COMISIÓN NACIONAL DE INVESTIGACION CIENTÍFICA Y TECNOLÓGICA

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Nº PROYECTO : 3140632
DURACIÓN : 3 años
AÑO ETAPA : 2016

TÍTULO PROYECTO : OSMOTIC PRE-CONCENTRATION AS A STRATEGY FOR EFFICIENT ANAEROBIC TREATMENT OF SEWAGE

DISCIPLINA PRINCIPAL : INGENIERIA SANITARIA
GRUPO DE ESTUDIO : INGENIERIA 1
INVESTIGADOR(A) RESPONSABLE : ISAAC ELIECER REYES CANIUPAN
DIRECCIÓN :
COMUNA :
CIUDAD : TEMUCO
REGIÓN : IX REGION

FONDO NACIONAL DE DESARROLLO CIENTIFICO Y TECNOLOGICO (FONDECYT)
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## OBJETIVOS
Cumplimiento de los Objetivos planteados en la etapa final, o pendientes de cumplir. Recuerde que en esta sección debe referirse a objetivos desarrollados, NO listar actividades desarrolladas.

<table>
<thead>
<tr>
<th>Nº</th>
<th>OBJETIVOS</th>
<th>CUMPLIMIENTO</th>
<th>FUNDAMENTO</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>To analyse the osmotic potential of sewage and its components.</td>
<td>TOTAL</td>
<td>The composition of sewage treatment plant from Temuco was analyzed by standard methods. An ion balance was carried out to quantify the osmotic potential contribution of the ions present in sewage. The latter was confirmed by osmometry. All previous analyzes were performed to crude sewage and prefiltered sewage to know the contribution of suspended solids and soluble matter on osmotic potential.</td>
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<td>2</td>
<td>To study the use of FO for the concentration of sewage.</td>
<td>TOTAL</td>
<td>A first prototype was manufactured for forward osmosis (FO) experimentation. Three types of FO membranes were studied. The results included permeate flux, sewage concentration percentages and analysis of fouling in the membrane with better performance. A second larger-scale prototype was manufactured for FO experimentation. Different assays of sewage concentration using at least 5 liters as feed were performed for 4 days.</td>
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<td></td>
<td></td>
<td>TOTAL</td>
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<tr>
<td>3</td>
<td>To design an osmotic draw solution based on nanoparticles capable of providing the osmotic potential required for sewage concentration</td>
<td>The osmotic potential of different concentrations of nanoparticles based on silver nitrate (AgNO₃) were evaluated in order to use them in a concentration process of municipal wastewater by forward osmosis. The results showed that nanoparticles solutions have low osmotic potential (11 and 12 atm) compared to seawater (26 ATM). Thus, the synthesis of nanoparticles might need 3 times higher concentrations, representing a complex job and a high economic cost of synthesis. This is logical because the osmotic pressure is a colligative property of the solutions, that is, it depends only on the concentration, so must propose nanosuspensions according to the ease with which these can be synthesized. In addition, purity and stability must be considered. Use of nanoparticles as osmotic solution in the wastewater concentration forward osmosis is discarded due to the complexity of achieving high concentrations, it was concluded.</td>
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</tr>
<tr>
<td>4</td>
<td>To evaluate a recover regeneration strategy of draw solution and operating conditions of the RS step.</td>
<td>Reverse osmosis has been studied as a recover regeneration strategy of draw solution. Preliminary studies in a closed-loop FO/RO system and using NaCl and MgCl₂ as draw solution showed that the rejection of trace organic solutes (TOS) by FO membrane is less than RO membrane in closed-loop FO/RO. Therefore, an accumulation of TOS in closed-loop was estimated. A high RO rejection was found. However, the kind of DS would affect the FO rejection for neutral TOS. A FO/RO system will be considered in future. The FO/RO strategy could be the most appropriate in cases where seawater no available, as a wastewater treatment plant. In coastal areas of Chile where there is free access to seawater, the concentration process wastewater could occur without the need to concentrate the osmotic solution. Furthermore the residual discharge water would dilute or lower NaCl concentration sea.</td>
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<td>5</td>
<td>To evaluate the right technology for anaerobic treatment of concentrated sewage.</td>
<td>Measurements of methanogenic potential of sewage and prefiltered have been made. A inhibition due to NaCl from reverse flux and other components in the sewage is currently studying. An UASB reactor with concentrated sewage as feed will be studied in the near future.</td>
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</table>

Otro(s) aspecto(s) que Ud. considere importante(s) en la evaluación del cumplimiento de objetivos planteados en la propuesta original o en las modificaciones autorizadas por los Consejos.
RESULTS OBTAINED:
For each specific goal, describe or summarize the results obtained. Relate each one to work already published and/or manuscripts submitted. In the Annex section include additional information deemed pertinent and relevant to the evaluation process. The maximum length for this section is 5 pages. (Arial or Verdana, font size 10).

Specific objective 1): To analyse the osmotic potential of sewage and its components.
Among the physicochemical parameters measured in total-WWTP a total chemical oxygen demand of 477.4 mg/L, a concentration of total solids of 0.69 g/L, a concentration of 40.27 mg/L of NH₄⁺, a concentration of carbohydrates of 54.69 mg/L, 340 mg/L for protein, a conductivity of 0,90 mS/cm and a pH of 6,99 were quantified. The total-WWTP was fractionated with ultrafiltration membranes to quantify the contribution of the ions in the osmotic potential of the wastewater. Values of 0.023 (1kDa), 0.026 (3kDa), 0.026 (5kDa), 0.027 (10kDa), 0.028 (30kDa), 0.029 (100 kDa) Osmol/Kg H₂O were measurement in different fractions by a cryoscopic osmometer. The ionic composition of total- and filtered-WWTP (0.22 µm) showed that ion concentrations of both fractions does not vary greatly except for aluminum and chloride may due to samples were taken at different summer period (summer and fall). The osmotic potential calculated for total- and filtered-WWTP were 0.022 Osmol/Kg H₂O and 0.015 Osmol/Kg H₂O, respectively. These values fit very well with the observed fractionation by osmometer analysis. The contribution of each ion in the osmotic potential was studied for total- and filtered-WWTP. The results showed that inorganic carbon (IC) provides between 35-40% of the osmotic potential. Then, total-WWTP mainly comprise, among sodium chloride, aluminum, ammonium, and IC with 89%. For filtered-WWTP are chlorides, sodium, ammonium, and IC with 88% of the total osmotic potential. The results of this specific objective are part of the first publication in Chemical Engineering Journal 306 (2016).

Specific objective 2): To study the use of FO for the concentration of sewage.
An prototype was manufactured for forward osmosis (FO) experimentation. Three types of FO membranes were studied. The results included permeate flux, sewage concentration percentages and analysis of fouling in the membrane with better performance. Assays with TFC-ES membrane achieved higher fluxes using UPW how feed solution. Also, the effect of suspended solids on the feed was assessed using total and filtered-WWTP as feed, the results not showing significant differences of performances within them.

Continuous concentration assays were carried out with t.WWTP and f.WWTP using NaCl as osmotic solute, maintaining a concentration of 35g/L during assay. A total feed of 500 mL in each module was used. Water flux (Jw) and reverse salt flux (Js) were registered over a period of 10 hours. The assays results indicated that initial fouling not affect significantly the concentration process of WWTP during short periods of time. Therefore, continuously concentration assay with sufficient agitation for resuspend settleable solids were assessed. The results show that for the same stirring condition and operating time (40-48 hrs) Jw of t.WWTP (Jw-t) and Jw of f.WWTP (Jw-f) show a decreasing trend similar but Jw-f is slightly larger than Jw-t. The results for Js of f.WWTP (Js-f) and Js of f.WWTP (Js-f) showed an increase in time but without significant differences between them. Indeed, both experiments show increased Js and a decrease of Jw past 20 hours of operation, this is mainly due to fouling. In this context, migration unwanted salts becomes relevant in WWTP preconcentration by FO for a subsequent AD. Because Na⁺ and Cl⁻ are inhibitors of methanogenesis, as well as also K⁺, Ca²⁺ and Mg²⁺ present in seawater, if seawater is used as osmotic solute. Therefore, to maintain a low Js, maintain Jw as high as possible, is necessary. Because Jw/Js ratio is inversely proportional.

The concentration results of total-WWTP and filtered-WWTP showed a percentage increase of various components of WWTP. The most important percent increments in total-filtered WWTP was COD (250%-300%), total solids (1850%-142%), proteins (741%-971%), Na⁺ (6500%-4500%) and Cl⁻ (9900%-5900%), the conductivity increment with salt concentration increment. The NH₄⁺ decreases because this permeate TFC membrane from feed solution to DS in a (-39%) and (-60%). The results of this specific objective are part of the first publication in Chemical Engineering Journal 306 (2016).

Composition of fouling in continuous trials with TFC membrane.
Samples of membrane were analysed by SEM microscopy, in order to observe membrane fouling, promoted by sewage and filtered-sewage concentration. Comparison of images revealed that fouling layer formed during operation with filtered-sewage was more compact, homogeneous and
thin (approximately 5 µm) than that observed in the membrane from sewage concentration (approximately 15 µm). Thicker fouling layer is expected to promote a higher concentration-polarization effect, reducing water flux. Lower water flux will reduce dilution of draw solution on the vicinity of the membrane (draw solution side), enhancing salt flux. This would result in an increase of the relation $J_s/J_w$, as was indeed observed. The formation of fouling layers may be at some extent controlled by increasing shear over membrane surface, by promoting turbulence. A high cross-flow velocity is a common way to achieve such goal (Lutchmiah et al. 2014).

A semi-quantitative analysis of the elemental chemical composition of the fouling layers was performed by energy dispersive X-ray spectroscopy. Results (Table 1) show that fouling layers were mainly formed by carbon, oxygen and nitrogen. High content of nitrogen, especially for the case of filtered sewage, indicates a high content of proteins. Accumulation of protein over membrane surface may been enhanced by the presence of ions coming from the draw solution, which may have reduced protein solubility by salting out effect (Lee et al. 2010; Salis et al. 2011). Indeed, a relevant presence of sodium in the fouling layer (2-3 wt %). Moreover, the application of low levels of surface shear may have enabled the stabilization and growth of the fouling layer (Lee et al. 2010). The results of this specific objective are part of the first publication in Chemical Engineering Journal 306 (2016).

### Table 1. TFC-ES semi-quantitative analysis of the elemental chemical composition of fouling layers formed over FO membrane. Analysis considered 6 locations on the fouling layer that were analysed independently. Average values are presented along with standard deviation (between parentheses).

<table>
<thead>
<tr>
<th></th>
<th>Sewage wt %</th>
<th>Filtered-sewage wt %</th>
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<tbody>
<tr>
<td>C</td>
<td>53.8 (2.7)</td>
<td>60.5 (3.4)</td>
</tr>
<tr>
<td>O</td>
<td>34.5 (2.4)</td>
<td>27.5 (1.8)</td>
</tr>
<tr>
<td>N</td>
<td>9.66 (0.94)</td>
<td>12.7 (0.85)</td>
</tr>
<tr>
<td>Na</td>
<td>2.79 (0.18)</td>
<td>3.74 (0.3)</td>
</tr>
<tr>
<td>Al</td>
<td>0.82 (0.27)</td>
<td>-</td>
</tr>
<tr>
<td>P</td>
<td>1.45 (0.08)</td>
<td>1.23 (0.16)</td>
</tr>
<tr>
<td>S</td>
<td>1.15 (0.09)</td>
<td>3.79 (0.32)</td>
</tr>
<tr>
<td>Cl</td>
<td>2.52 (0.08)</td>
<td>3.01 (0.24)</td>
</tr>
<tr>
<td>Ca</td>
<td>1.93 (0.05)</td>
<td>0.76 (0.04)</td>
</tr>
</tbody>
</table>

**Ammonia rejection during sewage concentration**

As already commented, during concentration experiments ammonia showed negative concentration factors, suggesting little membrane rejection. In order to determine ammonia rejection, further assays were performed with ammonia solutions and a new TFC-ES membrane for a period of 8 hours. Initial ammonia concentrations of 20 mg/L and 40 mg/L, and 35 g/L of NaCl as draw solution (concentration of 20 and 50 g/L of NaCl were studied additionally) were studied. The evolution of ammonia concentration was measured on both sides of the membrane. The results basically showed low levels of ammonia rejection, independently of the initial concentration tested. Results also show that concentration of draw solution produced little or no influence on concentration evolution, indicating that ammonia transport is not related with difference of osmotic potential of both sides of the membrane. A similar behaviour was observed by Lu et al. (2014). Therefore, the differences in concentration factors observed would be the result of a transport-retarding effect provided by the different fouling layers formed over membrane surface, when concentrating sewage and filtered-sewage. Indeed, thicker fouling layer formed during sewage filtration may have provide extra resistance for ammonia transfer to draw solution, promoting a less negative concentration factor than for filtered-sewage. A low level of ammonia rejection represents a drawback for FO as a concentration technology for sewage. Depending on the operation used for draw solution re-concentration, that ammonia could represent an issue to be considered. The results of this specific objective are part of the first publication in Chemical Engineering Journal 306 (2016).

**Specific objective 3): To design an osmotic draw solution based on nanoparticles capable of providing the osmotic potential required for sewage concentration.**
The osmotic potential of different concentrations of nanoparticles based on silver nitrate (AgNO₃) were evaluated in order to use them in a concentration process of municipal wastewater by forward osmosis. A fungus extract (S.hirsutum, 3mm, 59nm) and a plant extract (G.officinalis, 5mm/55nm) were used for the synthesis of nanoparticles. Van't Hoff model was used to estimate the theoretical osmotic potential of nanosuspensions. Furthermore, the osmotic potential was determined using a cryoscopic osmometer. The results were compared with the osmotic potential (26 atm) of seawater with a typical concentration of NaCl 35 g/L. The results showed that nanoparticles solutions have low osmotic potential (11 and 12 atm) compared to seawater. Thus, the synthesis of nanoparticles might need 3 times higher concentrations, representing a complex job and a high economic cost of synthesis. This is logical because the osmotic pressure is a colligative property of the solutions, that is, it depends only on the concentration, so must propose nanosuspensions according to the ease with which these can be synthesized. In addition, purity and stability must be considered. Use of nanoparticles as osmotic solution in the wastewater concentrates forward osmosis is discarded due to the complexity of achieving high concentrations, it was concluded.

Specific objective 4): To evaluate a recover regeneration strategy of draw solution and operating conditions of the RS step.

Reverse osmosis has been studied as a recover regeneration strategy of draw solution. Preliminary studies in a closed-loop FO/RO system and using NaCl and MgCl₂ as draw solution showed that the rejection of trace organic solutes (TOS) by FO membrane is less than RO membrane in closed-loop FO/RO. Therefore, an accumulation of TOS in closed-loop was estimated. A high RO rejection was found. However, the kind of DS would affect the FO rejection for neutral TOS. A FO/RO system will be considered in a future research.

Specific objective 5): To evaluate the right technology for anaerobic treatment of concentrated sewage.

Sewage from Temuco treatment plant was concentrated using 3 membrane processes: Forward osmosis (FO), microfiltration (MF) and, ultrafiltration (UF). For FO concentration, a 0.6 M NaCl solution as draw solution was used. A lab-scale filtration unit using a CTA membrane (HTI, USA) of 0.03 m² was used for FO. For MF concentration, a tubular ceramic membrane (Al₂O₃) with 0.0094 m² (Atech Innovations, Germany) and with a pore diameter of 0.2 µm was used. During UF concentration, a polymeric tubular membrane (X-Flow Norit, The Netherlands) with a pore diameter of 30 nm. and 0.0176 m² was used. All membranes were operated under cross-flow mode.

The biogenic methane potential (BMP) assays were carried out in closed bottles using a granular sludge form a UASB reactor as inoculum. A substrate/inoculum ratio of 1 gCOD*1 gVS-1 was applied. After flashing the bottles were incubated at 35°C. The evolution of the headspace pressure was determined with a pressure transducer and biogas composition was measured by gas chromatography. In order to determine the influence of the NaCl concentration on sludge used for BMP tests, specific methanogenic activity (SMA) was determined at different NaCl concentrations. The SMA assays were carried out using the same methodology to BMP. Methane production was measured by gas chromatography. SMA was evaluated determining the maximum production of methane observed during the assay. COD, total solids (TS) and volatile solids (VS) were determined according to Standard Methods (APHA, 2005). Na⁺ was analyzed using an ICP Mass Spectrometer NexION 350D.

Times required to achieve such levels of volume reduction were quite higher for FO (~70 h) than MF and UF (~10 h), as a result of the observed differences in permeate flux. Higher membrane areas or the use of a more concentrated draw solution would be required to decrease the time observed for FO.

Figure 1a shows COD content of the concentrates obtained, together with the degree of COD recovery. Latter value was calculated based on the ratio between actual and “expected” COD concentration, based on volume reduction factor, and assuming complete COD rejection (100% of COD rejection). This analysis shows a similarity between membranes performances. On MF and UF the assay time lasted 10 h, in this time is likely to be lost a 30–45% of COD on a filtration
process, because, 20–25% are going with the permeate water, and the 10–20% are lost as waste inside the tubing and pumps.

The assay time on FO concentration was 70 h, where a 38% of initial COD is lost due to biodegradation. The FO membrane mechanism is diffusive, the high retention prevent leakage of COD as it happens in MF and UF. Nevertheless, the long time of operation favors the biodegradation. An interesting aspect because for FO need increase 7 time the membrane area for achieve a similar time of concentration like MF or UF process, which increases the COD recovery.

BMP assays were conducted for the 3 concentrates. Results are presented in Figure 1c, which shows the evolution of methane production in time. BMP was very similar for MF and UF, close to 150 NmL gVS⁻¹. BMP was higher for FO concentrate (around 200 NmL gVS⁻¹), but the kinetics of methane production were lower in comparison to MF and UF. Such behavior is most likely the result of different COD quality in the concentrates coming from membrane processes, based on the different rejection characteristics of tested membranes. Moreover, FO concentration process took long time, which most likely produced some biological degradation. In the case of FO, the presence of Na⁺ or other ions as a result of reverse salt flux and the concentration of ions (due to the high rejection of FO membrane), may have also affected kinetics of methane formation. Figure 1b presents the effect of Na⁺ concentration on SMA of the anaerobic sludge used for BMP determination. A concentration of 2.5 gNa⁺L⁻¹ already produces a decrease of 20% for SMP. Sodium concentration during BMP tests for FO concentrate was close to 2 g/L, so this factor may have played a role in the methane kinetics observed.

FO membrane used has a sodium rejection factor close to 95%. The permeation of Na⁺ to the sewage is the result of the high filtration time, resulted from the low observed fluxes and the relation membrane area/initial feed volume.

There are no reports of biogas production from concentrate municipal sewage by Forward Osmosis Process. However, some studies like Lutchmiah et al., 2014, who evaluated the municipal sewage concentration with a CTA membrane (provide by HTI) and mention the possibility of biogas production from a concentrated municipal sewage. This study shows, for first time, the biogas production possibility and the effect of reverse salt flux over the biogas production.

Based on BMP results, the potential energy contained in the concentrates was estimated, considering calorific power of generated methane. Results are presented in Figure 1d as Wh per g of COD contained in concentrated sewage. Potential energy presents as a function of the volume of sewage (before concentration). As expected, energy potential of FO-concentrate sewage, when expressed per g COD, was higher, as a result of the higher BMP.
Biogas production is higher with the FO's concentrated-sewage than the MF and UF's concentrated-sewage, due to more high FO retention performance. Therefore a FO-concentrate maintains a best COD quality than MF and UF in a similar concentration process. The FO's sewage concentration has proven to be technically feasible. However, some drawbacks need to be overcome such as low water-flux and more high membrane area is required. The results presented here are being compiled in a manuscript in progress entitled: "Biogas production from concentrated municipal sewage by forward osmosis, micro and ultrafiltration”

References


OTHER ACHIEVEMENTS OF THE PROJECT:
- Research visit(s) to other institution(s).
- Outreach activities related to the project’s main topic.
- Any other contribution, not addressed elsewhere, that you consider important.

The maximum length for this section is 1 page. (Arial or Verdana, font size 10).

a) Human resources training and informed tesistas except:

Postgraduate training

The results of the research project FONDECYT 3140632 were useful for work doctoral thesis by Juan Carlos Ortega, 2015. Thesis title: "Forward Osmosis: an alternative for the concentration of sewage". Doctoral Program on Engineering”, November 2015, University of La Frontera.

Undergraduate training

Thesis

1) The results of the research project FONDECYT 3140632 were useful for the undergraduate thesis at Jose Molina Quitral, 2016. Thesis title: "Evaluation of ionic compounds rejection by Forwards Osmosis Treatment as an Alternative Drains Acids Miners". Environmental Civil Engineering, University of La Frontera.

2) Training in course of candidate engineer Mr. Victor Hidalgo Zúñiga with his work entitled: "Effect of shear stress on the fouling formed during the concentration of wastewater protein rich by forward osmosis". Working for the civil engineering degree in Biotechnology, 2016, University of La Frontera.

Laboratory Practices:


2) Jose Molina Quitral, 2016. "Using nanoparticles as osmotic solution in the concentration of municipal wastewater”, University of La Frontera.


B) Outreach Activities:

1. The knowledge gained in this research was diffused in a practical class, as part of the course "Laboratory of Environmental Engineering", Code: IIQ606 of Engineering department at University of La Frontera. This outreach activity was directed by Isaac Reyes, Victor Hidalgo, and Javier Pavez at BIOREN centre (First half 2016).

2. An overview and associated facilities to postdoctoral project (3140632) was released for educational purposes at community from Temuco in the "Feria de Investigación (FIUFRO) Universidad de La Frontera, 2016". This was on August 31th 2016 at the Convention Center at Dreams Hotel, Temuco, Chile. Associated link: [http://feriainvestigacion.ufro.cl](http://feriainvestigacion.ufro.cl).
The evaluation of Dr. Reyes work is positive.

Dr. Reyes was able to overcome the challenges and problems that research in a new subject involves. He collaborated on the supervision of a PhD thesis and supervised few BSc students. Results from his research are a contribution to knowledge about application of Forward Osmosis process.

Work done by Dr. Reyes enabled to the publication of a paper in a high impact journal. Moreover, a second paper is currently being written, and submission is expected to be completed this year.

Project also enabled the participation in a couple of international conferences, and outreach activities were also performed, contributing to share the results provided by the project to different audiences.

Finally, Dr Reyes supervised a BSc student on the use of Forward Osmosis filtration process for the removal of metals from mining wastewaters. Even though application of this filtration technique to mining wastewaters was not considered in the original project, this effort is interpreted as positive, since it contributed to expand the potential applications of forward osmosis to other types of wastewaters other than sewage.
ARTÍCULOS
Para trabajos en Prensa/Aceptados/Enviados adjunte copia de carta de aceptación o de recepción.

Nº : 1
Autor (a)(es/as) : Ortega-Bravo, J.C.; Ruiz, G; Donoso, A.; Reyes-Caniupan I.; Jeison D.
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OTRAS PUBLICACIONES / PRODUCTOS

Sin información ingresada.

CONGRESOS

Nº : 1
Autor (a)(es/as) : Ortega, J.C.; Jeison, D.; Reyes I.
Título (Idioma original) : Municipal sewage concentration by forward osmosis
Nombre del Congreso : 5th International Workshop in Advances in Science and Technology of Bioresources
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ANEXOS

A continuación se detallan los anexos físicos/papel que no se incluyen en el informe en formato PDF.