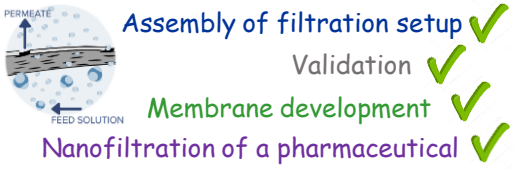
SZAKMAI ZÁRÓJELENTÉS / FINAL REPORT

NKFI-KH/126498

Project information

Title: Improvement of the selective layer of composite membranes by graphene oxide
PI: Dr Tamas Szabo
Duration: 2017-12-01 to 2020-02-29 (27 months)



Introduction

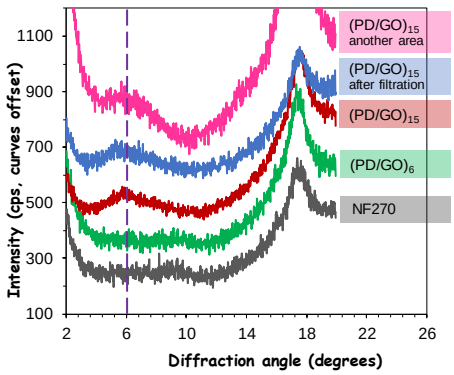
The present project focused on the development of the active layers of polymer-based filtration membranes by using graphene oxide nanoflakes as surface modifiers. In accordance with the original research plan, the work was divided into two separate directions. The first direction was the formulation of thicker, paper-like layers of micrometer-range cross-section using controlled deposition of particles from aqueous graphene oxide dispersions. Pristine and pillared derivatives were then envisioned to constitute thin films consisting a torturous path of different channel widths to achieve selective nanofiltration of model pollutant molecules of pharmaceuticals.

Regarding the second direction, we aimed to deposit ultrathin hybrid multilayers by the so-called layer-by-layer self-assembly technique, which relies on the charge regulated deposition of alternating assemblies of colloidal particle or macromolecular monolayers. Since GO consists of elementary lamellae of negative surface charge, we chose polycations for sticking the multilayered structure. The formed intercalation structures were characterized, and their interlayer expansion was precisely determined.

Finally, our goal was also to establish a new membrane laboratory at the university of Szeged, with a prototype device that was successfully assembled within the frame of the project. We have used this cross-flow filtration setup for the determination of the characteristic selectivity and flux values of the composite membranes in the characteristic pressure range of nanofiltration under dynamic cross-flow conditions.

Progress of the research

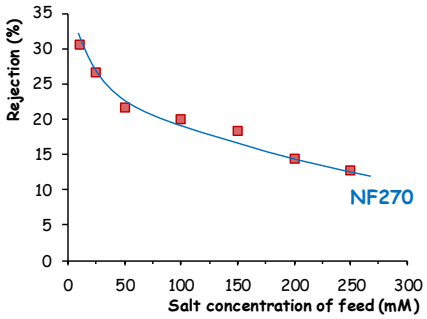
Commercially available PAM membranes were purchased and used throughout the project. These and several well-characterized membranes without GO coating, originating from the En.sur.E water lab of Politecnico di Torino were also used as reference. LbL self-assembled graphene oxide/cationic polyelectrolyte films were then deposited on the membrane surfaces. The outermost layer facing the solution was negatively charged in order to hinder the potential attachment of negatively charged foulants. Preliminary experiments on vacuum filtration deposition of GO papers were performed, but these were mostly related to the second year. Pure water and saline solutions were used to prepare processable GO dispersions. A paper related to their colloidal stability was published (*Szabo et al. Carbon, 2020*). Layer-by-layer coatings were then characterized by optical microscopy and contact angle measurements. The latter proved that the both the pristine polyamide, and the multilayer-coated membrane surfaces are very well wettable (contact angle around 0°) by water possibly due to the high intrinsic roughness.



X-ray diffractograms (*figure to the left*) of poly(diallyl-dimethylammonium)chloride/GO multilayers on quartz substrates revealed an ordered intercalation structure characterized by the expansion of the interlayer spacing from ca. 0.6 to 0.8-0.9 nm in air-dry state. Selected

specimens of such ultrathin layers were found to be responsive to water vapors but the correlation of the film structure and the factors determining the extent of swelling is still unclear. However, we could collect valuable surface zeta potential data at the Politecnico di Torino of the LbL GO films using their flat-sheet membrane samples. Part of the MSc thesis of an undergraduate student (*M. Hancsárik*) was about the partial hydrophobization of graphite oxides with surfactants and their swelling was also monitored by XRD. A study on the comparison of GO with humic acids is published (*Tombacz et al. J Mol Liq,* 2020).

Regarding the most fundamental part of the whole project, we managed to purchase parts and assemble a cross-flow membrane filtration apparatus. It took 9-10 months until all components have been purchased and successfully integrated into the setup by the undergraduate student, handymen and the project leader. We consider it a success, since a similar setup was built at the PoliTorino roughly for the same time span by engineers. The student (*M Hancsárik*) also helped in the knowledge transfer of nanofiltration by spending 2 months in the Italian laboratory. To test the nanofiltration performance and validate the setup in Szeged, several salt solutions ($MgSO_4$, $MgCl_2$ and NaCl) were filtered by three types of commercial PAM membranes at applied hydraulic pressures between 10-20 bars. Measurement of the water flux and of the concentration of solutes in the permeate solution allowed the calculation of the intrinsic membrane parameters, which showed an excellent agreement with literature values including those found by the Italian experts (see e.g. *the figure to the left*, on the concentration dependence of the rejection for NaCl solutions on NF270 PAM membrane). This confirms that (1) the setup is correctly built, (2) the base membranes are of good quality and (3) the experimental protocol is correct and the team in Szeged is capable to obtain reliable data for membrane performance.



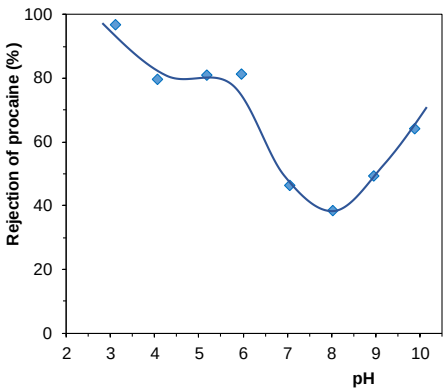
Since the degree of oxidation is expected to influence both the surface chemistry, surface polarity and morphology of GO flakes, and thus the interaction of GO surfaces with water and the solutes, we were producing a series of samples of different degrees of oxidation at the beginning of the second year of the project (a paper on their optical properties is submitted for publication). Contrary to our expectations, the ultrathin coatings of GO were less prone to cracks and mechanical damage than the paper-like coatings. This was evidenced by the good reproducibility of rejection (around 1%) and flux (less than 20%) values. Layer-by-layer deposition of GO particles with both poly(diallyldimethylammonium) chloride, a polyelectrolyte with constant line charge density, and protamine sulphate, a smaller positively charged polypeptide, were also performed. For the former, the layer construction process was varied so that between 1 up to 10-15 bilayers would constitute the ultrathin coating on the active side of the PAM membranes. We also found that highly aged protamine and GO samples (samples stored for years) afforded multilayers of similar structure as fresh samples.

Regarding structural characterization, samples were delivered by the PI to one of the most advanced electron microscopy of Central-East Europe (Politecnica Bucharest), where membrane surfaces were characterized by SEM, and high magnification images of the GO platelets were also recorded by STEM SEM-STEM-ZC-EDX simultaneous co-localized measurements with the aid of a PhD student (O. Lazar). The delamination could only be studied qualitatively at this point, because the membranes subjected to the cross-flow feed streams are not readily measured by UV-DR spectroscopy. As of follow-up of this project we will aim at the construction of a cell that allows in situ monitoring of the optical film thickness.

A good advancement and great achievements can be reported regarding the membrane performance studies of a model pharmaceutical compound found in aquatic systems. A common drug, procaine hydrochloride, a benzoic acid derivative with local anesthetic and antiarrhythmic properties we chosen for nanofiltration tests. Firstly, we needed to develop a proper protocol for

the correct quantitative analysis of the procaine contents of aqueous feed and permeate solutions because conductometry is inadequate for analysis at the relevant concentration range. However, UV-photometry is capable for providing data for evaluating the membrane rejection in case the pH-dependent spectral features of the compound are taken into account. The assessment of the long-term pH-stability of the compound is still under progress, but it can be stated that diluted (below millimolar) and more concentrated (tens of millimolar) solutions are very stable chemically, while the compound slowly decomposes already in moderately acidic and alkaline conditions.

More than 100, day-long measurements were performed on self-assembled PDDA/GO multilayers by the cross-flow filtration apparatus assembled in the first year of the project, and the measurement of the water flux and of the concentration of procaine in the permeate solution let us calculate the intrinsic membrane parameters. Most remarkably, the rejection found for the bare NF270 nanofiltration membranes were typically around 40%, which increased up to around 56% using the aforementioned multilayers containing 10 bilayers of the polyelectrolyte/graphene oxide composite structure. This is remarkable result considering that the permeance of the membrane have not shown a simultaneous magnitude-scale decrease, as often found for surface-modified NF membranes. The dependence of intrinsic membrane parameters on the bilayer number was also determined and found to saturate above bilayer numbers of 6. Finally, we have very promising preliminary results regarding the nanofiltration performance of graphene-oxide modified LbL coatings, which employ protamine sulphate instead of the synthetic high-molecular weight PDDA. One of the last experiments performed with the model drug solution was the characterization of the huge pH dependence of its rejection (*figure to the right*).



Problems emerged during the research and their mitigation

The purchase of proper PAM membranes took unusually long time because they are sold as an integral part of filtration elements. We found that the base membranes are hardly removable from these items without significant damage, making them unreliable for further studies. We found only one company in the USA which sells bare flat-sheet nanofiltration membranes. Their purchase posed unexpected administrative problems as well, but after 2 months we managed to purchase them. Meanwhile, we performed studies on the deposition of LbL films on quartz substrates.

In general, we had troubles to deposit homogeneous paper-like membranes with the envisioned spacers. We can still exert effort to obtain uniform and stable films by co-filtration. However, it seems that the layer-by-layer process is far more efficient for the preparation of uniform coatings on commercial polyamide membranes, and we took more action into this direction. Contrary to our expectations, the ultrathin coatings were less prone to cracks and mechanical damage than the paper-like coatings. This was evidenced by the good reproducibility of rejection (around 1%) and flux (less than 20%) values.

Changes in the personnel and their influence on the progress of research

Considering the relatively short time of the project, there was a significant rotation in the staff responsible for the experimental work. We planned to employ a researcher in full time, for the duration of two years. Instead, we managed to employ only one researcher for a year, and another for 6 months. Therefore, we needed to rely heavily on the contribution of students. Unfortunately, all of them left the group after graduation. The fact that all participants needed to be trained and worked for relatively short time greatly hindered the progress of research. Despite this, we consider the project as successful, based on the achievement as detailed in the next point.

Achievements of the project

A) Material achievements

The financial support allowed the purchase of equipment which were not only inevitable for the successful realization of experiments but enabled the establishment of the core of a membrane filtration laboratory at the Institute of Chemistry, University of Szeged. Additionally, the support enabled to purchase a gel electrophoresis setup, which is useful for the evaluation of preliminary antifouling tests, and for protein-related studies. The rest of investments enabled to upgrade a part of the laboratory and computer infrastructure.

B) Intellectual/scientific achievements

Regarding the scientific benefit of the project, we first need to mention that a new knowledge base was established in our laboratory on membrane filtration technology. The PI and, of equal importance, the participating young researchers and students gained basic knowledge in this completely new field. Training of students, especially for M. Hancsárik in the expert foreign partner's laboratory was significant. The main hypotheses were tested and were partially confirmed, but we also revealed some surprising scientific facts. In more detail, we (1) demonstrated for the first time that LbL multilayers can be deposited on commercial PAM membranes, and they have considerable, although not complete physical stability (largely preserved film structure after long filtration runs) under dynamic cross-flow conditions, without chemical grafting of GO sheets on the bare membrane surface. We have also shown that (2) the rejection of the surface modified membranes is greater than that of the pristine membranes when a common, cationic pharmaceutical molecule is removed from aqueous solution. These basic findings open the way for investigating a great diversity of other interesting scientific questions, e.g. regarding the pH dependence of the membrane performance parameters, or the generic features of rejection enhancement. However, we also found that the expected easy construction of multilayered GO papers with the spacers envisioned is more challenging and was not yet solved during the project.

C) Publications

According to the work plan, we expected the publication of 5 research papers and 5 conference contributions. We failed to publish all results of the project within the time frame of the project and until the submission of the final report. With the publication of the remaining results, the expectation regarding the number of scientific publications will be fulfilled. We have already exceeded the number of foreseen conference contributions.

	Dissemination (total)	*Dissemination (item/FTE/year)*	*Quality (SJR / Impact Factor)*
Papers published	2	0.53	D1 / 7.466 Q1 / 4.561
Papers under review	1	0.27	D1 / 4.309
Manuscripts under prep.[1]	2	0.53	Q1 expected
PAPERS SUBTOTAL	5	1.33	≥ Q1
Poster presentations			
intl. conf. abroad	2	0.53	N/A
intl. conf. Hungary	3	0.8	best poster prize
POSTERS SUBTOTAL	5	1.33	

[1] We consider „manuscripts under preparation", which already have full dataset (>95% of data are already collected), the manuscript was conceptualized, the experimental part is written and at least parts of display items are prepared.

	Dissemination (total)	*Dissemination (item/FTE/year)*	*Quality (SJR / Impact Factor)*
Oral presentations			
intl. conf. abroad	2	0.53	regular
intl. conf. Hungary	4	1.07	regular
ORAL PRES. SUBTOTAL	6	1.6	
Dissertations[2]			
B.Sc. theses	2		N/A
M.Sc. theses	1		N/A
THESES SUBTOTAL	3		

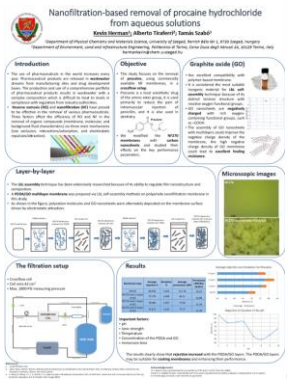
D) Other achievements

The project resulted in the extension of the international collaboration potential of the PI's laboratory. The PI undertook a short-term scientific mission in the advanced structural characterization laboratory of Prof. M. Enachescu, at the Politechnica Bucharest, Romania. Likewise, existing ties with partner laboratories at Umeå University, Sweden and Politecnico di Torino, Italy, were strengthened.

The project funding allowed us to invite the former postdoc supervisor of the PI, who is a Professor Emeritus at the Catholic University of Leuven, Belgium. The guest professor gave a keynote and an invited lecture at a local international conference and one at the meeting of the local academic committee. The PI thinks that the local materials science community and the young scientist generation benefited from the attendance of these talks on zeolites and functional clay mineral films.

The student Martin Hancsárik completed a two-months professional practice in the en.sur.e Water Lab at the Politechnic University of Turin. Although this training was financially supported by the Erasmus+ programme, this visit was beneficial for the progression of the present project and for the professional development of a young chemist.

Another remarkable achievement is the "Best student poster" prize of K. Herman from "PERMEA 2019" - Membrane Conference of Visegrad Countries. This congress is a biannual meeting of the researchers who are expert in the field of membrane science and technology. Considering the fact that we are newcomers in membrane science with only around two years of experience at the closure of this project, we think that this prize is a great acknowledgement of our initial studies, and provides realistic hope that the two unfinished manuscripts are publishable in high-rank journals.



Finally, the training aspects of the project were noteworthy. Upon the two years, seven undergraduate students (N. Alsharif, Á. Dernovics, K. Herman, M. Hancsárik MSc students; V. Konkoly, M. Gregus, P. Gyenes BSc students) have participated in the research programme and gained important professional skills. A total of 3 theses are in relation of this project; two students will defend their BSc theses shortly after the project closure, in 2020 May.

[2] Performance indicators (items/FTE/year) were not calculated for Student Theses because students do not bear FTE in the project.

Progress of the project, milestones

- **2017 December: project kick-off**
- 2018 January: N. Alsharif progresses with LbL deposition and later aids other students to master the technique. M. Hancsárik participates as MSc student
- 2018 February to May: Á. Dernovics MSc student joins the lab
- 2018 March to April: M. Hancsárik spends 2 months in the En.Sur.E water lab at the Politecnico di Torino in the frame of Erasmus+ professional practice
- 2018 May: T. Szabo and Á. Dernovics participates at the 11th Conference on Colloid Chemistry" conference. T. Szabo contributes also as the secretary of the conference.
- 2018 Aug: assembly of the base of the membrane filtration setup is finalized by the Workshop team, M. Hancsárik, and T. Szabo
- 2018 Sept: K. Herman joins the group as full-time researcher
- 2018 Oct: The filtration setup is complete.
- 2018 Oct: T. Szabo oral presentation at the 8th SIWAN conference. R. Schoonheydt (KULeuven, Belgium) is a guest professor of the group.
- 2018 Nov. membranes arrived. K. Herman makes successful filtration experiments and validates the setup with the PI
- **2018 December: start-up of the second year of the project**
- 2019 February: V. Konkoly is trained for LbL deposition
- 2019 March: A. M. Butt joins the research group as full-time researcher
- 2019 June: T. Szabó and K. S. Herman participates at the PCBCI conference in Eger.
- 2019 June-July: T. Szabó visits the Politecnica Bucharest (group of prof M. Enachescu) in the frame of a COST Short-term scientific exchange program. Some membrane surfaces are characterized by scanning electron microscopy
- 2019 July: T. Szabó attends the World Carbon 2019 conference and its Satellite Workshop ("Beyond adsorption II") both held in the United States. He gives two oral presentations
- 2019 August: K. Herman and T. Szabó is at the Permea 2019 (Membrane Conference of the Visegrad countries). The PI gave an oral presentation on membrane filtration by LbL assemblies, while K. Herman exhibits a poster by which one of the two Best Student Poster prizes is awarded to him.
- 2019 August: zeta potential test measurements of bare and modified membranes are kindly allowed by Anton Paar, using their SurPass TM 3 Instrument
- 2019 September: A. M. Butt and K. S. Herman leaves the group. Filtration tests are affiliated to an undergraduate student (P. Gyenes)
- 2019 October: Arrival and instalment of the new SDS PAGE apparatus
- 2019 November: V. Konkoly completes pH-controlled deposition measurements for LbL assemblies.
- 2020 February: P Gyenes completes nanofiltration experiments with a pharmaceutical using LbL multilayer-modified membranes. BSc students start writing their theses.
- **2020 March: the project is terminated**

Szeged, 14th April, 2020

Tamas Szabo, PhD
Principal Investigator

National Research, Development and Innovation Office Hungary
PROGRAM FINANCED FROM THE NRDI FUND
MOMENTUM OF INNOVATION