Harnessing Natural and Biowaste Adsorbents to Eliminate Contaminants of Emerging Concern in Water

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Introduction

In the ongoing pursuit of environmental sustainability, addressing water quality emerges as a paramount challenge in the 21st century. Wastewater treatment plants (WWTPs) play a crucial role in mitigating the impact of industrial and urban wastewater by implementing various treatments. However, despite their effectiveness, WWTPs pose a significant concern as a source of emerging organic contaminants in aquatic environments. The presence of these pollutants not only jeopardizes human health but also poses a threat to the delicate balance of ecosystems.

Conventional WWTPs, while effective in treating conventional pollutants, are ill-equipped to eliminate contaminants of emerging concern, which persist in aquatic ecosystems with potentially harmful consequences for both human and environmental well-being. To counter this issue, additional treatments are imperative, and among the explored avenues, natural and biowaste adsorbents stand out as a promising but relatively unexplored frontier.

This exploration delves into the realm of bioadsorbents, including agro-industrial wastes, wood bark, different types of biomass, as potentials agents for the removal of contaminants of emerging concern from wastewater. The investigation aims not only to enhance our understanding of these treatments, but also to contribute valuable insights towards sustainable water management practices.

The aim of this study is to investigate three bioadsorbents (chestnut shells wastes, almond shells wastes, and expanded burnt cork) as potential materials for the removal of emerging pollutants identified in WWTPs, as well as for their applications as part of nature-based strategies for wastewater treatment and regeneration (e.g. constructed wetlands).

Methodology

In this study Chestnut Shell Waste (CSW), Almond Shell Waste (ASW) and Expanded Burnt Cork (EBC) were used as a bioadsorbents. These bioadsorbents were characterized for their elemental analysis (C, H, N, S, O) and ash content. In addition, FTIR technique was applied in order to determine the main functional groups on the surface of the bioadsorbents.

A solution of 17 selected micropollutants (MP) was prepared at 1 µg/L in water. For kinetics studies, 2.5 g of adsorbent were added to 250 mL of 1 µg/L MP solution. Mixtures were stirred at room-temperature, 20 ºC, in multipoint agitation plate. At different times (from 0.5 to 144 hours), samples were taken and filtered. The residual MPs concentration in water was analyzed in a Water Acquity Ultra-Performance liquid chromatography system (UPLC) coupled to a Xevo TQ-S tandem quadrupole mass spectrometer with ESI source. Moreover, the most representative compounds from the mixture were chosen to carry out individual biosorption studies.

Results

The biosorbents displayed different chemical characteristics: EBC was characterized by a high carbon content (70.78%) respect to CSW and ASW that approximately were 49% and 50%, respectively. The content of ashes for the three biosorbents were 1% approximately. These values implied the presence of different quantities of oxygen between EBC (around 28%) and CSW and ASW, approximately 49% in both cases. Respect FTIR analysis, the main functional groups on surface for CSW and ASW were O-H stretching vibration (3500-3200 cm^{-1}) belonging to alcohol, phenol or carboxylic group, aliphatic groups (CH_2 or CH_3) around 2900 and 1460 cm^{-1}, carboxylic or carbonyl groups (~ 1750 cm^{-1}) and C=C stretching vibration due to the presence of possible aromatic rings (1580-1650 cm^{-1}). In the case of EBC, some of the FTIR bands showed lower transmittance compared to CSW and ASW. This could be due to the loss of functional groups during the burning process of the material.

The multi biosorption results after 6 days of process are shown in Figure 1. As can be seen, CSW and EBC can remove most of the pollutants (16 of 17) between 20 and 90%, only remain in water fenopropimorph in the case of CSW and fluconazole for EBC. Maximum bioadsorption was observed for trimethoprim (up to 90%) and metropolol (approx. 85%) in the three biosorbents. Respect ASW only eliminate 12 of the 17 pollutants from 10% to 90%, and caffeine, carbamazepine, fluconazole, primidone, and gemfibrozil remain in water. So, these results suggest different chemical interactions occurs during the bioadsorption.

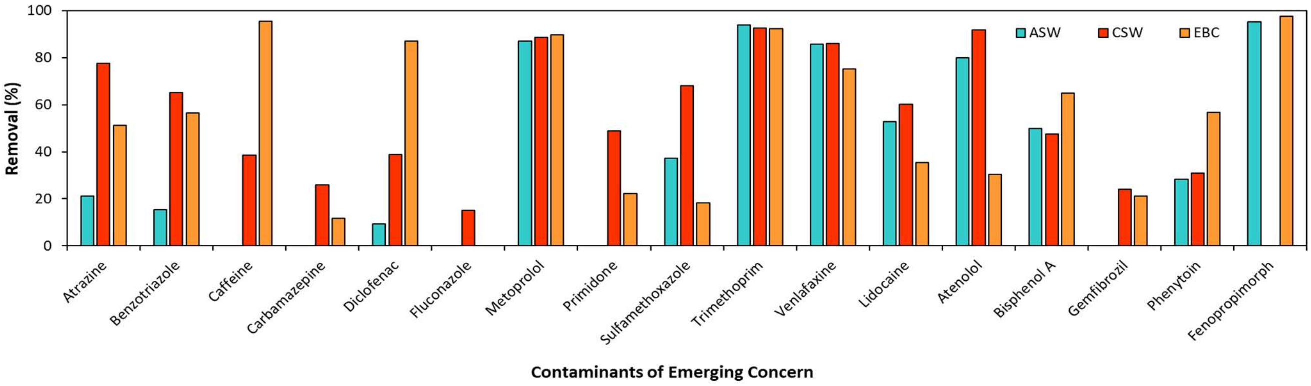

Figure 1. Percentage of removal for multisorption in the biosorbents after 6 days

For example, in the case of atrazine (Figure 2), maximum bioadsorption occur after 24 hours in the case of CSW (up to 80% of removal), and after 6 days for EBC and ASW with approximately 50 % and 20 % of removal. These differences can be due to the competition with other pollutants for the same places of bioadsorption and/or possible π-π interactions produced between aromatic bonds of biosorbents and the pollutant. In general, in this study, the time retention for most pollutants in CSW and EBC achieved after 24 hours, and in ASW after 6 days except for diclofenac and benzotriazole that were of 24 hours. In addition, other factors as molar volume, pka and log kow of the pollutants could influence in the biosorption process.

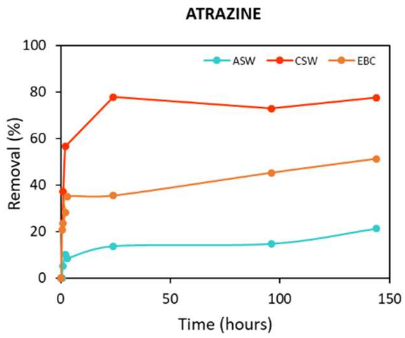

Figure 2. Kinetics of atrazine in multiadsorption for 6 days

Conclusions

The characterization of bioadsorbents revealed high carbon and oxygen content, along with various functional groups such as carboxylic and aromatic bounds. These groups were responsible for facilitating chemical interactions such as π-π interactions or hydrogen bonding, which play a crucial role in the biosorption of emerging micropollutants. Additionally, the physical and chemical properties of micropollutants also effect of biosorption process. The utilization of chestnut and almond shell waste as adsorbents has demonstrated significant potential for positively impacting the circular economy in the future.

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