Nanomodified activated carbon produced from yeast residues: application in the removal of hormones in water

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Introduction

Due to the advances in medical researches, the use of hormones in several drugs, such as contraceptives, has become increasingly common. Consequently, this fact has led to an increase in these contaminants in water bodies and has been characterized as a global problem, causing several health problems to living organisms. In addition, it has contributed to environmental imbalance, and water or sewage treatment plants cannot remove these substances (Debs et al., 2019). Biosorption arises in the face of this pollution concern, considered a sustainable, efficient, and low-cost option. The process consists of retaining contaminants from an aqueous medium from naturally occurring solids or their derivatives (Wang et al., 2019). Activated carbon is a biosorbent with great adsorbent power due to its high surface area and the presence of several functional groups on its surface, being a highly porous material and presenting a broad range of pore sizes (Jeirani et al., 2017). Nanotechnology allows obtaining biomass particles at the nanoscale. The impregnation of magnetic nanoparticles is reported as an alternative to improve the sorption capacity of the material, enhancing this process (Barbosa et al., 2020). This work proposes to evaluate the potential of a biosorbent produced from yeast residues of the sugar and alcohol industries and its nanomodification with magnetite (Fe_3O_4) to be used in the removal of estrone (E1) from contaminated aquatic environments.

Methods

The activated carbon (AC) was obtained from dry yeast residues from fermentation processes in the sugar and alcohol industry. The AC was produced by activating yeast biomass (YB) with $ZnCl_2$ in a 1:0.8 ratio in a chemical activation process (Modesto et al., 2020).

Preparation of magnetite nanoparticles (MNP) and yeast activated carbon magnetic nanocomposite (YAC-MNP): MNP and YAC-NP were synthesized using the coprecipitation method (Panneerselvam et al., 2011). This method employed solutions of Fe(II) and Fe(III) in a molar ratio of 1: 2 in an acid medium (HCl 1 mol/L). Then, 0.7 mol/L NH_4OH solution was slowly added for 30 min. The synthesis of the nanocomposite YAC-MNP was performed by adding yeast activated carbon (YAC) to this solution, under stirring at 80 ºC for 30 min to form YAC-NP. All reagents ($FeCl_3\cdot 6H_2O$, $FeSO_4\cdot 4H_2O$, HCl and NH_4OH) were PA grade (LabSynth, São Paulo, Brazil).

Point of zero charge (pH_{PZC}) and pH assessment: The point of zero charge (pH_{PZC}) indicates the pH value at which a solid has the number of positive charges equal to the number of negative charges. The pH_{PZC} determination was carried out by mixing 10 mg of the adsorbent with 10 mL of 0.1 mol/L NaCl solution at increasing pH values (1-12) adjusted with HCl and NaOH solutions, under agitation (185 rpm) at 25 ºC. After 24 hours of equilibrium, the solutions were filtered, and the final pH of each resulting solution was measured. After determining the pH_{PZC}, estrone (E1) sorption at pH values lower than pH_{PZC} was evaluated by mixing 10 mg of YAC-MNP with 10 mL of 20 mg/L E1 solution. The mixtures were kept under stirring at 185 rpm for 15 min, and the supernatants were analyzed by UV–Vis absorption spectroscopy (Genesys, 10S, Thermo Fisher Scientific, USA) for E1 determination. These assays were performed in duplicate.

Kinetic studies: The kinetic study of estrone (E1) was performed using 10 mg of YAC-MNP and 10 ml of 20 mg/L E1 solution, kept under constant stirring at 185 rpm. The supernatants were removed at intervals of 5, 10, 30, 60, and 90 minutes, with subsequent determination by UV-Vis at 230 nm. The kinetic models of pseudo-first and pseudo-second-order reactions were applied to the experimental data.

Results and discussion

The point of zero charge (pH_{PZC}) corresponds to where the pH remains constant after the system reaches equilibrium. It was possible to calculate the pH_{PZC} using the arithmetic mean of the points where the final pH stays constant. Based on the results, the YAC-MNP pH_{PZC} was determined to be 6.05. In aqueous solutions with pH values below pH_{PZC}, the adsorbent surface is positively charged, more effectively removing anionic species. When the pH of the aqueous solution is above pH_{PZC}, the surface is negatively charged and, preferably, adsorbs cations. In our study, the E1 sorption tests were performed at pH under pH_{PZC} since the adsorbate is negatively charged.

The evaluation of the effect of pH on the sorption process was carried out in the 2-6 pH range (Fig. 1). The results show that the sorption of E1 by YAC-MNP was equally favorable in all pH values, with no need to adjust the pH value of the solution (approximately 6.3) in future procedures.

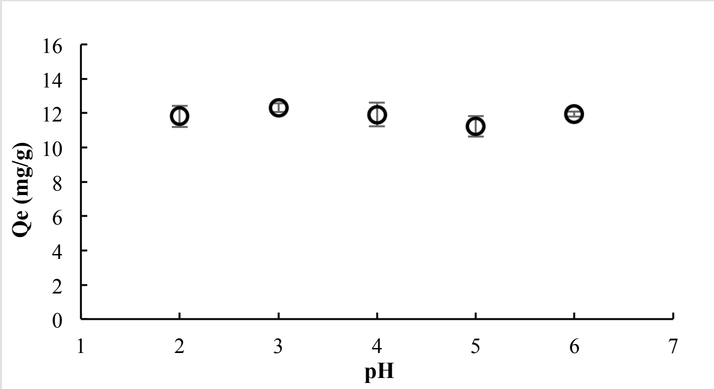

Figure 1. Effect of pH increase on the removal capacity of E1 by yeast activated carbon magnetic nanocomposite (YAC-NP), using 10 mg of the biosorbent with 10 mL solution of 20 mg/L of E1. n = 2

The kinetic tests are based on the adsorption rate of E1 by the biosorbent at increasing contact time in an aqueous medium. The study was carried out at the pH of the solution. As shown in Figure 2, it is possible to observe that the equilibrium in the sorption efficiency is reached at 30 min, with adsorption of 20.76 mg of the contaminant per gram of the biosorbent.

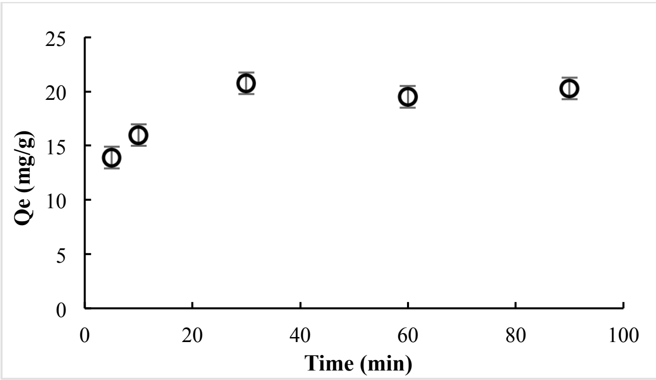

Figure 2. Effect of kinetic increase on the removal capacity of E1 by yeast activated carbon magnetic nanocomposite (YAC-MNP), using 10 mg of the biosorbent with 10 mL solution of 20 mg/L of E1.

Conclusion

The initial results indicate that the synthesized material presents itself as a promising biosorbent to remove estrone in aqueous medium at all pH values investigated, reaching equilibrium in 30 minutes. The presence of MNP facilitates the removal process of the E1-containing biosorbent. Therefore, YAC-MNP showed the potential as an efficient, abundant, and low-cost material produced from the sugar and alcohol industry residues to remove estrone from water.

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References

Barbosa, J. A.; Labuto, G.; Carrilho, E. N. V. M. Magnetic nanomodified activated carbon: characterization and use for organic acids sorption in aqueous medium. Chem. Eng. Commun., 1-14, 2020.

Debs, K. B.; Silva, H. D. T.; Moraes, M. L. L.; Carrilho, E. N. V. M.; Lemos, S. G.; Labuto, G. Biosorption of 17α-ethinylestradiol by yeast biomass from ethanol industry in the presence of estrone. Environ. Sci. Pollut. Res., 26: 28419-28428, 2019.

Jeirani, Z; Niu, C.; Soltan, J. Adsorption of emerging pollutants on activated carbon. Rev. Chem. Eng., 33: 491-522, 2017.

Modesto, H. R.; Lemos, S. G.; Santos, M. S.; Komatsu, J. S.; Gonçalves, M; Carvalho, W. A.; Carrilho, ENVM; Labuto, G. Activated carbon production from industrial yeast residue to boost up circular bioeconomy. Environmental Science and Pollution Research, 28:24694-24705, 2021.

Panneerselvam, P.; Morad, N.; Tan, K. Magnetic nanoparticle (Fe_3O_4) impregnated onto tea waste for the removal of nickel(II) from aqueous solution. J. Hazard. Mater., 186:160-168, 2011.

Wang, L.; Xiao, H.; He, N.; Sun, D.; Duan, S. Biosorption and Biodegradation of the Environmental Hormone Nonylphenol By Four Marine Microalgae. Sci. Rep., 9: 1-11, 2019.