Circular Economy: Recovery, Reuse & Valorization

Green Fertilizers

KEYWORDS: Nutrients Recovery / Low Footprint Crystallizers / NETmix / Oscillatory Flow Crystallizer / Adsorption / Microalgae

New solutions for nutrient recovery from wastewaters, including low-footprint crystallizers (NETmix and oscillatory flow crystallizer), adsorption processes using magnesium-modified cork biochars, and microalgae cultivation, promoting sustainable agriculture.

Introduction

Nutrient recovery technologies are rapidly expanding due to the need for the appropriate recycling of key elements from waste resources, reducing the depletion of non-renewable resources and the environmental impact linked to their extraction and manufacture. Current technologies devoted to nitrogen (N) and phosphorous (P) recovery from wastewater include (i) membrane-based technologies; (ii) crystallization-based systems (Struvite – $MgNH_4PO_4{\cdot}6H_2O$; Hydroxyapatite (HAP) – $Ca_5(PO_4)_3(OH)$, etc.); (iii) biological processes (algae biomass production, advanced biological systems, wetlands); (iv) physical-chemical adsorption and ion exchange; and (v) ammonia stripping and absorption.

The developments in struvite/HAP crystallization and recovery processes have renewed interest in nutrient recovery, but considerable work is needed in reactor design or conditions that increase its economic viability.

Another strategy to recover nutrients from wastewater is the cultivation of microalgae, which are photosynthetic microorganisms with high growth rates, requiring only carbon (C), N, and P. Microalgae biomass offers novel sources of plant growth promotors that enhance crop productivity and impart disease resistance. These beneficial effects could be attributed not only to the presence of N, P, and other inorganic micronutrients but also to the release of some secondary metabolites like vitamins, carotenoids, and amino acids, which help in plant growth promotion.

The main goal of this project is to foster nutrient recovery from wastewaters using precipitation/crystallization processes, adsorption, and microalgae cultivation, enabling to (i) produce nutrient-based fertilizers to ensure food security and sustainable agriculture (SDG2) and partially helping to reduce global warming by replacing synthetic fertilizers, generated in energy-intensive processes involving fossil fuels and raw materials intensive processes (SDG 13); (ii) minimize the environmental footprint of wastewater treatment through the reduced load of nutrients and reduced eutrophication (SDGs 6); and (iii) decrease the consumption of natural resources (mined phosphate rock) and save costs associated with N fixation (SGD 12).

Current Development

Nutrient recovery by struvite crystallization is under evaluation for centrate streams using two low-footprint crystallizers: NETmix (Fig 1) and oscillatory flow crystallizer (OFC) (Fig 2).

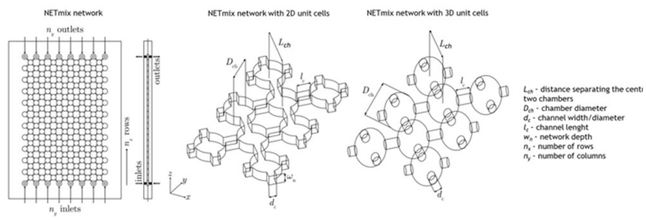

Fig 1. Schematic representations of the NETmix network.

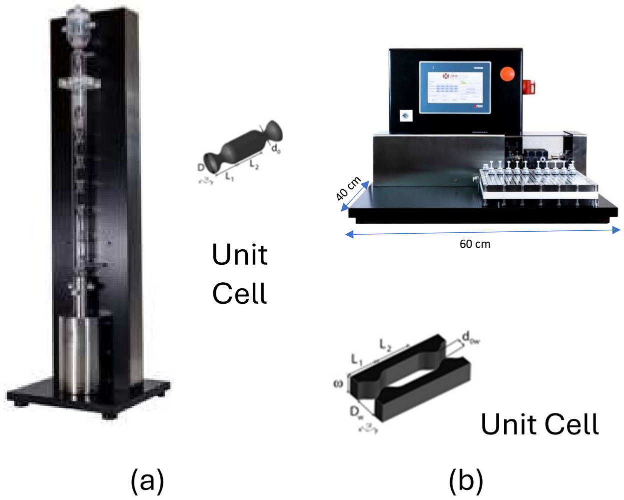

Fig 2. Oscillatory flow crystallizer apparatus based on (a) pipes and (b) channels arrangement.

The capacity of the NETmix reactor to efficiently mix two streams with dissimilar flowrates (wastewater and magnesium (Mg)/calcium (Ca) solution) and the same physical properties was studied numerically in terms of flow distribution and mass transfer. The simulations showed that the static mixer NETmix could generate a uniform flow distribution across its network and attain the desirable condition of similar outlet flow rates for several asymmetric inlet flow conditions. Regarding mixing performance, it was verified that the mass transfer phenomenon between two identical fluids was enhanced by increasing the inlet Reynolds number (*Re*), although outlet streams with tracer concentrations close to homogeneity were obtained in all the cases studied. The number of rows needed for tracer/water homogenization is smaller for the cases with a higher water inlet flow rate. The spectral analysis enabled the determination of the characteristic flow field oscillation frequencies from the velocities computed at the center of chamber C14. Then, two methods were employed to estimate the fraction of this chamber that is occupied by vortices. Fairly concordant values were obtained from both methods, and it was concluded that the increment of Re_l led to an increase in the area occupied by vortices in the NUB (NETmix Unit Block) chamber. The velocity fluctuations at the center of the NUB chambers were also analyzed. Intensities of turbulence around 0.25 were obtained for the cases with Re_l = 600 and close to 1.00 for the cases with Re_l = 1200. Tracer experiments conducted at the laboratory validated the numerical results obtained from the simulations with the 2D Double ExtendedNUB geometry. The same flow patterns and mixing structures were visualized for both the computer fluid dynamics (CFD) and the experimental results for the same conditions. In addition, a more efficient mixing was obtained in the experiments with $Re_{3D,water}$ = 1200, which was also concordant with the simulations.

Saturated Mg-cork biochars with 120-175 mg/g P content were obtained by adsorption from 100 mg/L P solutions. Crystals of magnesium phosphate were observed on the surface of biochar. Mg, C, and P, the main components of the P-laden biochar, are essential nutrients for a successful fertilizer. Therefore, it is proposed that this product, resulting from water treatment processes, can be reutilized as a fertilizer in the soil, providing a valuable fate for the captured P.

C. vulgaris cultivation was successfully applied for the bioremediation of a paper industry effluent after secondary treatment, fortified with a N source, targeting P removal. C. vulgaris was able to grow in all studied effluent conditions (in non-diluted and diluted ones). However, it was possible to conclude that growing on non-diluted effluent resulted in lower biomass productivity, which was also reflected in N and P removal efficiencies. From microalgal growth and nutrient removal points of view, the paper industry effluent diluted by a factor between 2 and 3 seems to be the most adequate, as microalgal growth was not inhibited in these conditions, and N/P mass removal was quite satisfactory.

Leachate obtained from an urban waste landfill located in northern Portugal was also used as a culture medium for microalgal growth (C. vulgaris e T. obliquus). Since the proposed microalgal treatment aimed to promote nutrient removal as part of the tertiary treatment, the effluent was collected after the biological treatment step (aerated lagooning + activated sludge biological oxidation). Both microalgal strains (C. vulgaris e T. obliquus) were able to grow in different leachate dilutions (from 5% (v/v) to 25% (v/v)). However, the landfill leachate without dilution exhibited an inhibitory effect on the studied microalgae. The highest biomass productivities were obtained in the experiments carried out with lower effluent concentrations. Similar behavior was observed for N uptake, as the highest removal efficiencies were obtained for the lowest effluent concentration studied.

Novel configurations for tubular photobioreactors (PBRs) (Fig 3) were tested, illuminated with specific and adequate light wavelength provided by LEDs, enabling a more uniform (spatial and temporal) distribution of light inside the culture medium and a low heat generation, aiming for a higher light utilization efficiency and photosynthetic activity. The PBRs are characterized by an involute/flat reflective surface around/below a cylindrical borosilicate glass tube. Depending on the reflector design, almost all the light arriving at the collector aperture can be collected and available for microalgae cultivation. A LED box is located above the collector. C. vulgaris growth was evaluated as a function of the reflective surface geometry (flat (F), simple double parabola (SP) and traditional double parabola (DP)) and material (anodized aluminum with (MS) and without (R85) protective coating and stainless steel (SS)). C. vulgaris growth as a function of time was found to be in good agreement with the actinometric results, where the parabolic reflectors (SP and DP), made of materials with higher specular reflectance (R85 and MS), showed the best results. This behavior is related to the fact that light reflected by the parabolic optics is distributed around the back of the tubular photoreactor so that most of the borosilicate glass tube circumference is illuminated. Conversely, energy-based specific growth rates slightly increased as the photon flux decreased, signalizing an energetic efficiency loss due to the low transmissibility of the microalgae suspensions. Additional tests using two absorber tubes (spaced between 12.5 and 75.0 mm) over the R85-F reflector were also carried out, showing that the distance of 50.0 mm led to the best compromise between the specific growth rates and biomass productivity per square meter of solar collector. Under these conditions, higher efficiency in the photonic energy usage was attained compared to the test with one tube. In short, tubular PBRs composed of flat reflectors can represent an enormous potential as an effective platform for microalgal biomass production due to (i) low constructive complexity; (ii) low area requirements; and (iii) higher energy efficiency.

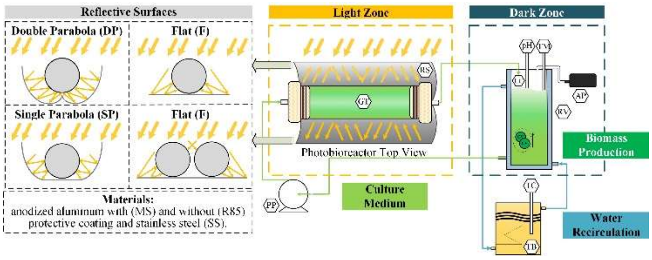

Fig 3. Schematic representation of the reflective surfaces and experimental setup used for C. vulgaris cultivation.

Future Perspectives

Assessment of struvite/HAP precipitation/crystallization regarding the feeding scheme to the network, superficial liquid velocity, frequency and amplitude, reactants' type and dose, temperature, pH, and centrate stream constituents.

Evaluation of the effectiveness of saturated P biochar application as a soil amendment in collaboration with Cork Technological Centre (CTCOR). The assessment will be done through P leaching tests in soil and pot trials for the growth of different vegetable species. Furthermore, the elution of P from the biochar can also be equated and studied using different nontoxic solutions to produce added-value concentrates.

Related Sustainable Development Goals

Outputs

PhD Theses

[1] Bruna Porto, Microalgal biomass production and nutrients removal from industrial wastewaters using different culture systems, FEUP/UFSC, 2021

[2] Ana Filipa Cruz Esteves, Effect of light spectrum in nutrient uptake and biochemical composition of microalgae, PDEA, FEUP, on-going, 2020-2024

[3] Luiza Maria Gomes de Sena, Continuous oscillatory flow crystallizer for nutrients recovery from sidestream digestate, PDEA, FEUP, on-going, 2023-2027

Master Dissertations

[1] Ana Filipa Cruz Esteves, Avaliação do efeito de diferentes comprimentos de onda da luz no crescimento de microalgas e remoção de nutrientes, MIEA, FEUP, 2019

[2] Maria Isabel Carvalho Neto Gabriel Silva, Paper industry effluents towards the development of energy-driven biorefineries: an experimental and techno-economic approach, MIEA, FEUP, 2020.

[3] Nuno Sousa, Produção de biocarvões de cortiça para recuperação de fosfato de águas, M.EA, FEUP, 2022.

[4] Laura Joana Ribeiro Cullen, NETmix crystallizer for nutrients recovery from side-stream digestate, M.EQ, FEUP, 2023

[5] Diogo Moura, Valorização de resíduos de cortiça pela produção de biocarvões fertilizantes, M.EA, FEUP, 2023.

Selected Publications

[1] B. Porto et al., Applied Sciences 10, 3009 (2020)
[2] B. Porto et al., Chem. Eng. J. 413, 127546 (2021)
[3] M.I. Silva et al., Sustainability 13, 1314 (2021)
[4] B. Porto et al., Chem. Eng. J. 435, 134747 (2022)

Patents

[1] Ariana Pintor, Salomé Soares, Cidália Botelho, Nuno Sousa, Fernando Pereira, Adsorbent composition modified by a metal, its preparation method, method of adsorbing phosphorus or phosphate,

composition comprising adsorbed phosphorus or phosphate, and its use as a fertilizer. Patent Pending PT 118599, filed 2023.

Team

Vítor Vilar Principal Researcher; Cidália B. Professor; Ricardo J. Auxiliar Researcher; Ariana Pintor Junior Researcher; Luiza Sena, PhD Student; **Ana Esteves**, PhD Student; **Laura Cullen**, Project Researcher

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