Adsorption coupled to AOPs to have a quick and definitive elimination treatment of pharmaceuticals from real wastewaters.

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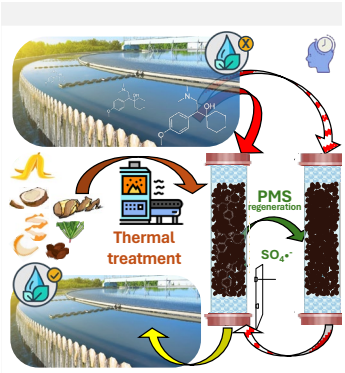

Pharmaceuticals are stable to traditional biological degradation and consequently these recalcitrant pollutants can reach the environment. Adsorption is a quick remediation process which could be easily coupled to wastewater treatment plants (WWTP). In order to increase the green character of this study, agroindustry residues were thermally treated to attain suitable adsorbents for pharmaceuticals. However, the spent adsorbent disposal is not an option and consequently Advanced Oxidation Processes (AOPs) are proposed as a regeneration alternative. In this manner, AOPs are employed for the treatment of highly polluted solid matrixes, favouring their efficiency. Among AOPs, peroxymonosulphate (PMS) and peroxydisulphate (PDS) processes were essayed considering the carbonaceous structure of the synthesized adsorbents could act as catalyst for their activation, avoiding additional costs and pollution associated to traditional AOPs catalysts. With this process, the antidepressant fluoxetine was quickly and efficiently removed.

Introduction

Pharmaceutical compounds are usually toxic to microorganisms and thus, they are persistent to the traditional biological processes on the WWTP. Consequently, pharmaceuticals get released and reach the environment where they impact negatively to flora, fauna and humans. Thus, adsorption processes can be coupled to the effluents on WWTP, trapping quickly the recalcitrant pharmaceuticals which otherwise would be released to the environment [1]. Thus, the low concentration of pharmaceuticals on real wastewaters would possibility the treatment of huge amounts of effluents with a given adsorbent. Various materials can be used as adsorbent among which activated carbon is one of the most efficient. Thermically obtained carbonaceous materials, so-named chars, have been proposed as a greener alternative. These chars present several advantages such as the option of attaining them from the thermal treatment on agroindustry residues, fitting them within circular economy. Among the treatment alternatives, pyrolysis (attaining so-called biochar) and hydrothermal (hydrochar) treatments are suitable for the attaining of materials rich on, respectively, nitrogen and oxygen functional groups which promote adsorption and catalytic behaviours.

It should be noted that spent adsorbents, which would have concentrated high amounts of recalcitrant compounds, should be treated in order to avoid their disposal and favour their reuse. AOPs are well known for their high capacity to degrade non-selectively the organic matter. Hence, they are proposed as an alternative for the regeneration of spent adsorbents. Among AOPs, PMS and PDS oxidations are proposed as a suitable alternative, considering they can be easily activated to generate sulphate radicals ($SO_4^{\bullet-}$). Thus, the utilized chars could *in situ* activate PMS or PDS, acting as catalytic adsorbents. In this manner, the necessity of expensive and pollutant extraction procedures or the usage of metallic catalysts for other AOPs processes, is avoided. Hence, this process has the potential to be easier and more economic to apply than the so far reported ones. This was validated for the elimination of the antidepressant fluoxetine by agroindustry residues and an AOPs regeneration process optimization.

Material and Methods

Agro-industrial by-products, including spent coffee (SC) grounds, spinach stems (SS), rice bran (RB), and the peels from potatoes (PP), bananas (BP), and chestnuts (CP), underwent cleaning, drying, and milling processes before being used for char synthesis.

In hydrothermal synthesis, a 50 mL autoclave was utilized. Into this, 50 mL of water and 8 g of agro-industrial waste were combined. The synthesis process was carried out for 2 h at a temperature of 220°C, resulting in the production of materials known as hydrochars (HC).

For pyrolytic synthesis, an Aero-360 tubular furnace was employed with a N_2 flow of 2 L/min where 8 g of sample were placed. Initial temperature trials were conducted at both 400°C and 800°C to gauge performance, with the most effective materials undergoing further refinement. The process involved heat-treating the residues for 2 h, with a temperature ramp of 10°C/min, leading to the creation of what are termed biochars (BC). The effectiveness of removing fluoxetine was assessed using the prepared chars. Thus, 10 mg of char was mixed with

50 mL of a fluoxetine solution (30 ppm) in a glass tube, which was placed on a rotary shaker. Adsorption experiments were conducted over 24 h at a rotation speed of 80 rpm. In the case of AOPs, either 2 mM of PMS or PDS were introduced into the reaction tubes, and a sample was collected during a 1-h reaction period.

The attained chars as well as the raw materials were deeply characterized in terms of porosity, point of zero charge (PZC), electrochemical properties such as electrochemical impedance spectroscopy (EIS) or the electrochemical active surface area (ECSA), surface state (XPS), order (XRD) and functional groups (FTIR).

Results and Discussion

The assessment of the adsorption capabilities of the synthesized materials revealed that the majority exhibited a satisfactory adsorption capacity (Figure 1), surpassing uptakes of 50 mg/g on most cases. This outperforms previous studies [2]. The choice of the heat-treatment method and the applied temperature significantly influence the adsorption efficiency.

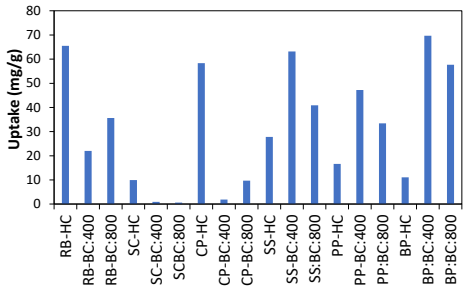

Figure 1. Adsorption efficiency comparison of the attained chars.

Subsequently, the adsorbents were regenerated through PDS and PMS, having the latter a much better performance. As it can be seen on figure 2, the majority of chars were regenerated more than 60 %, providing the possibility of reutilization. This is in concordance with the fact that AOPs are efficient at high pollutant concentrations within solid matrixes [2]. Among the worst regenerating performances, biochar attained from rice bran at 400 and 800 ºC are highlighted. This can be related to their lower PZC which promoted the char to be more negatively charged, attracting fluoxetine more strongly. Moreover, the nitrogen content is more elevated than in other chars, favouring π-π interactions which promote the strong union between pollutant and chars, making the degradation process more difficult.

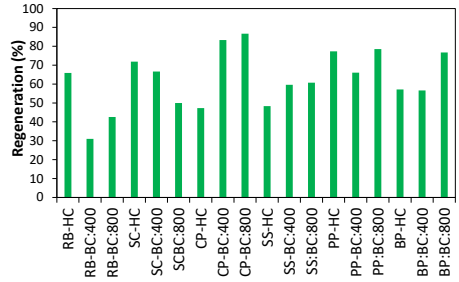

Figure 2. Chars' regeneration after 1 h with PMS (2.5 mM).

Considering an equilibrium between high uptakes and regenerations, biochar attained from banana peels at 800 ºC (BP-BC:800) was selected as the optimal char. This material was reused up to three times attaining uptakes of, subsequently, 57.9, 51.4, 30.5 mg/g. This detriment was explained by the physic-chemical characterization of both initial and regenerated BP-BC:800 where it was found that the structure was damaged and the surface extremely oxidated. However, the performance of this process is comparable to previous studies and proposes a cheaper and greener alternative for the treatment of stable pollutants.

In any case, real wastewaters provided by the WWTP of Guillarei, Galicia were used as working matrix, attaining a fluoxetine uptake of 54.1 mg/g and a PMS regeneration of 75 %. This fact demonstrated that the process can cope with higher effluent complexities, one of the advantages of PMS processes.

Under this conditions column adsorption and subsequent PMS regeneration was carried out, attaining less than 20 % detriment when compared to batch tubes tests, fact associated to preferential pathways generation throughout the adsorbent column. In any case, the high performance attained demonstrates the suitability of this process for real scenarios.

Conclusions

Several agroindustry residues were thermally treated either by N_2-pyrolisis or hydrothermal treatment. The attained materials, respectively BC and HC, showed a remarkable adsorption capacity. Moreover, these carbonaceous materials acted as effective PMS catalysts, favouring the *in situ* regeneration of the spent adsorbents, increasing the suitability of this process for real scenarios. PMS resulted to damage the catalytic adsorbent structure and consequently further studies would be based on the subsequential addition of smaller PMS concentrations, in order to avoid excessive surface oxidation. With this, the reusability of the materials could be increased. This process was suitable for a column adsorption-regeneration process for the treatment of real wastewaters.

Acknowledgments

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