

3.2 Water Management

3.2.2 Water Pollution Prevention, Mitigation & Sustainability

KEYWORDS: Municipal Sewage Network / Industrial Pollution Hotspots / Wastewater Treatment / AFM Filtration / Coagulation

Innovative methods were studied in real environmental compartments with close collaboration of water management entities to assess the occurrence, impact, and removal of pollutants, contributing to water sustainability.

Introduction

Wastewater treatment plants (WWTPs) performance is routinely verified by assessing wastewater influents and effluents in terms of chemical and biochemical oxygen demand (COD and BOD, respectively), total suspended solids (TSS), total nitrogen (TN), and total phosphorous (TP) contents, among other current physicochemical parameters. These general wastewater quality parameters are normally required to overview legal compliance and are used as the basis for the design of WWTPs. Nonetheless, those parameters are indicative and do not provide detailed information on the properties of specific components of dissolved organic matter (DOM), nor the presence or identification of contaminants that reach the WWTP and that may impact the treatment performance, especially the biological treatment stage. Thus, to ensure the proper operation of WWTPs, it is essential to check the presence of (organic) microcontaminants and characterize DOM throughout the sewage network, allowing the detection of specific hotspots and the implementation of preventive measures at their source.

Concerning this topic, the efficiency of a tertiary treatment conducted in a pilot facility based on a filtration system that uses an activated glass granular medium (CAFE) was evaluated in a WWTP. The performance of the system was analyzed for one year (2021) by weekly determining several water quality parameters (TSS, TN, TP, dissolved copper, *E. coli*, and total coliforms), and the removal rate of 20 emerging pollutants, including 12 pharmaceuticals and 8 pesticides.

Coagulation/flocculation is one of the most common treatment processes in water, urban wastewater, and industrial effluent treatment systems. As an alternative to traditional coagulants, natural coagulants, particularly tannin-based (TB) ones, have been extensively researched for the past 10 to 15 years. Over the last 5 years, our focus has been on studying tannin extraction from eucalyptus bark, chestnut shell, and cork powder. Furthermore, tannin-based coagulants for water and wastewater treatment have been produced through aminomethylation.

Current Development

The impact of industrial wastewater discharges on the performance of the Ave WWTP located in Vila do Conde, Portugal, was assessed in close collaboration with EFACEC, Águas do Norte, INDAQUA, the municipal council of Vila do Conde and the municipal council of Póvoa de Varzim. This study was compelled by the occurrence of operational problems reported by the Ave municipal WWTP, such as (i) inhibition of nitrification in the activated sludge reactor, (ii) poor settling characteristics of the activated sludge, impairing the efficiency of the secondary settling tank and the UV disinfection step, (iii) high amounts of foam within the secondary and tertiary treatment steps and in treated wastewater discharged to water compartments, and (iv) high content of linear alkylbenzene sulfonates (LAS) in dry sludge.

Taking this, to assess the impact of industrial effluents on the composition of urban wastewater and the efficiency of WWTPs, an exhaustive physicochemical characterization of 24 wastewater samples was performed (3 monitoring campaigns, each with 8 sampling points: 6 throughout the sewer network, plus the WWTP influent and effluent) (Fig 1).

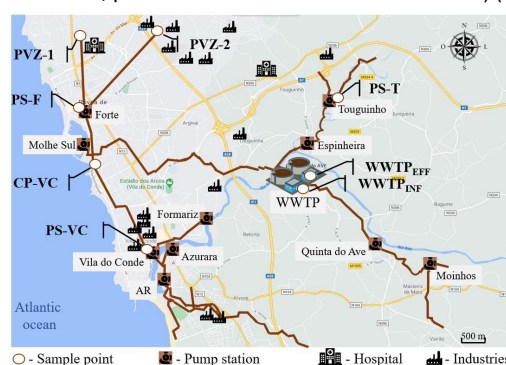


Fig 1. Map representing the sewage network and sampling locations.

Furthermore, advanced analytical tools such as fluorescence excitation/emission matrix-parallel factor analysis (EEM-PARAFAC), size exclusion chromatography with organic carbon detector (SEC-OCD), and liquid chromatography with mass detection (LC-HRMS) were employed to characterize DOM properties and origins and identify contaminants (particularly, surfactants) potentially related to the problems detected at the WWTP. The Ave WWTP complied with the legal values for discharge as regards COD, BOD, and TSS. However, TN values (~ 50 mg N/L) remained above the emission limit values, indicating the occurrence of constraints in the biological treatment. High amounts of surfactants (cationic, anionic, and non-ionic) were detected in almost all sampling locations (up to ~ 50 mg/L for CP-VC, at campaign 2), including in the WWTP-INF (up to 6.1 and 13.5 mg/L, for non-ionic and anionic surfactants, respectively). In turn, low surfactant concentrations were observed at WWTP-EFF, suggesting that their loads were reduced during the treatment. In the sludge control analyses, concentrations between 4.7 - 9.7 mg LAS/g dry sludge were measured, reflecting a significant occurrence of LAS adsorption mechanisms in the activated sludge. All sewer samples have been classified as biodegradable. However, the continuous addition of a pollutant load from CP-VC (which presented the highest surfactant levels) led to a modification in the sludge characteristics. From microscopic analysis, filamentous and flagellate organisms were observed, as well as the disaggregation of biological flocs, which are clear indicators of increased difficulties in sludge settling and decreased efficiency for organic matter removal. EEM-PARAFAC (collaboration with the University of Arizona - Water and Energy Sustainable Technology (WEST) Center, USA) showed a high fluorescence intensity for protein-like component (C2), particularly in sampling points CP-VC (near seafood industries) and PVZ-1 (near a hospital), associated with the presence of surfactants (up to ~ 50 mg/L) and pharmaceuticals/healthcare products, respectively. SEC-OCD results were consistent with PARAFAC, highlighting the

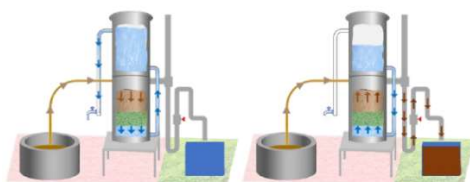
WWTP efficiency in removing low molecular weight acids and neutrals. LC-HRMS (collaboration with the Department of Analytical Chemistry from the University of Santiago Compostela (USC), Spain) identified 108 compounds of emerging concern (CECs) (56% pharmaceuticals and 15% metabolites), and similar detection patterns were obtained for all wastewater samples, except for PVZ-2 (lower detection). 111 surfactants were detected, and the classes more frequently found were alcohol ethoxylates (AEOs), nonylphenol polyethoxylates (NPEOs), and LAS. The continuous presence of LAS and NPEOs allied to surfactant concentrations in the WWTPINF of 15-20 mg/L, with CP-VC location (linked with food industries) as an important contributor, explain the changes in the characteristics of the activated sludge and high content of LAS in the dewatered sludge.

The CAFE system, using activated glass filter medium AFM, was installed at Olhalvas WWTP, located in Leiria (Fig 2). This project was developed in close collaboration with InnovWise, and it was compelled by the interest in studying its efficiency in removing dissolved organic matter from wastewater after current treatment at the WWTP. Significant mean removal rates were obtained for total suspended solids (56%). The mean reduction of TN (16%), TP (4%), and microorganisms (67% for *E. coli* bacteria and 51% for total coliform bacteria) was lower than desirable. All 20 emerging pollutants analyzed were identified in at least one sample, and anti-inflammatory drugs were found at higher concentrations, reaching values in the tens of micrograms. The median removal rate of emerging pollutants was below 30%, except for atenolol (36%), trimethoprim (90%), diuron (41%), thiachloprid (55%), acetamipride (64%), and thiamethoxam (70%).

In conclusion, the CAFE system was demonstrated to be a valid option for the tertiary treatment of wastewater when the objective is to remove suspended solids. With a subsequent disinfection process, there is a possibility of reusing the filtered water, namely for irrigation. CAFE appeared to be ineffective in removing most of the emerging pollutants, although it reduced the environmental risk for all quantified compounds.



(1)



(2)

Fig 2. (1) CAFE Filtration System installed as tertiary treatment in Olhalvas WWTP; (2) Water circuit in the filtration process (left) and backwashing (right).

Eucalyptus globulus bark (EGB) and chestnut shells (CS) were used as tannin sources. The extraction of polyphenols from both sources was studied using water as solvent (Fig 3). The extract generated under optimized conditions presented

a condensed tannin content of 645 mg/g for EGB and 1300 mg/g for CS, expressed in terms of catechin equivalents. Tannins extracted from chestnut shells were subjected to aminomethylation using varying concentrations of tannin, ammonium chloride, and formaldehyde (FA). Zeta potential measurements and chemical analysis confirmed successful cationization procedures. The coagulants' performance was evaluated through coagulation/flocculation-sedimentation experiments using synthetic and natural water samples. The coagulant efficacy was evaluated considering the minimization of formaldehyde usage. The most promising coagulant formulations were produced with tannin: NH_4Cl :FA molar ratios of 1:2.5:7.5 and 1:2.5:10. These coagulants reached remarkable removal rates, achieving over 95% turbidity reduction. The coagulants have also efficiently removed organic matter, phosphorus, and nitrogen. Chestnut shell tannins exhibited great potential as source material for producing natural coagulants, offering a sustainable and eco-friendly approach to water treatment.

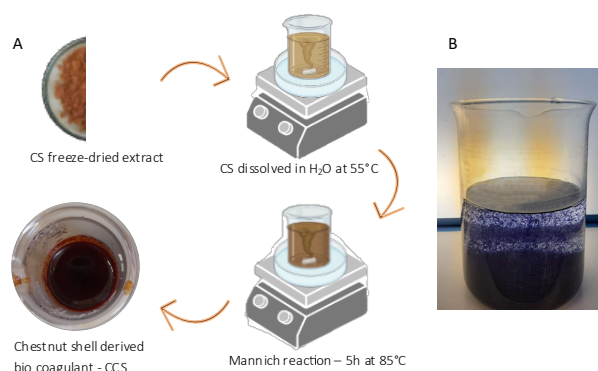


Fig 3. Coagulant production from freeze-dried chestnut shell (CS) extract (A) and coagulation test (B).

Future Perspectives

Studying processes of the uptake and transport of DOM in plants, particularly when treated wastewater is reclaimed for irrigation of agriculture or hydroponic production. Exploring the feasibility of achieving efficient coagulation with even lower formaldehyde dosages or potentially eliminating formaldehyde, offering valuable insights for advancements in this field. A comparative life-cycle assessment (LCA) will be conducted considering the extraction and cationization phase to compare the reactions (Mannich/Free-formaldehyde) in terms of environmental burden and help to select the best approach. Studying the coagulation-flocculation in continuous automated mode (lab/pilot scale) applied to textile wastewaters for efficient management of water in this sector.

Related Sustainable Development Goals



Outputs

Master Dissertations

- [1] António Pedro Ribeiro Antunes Duarte, Eficiência do tratamento terciário na ETAR de Olhalvas através de uma tecnologia de filtração, MEENA, ESTG-IPLeia, 2023.
- [2] Mariana Filomena Teixeira Sá, Estudo sobre o impacto dos contaminantes industriais na ETAR do Ave, MIEA, FEUP, 2019
- [3] Elisandra Centeio Lopes, Coagulantes derivados de taninos para aplicação no tratamento de efluentes têxteis, MIEA, FEUP, 2018.

Selected Publications

- [1] I.T. Tomasi et al., *J. Clean. Prod.* 395, 136452 (2023)

[2] I.T. Tomasi et al., Water 15(2), 317 (2023)

[3] I.T. Tomasi et al., Sci. Total. Environ. 822, 153454 (2022)

[4] M.F.T Sá et al., Sci. Total. Environ. 817, 152518 (2022)

[5] E.C. Lopes et al., J. Environ. Chem. Eng. 7, 103125 (2019)

Team

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