Production of a paper mill sludge-based activated carbon and application in the removal of pharmaceuticals from water

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The application of wastes as new resources is gaining increasing attention by the scientific and industrial community since it is completely in line with the new paradigm of a circular and sustainable economy. The use of industrial residues for the production of alternative adsorbents has been object of several studies. In this context, the use of primary sludge (PS) from the pulp and paper industry (which consists mainly of cellulose) as precursor for the production of carbon adsorbents has already shown to constitute a promising solution (Jaria et al, 2017), namely concerning its use for the removal of pharmaceuticals from water (Calisto et al., 2014; Calisto et al., 2015; Jaria et al., 2015; Ferreira et al., 2016). The use of paper mill sludge to produce alternative adsorbents can, therefore, address two great challenges: the remediation of contaminated waters and the management of an industrial waste in a sustainable way.

In this work, a full factorial design (FFD) was applied to the production of a chemically activated carbon using PS as precursor in order to determine the best production conditions. Four factors at two levels were studied, namely: *a)* temperature of pyrolysis (under N_2 atmosphere) (650 ºC and 800 ºC); *b)* residence time (60 minutes and 150 minutes); c*)* type of activating agent (KOH and K_2CO_3); and *d)* precursor-activating agent ratio (1:1 and 10:1). These factors are known to influence the properties and the adsorbent performance of the final material. The best experimental conditions were then determined by the application of a desirability function where multiple responses were analysed, specifically, the production yield, the adsorption capacity towards different pharmaceuticals (sulfamethoxazole (SMX), carbamazepine (CBZ) and paroxetine (PAR)), the organic carbon content and the specific surface area (S_{BET}). Physical and chemical characterization of the materials with the best responses were performed by means of Fourier Transform Infrared spectroscopy, determination of the zero point charge, determination of the carbons' surface functional groups by Boehm's titrations, proximate and ultimate analysis, and scanning electron microscopy. Very little differences between the two chemical activating agents used and the two residence times tested were observed. The higher temperature (800 ºC) and the 1:1 precursor-activating agent ratio showed the best adsorption performance, resulting, however, in the worst yields. Four production conditions of the FFD analysis presented very good results for the adsorption of the considered pharmaceuticals, indicating that the produced adsorbents are able to compete with commercial activated carbons (Table 1).

Table 1. Comparison between the results for the adsorption percentage (%) of SMX, PAR, and CBZ obtained for one of the produced adsorbents and for one commercial activated carbon.

Carbon adsorbent	SMX Adsorption (%)	PAR Adsorption (%)	CBZ Adsorption (%)
Produced AC	74.7	83.6	84.7
Commercial AC (Norit HDC)	25.8	28.6	13.5

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References

Calisto, V., Ferreira, C.I., Oliveira, J.A., Otero, M., Esteves, V.I., 2015. Adsorptive removal of pharmaceuticals from water by commercial and waste-based carbons. Journal of Environmental Management 152, 83-90.

Calisto, V., Ferreira, C.I., Santos, S.M., Gil, M.V., Otero, M., Esteves, V.I., 2014. Production of adsorbents by pyrolysis of paper mill sludge and application on the removal of citalopram from water. Bioresource Technology 166, 335-344.

Ferreira, C.I.A., Calisto, V., Otero, M., Nadais, H., Esteves, V.I., 2016. Comparative adsorption evaluation of biochars from paper mill sludge with commercial activated carbon for the removal of fish anaesthetics from water in Recirculating Aquaculture Systems. Aquacultural Engineering 74, 76-83.

Jaria, G., Calisto, V., Gil, M.V., Otero, M., Esteves, V.I., 2015. Removal of fluoxetine from water by adsorbent materials produced from paper mill sludge. Journal of Colloid and Interface Science 448, 32-40.

Jaria, G., Silva, C.P., Ferreira, C.I.A., Otero, M., Esteves, V.I., 2017. Sludge from paper mill effluent treatment as raw material to produce carbon adsorbents: An alternative waste management strategy. Journal of Environmental Management 188, 203-211.