Technologies for Pollution Control

Sorption/Biosorption Processes

KEYWORDS: Adsorption / Water / Cork / Tannins / Arsenic / Antimony / Phosphorus / Biochar

Water treatment systems for the removal of arsenic and antimony were built at a lab scale using iron-coated cork granulates and polymerized tannins from pine bark. Partnerships with industry for the treatment of groundwater contaminated with arsenic were established. A novel methodology for the production of magnesium-modified cork biochar for the recovery of phosphorus was optimized and intellectually protected. Adsorption experiments were carried out for the removal of emerging contaminants using biodegradable materials.

Introduction

The use of low-cost materials for the production of adsorbents, due to its environmental and economic advantages, has been a focus in adsorption research for water treatment. Namely, using natural materials of biological origin, such as agricultural and forestry residues, as precursors for tailored adsorbents has shown to be a convenient approach to a circular economy by upcycling wastes with presently very low value.

In our research group, we have concentrated on the use of cork-based materials and tannins for water treatment applications, and new biodegradable and safe materials for the simultaneous removal of emerging contaminants in water.

Cork is a natural, renewable material produced from the bark of *Quercus suber* L., traditionally used to manufacture cork stoppers. Industrial cork processing for this purpose generates over 75% wt of cork byproduct in the form of powder or granulates. Adding value to these byproducts is an important goal for this sector. Although this is a topic that had started to be explored in our lab in the previous decade, in the current period, we moved from the use of raw cork byproducts to modified cork-based materials with specific target pollutants.

On the other hand, tannins have been extracted from *Pinus pinaster* bark, a forest and industrial waste whose chemical richness is commonly ignored, and converted into adsorbents through polymerization.

Current Development

We have developed novel adsorbents from cork powder and granulates, and from polymerized tannins, chemically tailored for the uptake of pnictogens (group 15 elements), namely phosphorus (P), arsenic (As), and antimony (Sb). For the removal of emerging pollutants, films, particles and microparticles were developed from alginate, activated carbon, graphene, and polycaprolactone.

<u>A - Cork-based biosorbents</u>

An iron-coating procedure on cork granulates at room temperature was optimized to maximize their affinity for arsenic removal. The process resulted in iron (oxy)hydroxides deposition inside the cork's external cellular structure, amounting to a Fe content between 20-30 mg/g (around 2-3% in weight). Batch adsorption of arsenic onto iron-coated cork granulates (ICG) achieved maximum values of 4.9 ± 0.3 mg/g As(III) (pH 9) and 4.3 ± 0.1 mg/g As(V) (pH 3).

ICG were also shown to have good removal capacity for antimony. Maximum adsorption capacities in batch mode were estimated to be 5.8 ± 0.5 mg/g Sb(III) (pH 6), 8.2 ± 0.7 mg/g Sb(III) (pH 3), and 12 ± 2 mg/g Sb(V) (pH 3).

A lab-scale adsorption column with a fixed bed of ICG was operated in continuous mode for the adsorption of As and Sb, with an effective scale-up of the conditions studied in batch mode. Namely, it was shown that it was feasible to uptake arsenic in environmentally relevant conditions of contaminated groundwater, such as an initial concentration of 0.1 mg/L As, reducing the concentration to below the WHO legal limit of 0.01 mg/L for 550-900 bed volumes. The adsorbent was also successfully regenerated to about 50% of its initial capacity using NaOH 0.01 M for 5 cycles. For Sb, it was shown that the most favourable outcome was reached at pH 3, with total capacities equal to those achieved in batch mode; the results suggest that using ICG to remove this element may be more advantageous in matrices such as acid mine drainage. Regeneration of the Sb-saturated column was ineffective, as Sb desorption was only possible with acid eluents, which caused the simultaneous removal of the iron coating.

The use of an ICG lab-scale column for the treatment of arsenic-contaminated groundwater was validated in a relevant environment, that is, the treatment of real groundwater collected from contaminated sites, through partnerships with the Municipality of Mirandela, INDAQUA, and Águas do Marco, in Portugal, and with the NHL Stenden University of Applied Sciences, in the Netherlands, enabling the achievement of TRL 5 with this technology.

The business idea of the use of this treatment system was named FilterCork and submitted to several entrepreneurship programs, having benefited from the BluAct prize in 2022 from the Municipality of Matosinhos and INDAQUA, which included an incubation period at UPTEC that is currently in progress.

Multicomponent studies of pnictogen adsorption using ICG have shown that phosphorus is an interferent in the uptake of As and Sb. However, ICG capacity for adsorbing phosphorus is, objectively, low, sitting at 3.1 ± 0.5 mg/g P. Because phosphate is not a toxic ion, adsorption of phosphate is usually aimed for nutrient recovery, and much higher capacities are needed for good efficiency.

For this reason, another cork-based adsorbent was devised, which consists of a magnesium-modified biochar produced by cork powder or granulate impregnation followed by pyrolysis under a nitrogen-carbon dioxide atmosphere. The methodology parameters and the characteristics of the product are subject to intellectual property through a provisional patent.

This biochar has shown a remarkable adsorption capacity of 120-175 mg/g P (initial pH = 3), of which the majority is not removed by adsorption on the surface but by microprecipitation of magnesium phosphate on the biochar surface. The process was demonstrated to be selective in the presence of interferents.

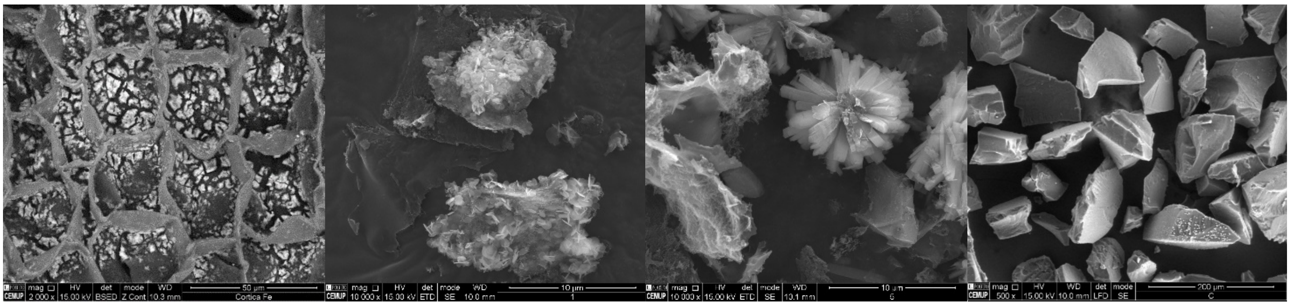


Fig 1. Scanning electron micrographs of low-cost adsorbents. From left to right: iron-coated cork granulates (2 000x magnification), magnesium-modified cork biochar (10 000x magnification), magnesium phosphate crystals on cork biochar (10 000x magnification), and tannin resins (500x magnification).

B – Tannin based biosorbents

Methods of tannin extraction and polymerization, oxidation and iron and calcium-loading of tannin resins were optimized. At 90 °C and using an alkaline solution, an extraction yield of 24.2% was achieved and 166 mg of formaldehyde-condensable phenols were extracted per gram of bark used. Polymerization of tannins, under the best conditions, presented an efficiency around 80%. Oxidation and iron loading yielded a tannin resin with an iron content of 22 mg/g. Calcium-loading yielded a tannin resins with a calcium content of 32 mg/g. None of the adsorbents produced was sufficiently efficient for phosphate uptake. Adsorption assays with As(III) presented negligible results. Equilibrium data obtained for As(V) adsorption by iron-loaded tannin resins showed a maximum adsorption capacity of 0.72 mg/g (pH 3, 20 °C). Tannin resin (unmodified) presented a good ability to uptake antimony, with maximum adsorption capacities, evaluated in batch mode, of 30-33 mg/g (Sb(III), pH 6, 20 °C) and 16-47 mg/g (Sb(V), pH 2, 20 °C). The applicability of the tannin resin on Sb(III) uptake was confirmed in continuous fixed-bed experiments. Breakthrough curves were obtained for different inlet adsorbate concentrations, bed heights, flow rates and aqueous media (distilled water and a simulated mine effluent). Desorption of Sb(III) and Sb(V) was assessed using different eluents. Strong alkaline solutions were found to be the most effective desorbing agent, although with still limited efficiency (27 % and 49 % desorption of Sb(III) and Sb(V), respectively) and leading to high levels of organic matter in solution.

C – Removal of Emerging Contaminants

Adsorbent materials are being optimized, namely films, particles and microparticles developed from alginate and polycaprolactone.

Results were obtained for the removal of several contaminants, namely the polycyclic aromatic compounds anthracene and benzo[a]pyrene, the pesticide chloropyrifos and copper used as a model for heavy metals. In addition, the interference of organic matter in the removal process is being also considered.

Future Perspectives

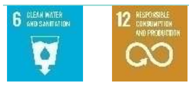
The main goal in the near future in this research line is to upscale the tested technologies and to evaluate them in comparison with current industry practices. This will involve, for instance, the assessment of environmental impact through Life-Cycle Analysis.

In the case of the arsenic removal system for groundwater treatment using ICG, we expect to partner with INDAQUA and Águas do Marco to invest in a pilot-scale installation that will allow to validate the technology *in situ* and at a closer dimension to industrial operation.

Regarding magnesium-modified cork biochars, these have only been tested in batch mode so far, so the next steps will comprise the design and operation of a lab-scale continuous mode installation. For a column setup, biochar agglomerates will need to be produced, possibly using a bio-based polymer. Another option is the use of perfectly mixed reactors.

For emerging contaminants, new tests are being carried out for the removal of drugs such as ibuprofen and translation to an applicable prototype in partnership with CR Inove Centro.

Related Sustainable Development Goals



Outputs

PhD Theses

[1] Hugo A. M. Bacelo, Tannin resins from maritime pine bark as adsorbents for water treatment and recovery of substances, PDEQB, FEUP, 2021.

Master Dissertations

[1] Diogo Moura, Valorização de resíduos de cortiça pela produção de biocarvões fertilizantes, MEA, FEUP, 2023.

[2] Nuno Sousa, Produção de biocarvões de cortiça para recuperação de fosfato de águas, MEA, FEUP, 2022.

Patents

[1] Pintor, Ariana M.A., Soares, O. Salomé G.P., Botelho, Cidália M.S., Sousa, Nuno F.R., Pereira, M. Fernando R., 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.

Selected Publications

[1] M. A. Carneiro et al., Journal of Hazardous Materials 432, 128657 (2022).

[2] D. Marques da Silva et al., Processes 10, 2300 (2022).

[3] H. Bacelo et al., Journal of Environmental Management, 302, 114100 (2022).

[4] A.M.A. Pintor et al., Separation and Purification Technology 233, 116020 (2020).

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