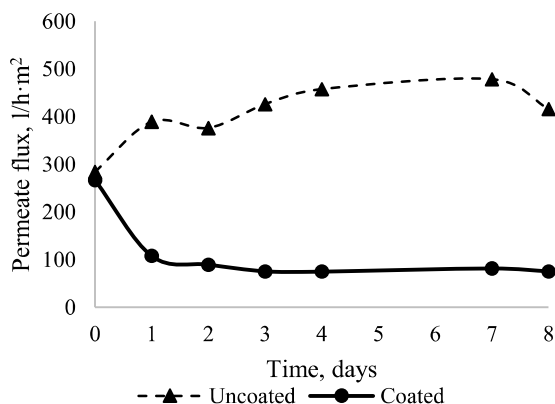


Fig. 2. Changes of permeate flux during the UF process under  $TMP = 0.34 \text{ MPa}$  and  $Q = 20 \text{ dm}^3/\text{h}$ .

The results showed that the flux of coated membranes decreased rapidly on the first day, later decrease slowed down. Average flux of coated membrane stabilizes and varies around practically acceptable 80 l/h·m<sup>2</sup> after two days of use. The uncoated control membrane showed higher flux (up to 479 l/h·m<sup>2</sup>) on next days of experiment.

During the ultrafiltration process no significant changes in water parameters between the permeate and tap water samples were detected. The average pH values before and after treatment were  $6.9 \pm 0.2$ , conductivity –  $519 \pm 65 \mu\text{S}/\text{cm}$  and RedOx potential values were  $204 \pm 38 \text{ mV}$ . The average temperature of all samples –  $22.4 \pm 1.2 \text{ }^\circ\text{C}$ .

It can be explained, that the coating, probably, does not dissolve in water or detach from membrane surface, as well it does not affect water quality parameters.

**DISCUSSION & CONCLUSIONS:** The coated membrane showed acceptable flux rate values, which are competitive to commercial UF membranes.

However, further research is needed in order to investigate the potential removal of various species of pathogens.

Due to the high flux rate of uncoated membrane the experiment should be repeated in order to confirm the accuracy of the obtained data.

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## The Set-up of a Photocatalytic Tubular Ceramic Membrane Reactor

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**INTRODUCTION:** Photocatalytic membrane reactors (PMR) have proven to be a promising technology for water purification and disinfection. The coupling of two processes, photocatalysis and membrane separation, in the same unit has allowed improving the removal and degradation of pollutants. Moreover, this has made it possible to improve the antifouling properties and permeability of the membrane, as well as, the stability of the photocatalyst. However, there are constraints for the development of a PMR that must be addressed to optimize the operations during the water treatment. Therefore, in this work, we report the set-up of a lab-scale photocatalytic tubular ceramic membrane reactor for water treatment.

**METHODS:** The design of the PMR was made taking into account various factors, such as the membrane characteristics, the photoactive surface, the properties of the photocatalyst, and the operating conditions.

**RESULTS:** A lab-scale photocatalytic photoreactor was made out of polymethyl methacrylate (PMMA) and has a total area of 2.16 m<sup>2</sup>, as shown in Figure 1a. The dimensions of the photoreactor are based on the configuration and size of the membrane module. A Titanium tubular ceramic membrane (300 KD, 1 channel, 0.004 m<sup>2</sup>, 10 mm OD x 250 mm, 1/Pk) was used in this work due to some advantages, such as the cross-flow filtration mode and high flux rates which reduces the fouling rate and pore blocking. The permeate side of the membrane was coated with a visible-light-driven photocatalyst (i.e., BiOI). Based on this, the membrane module was made out of PMMA to allow the activation of the photoactive surface, as shown in Figure 1b. In addition, as shown in Figure 1a, four 10W white light LED lamps were positioned surrounding the membrane and at an optimal distance in order to ensure a homogeneous irradiance of the outer surface of the membrane. Moreover, two fans were placed to maintain a constant inner temperature of the reactor and, thereby, the temperature of the solution in close

contact with the membrane surface was kept in ambient condition.

On the other hand, as shown in Figure 2, a diaphragm pump was connected to the feed tank for pumping the contaminated water to the membrane module. A flowmeter was positioned on the feed stream to measure the flux in a set pressure. A valve was placed on the retentate stream to control the pressure of the feed stream and, thereby, the transmembrane pressure (TMP). In order to measure both pressures, a pressure gauge and pressure transducer were installed on the feed and retentate side of the membrane unit, respectively. An electronic mass balance was placed at the end of the permeate stream to measure the permeate flux. Both the electronic mass balance and pressure transducer were interfaced with a data acquisition system LabView for taking data in real-time.

**DISCUSSION & CONCLUSIONS:** It was possible to build up a low-cost PMR, which could be used to study the efficiency of photocatalytic tubular ceramic membranes in the removal and degradation of contaminants of emerging concern.

**ACKNOWLEDGEMENTS:** This work was supported by the undergrad research program BiOX of the European project Hi-Water. The installation of the photocatalytic membrane reactor was performed at the Universidad Regional Amazónica Ikiam. Thanks to SENESCYT for having funded the project.

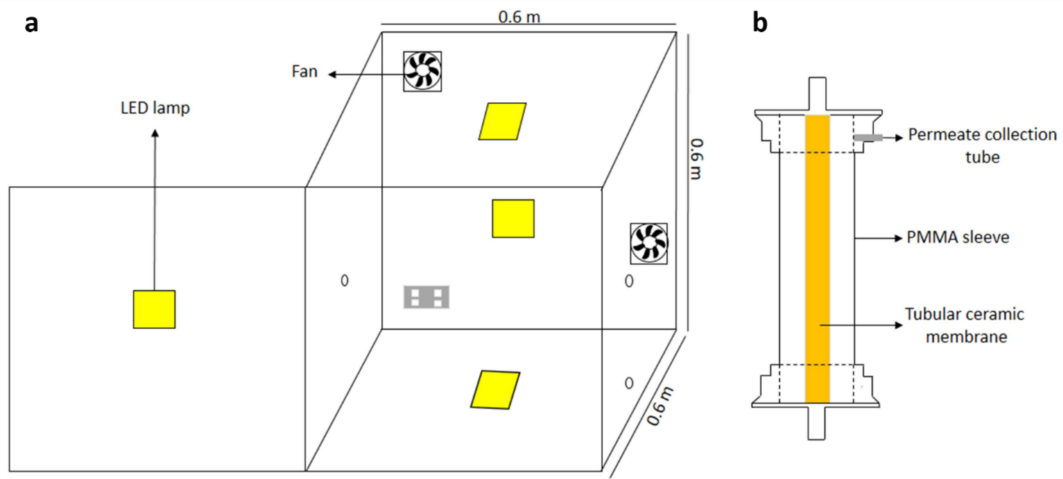


Fig 1. Design of the photoreactor for photocatalytic water treatment (a) and the transparent membrane module (b).

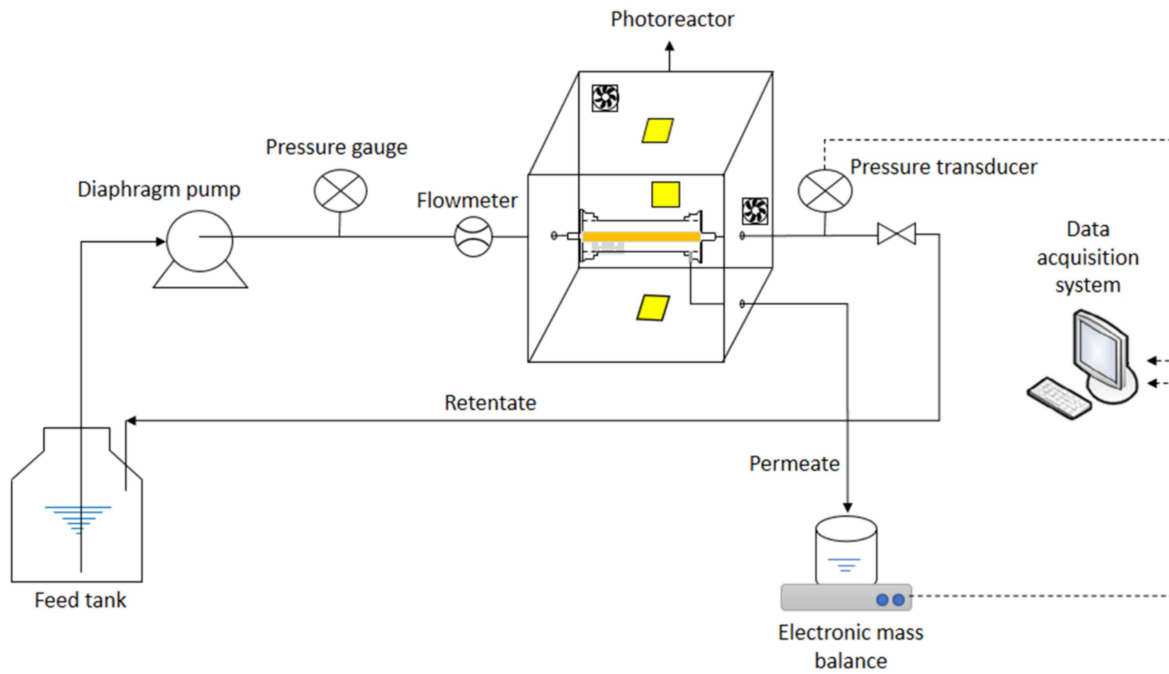


Fig. 2. Schematic diagram of the photocatalytic membrane filtration treatment system.

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