Valorization of spent coffee grounds as biosorbent for the retention of fluoxetine from water – a cost-effective alternative to activated carbon

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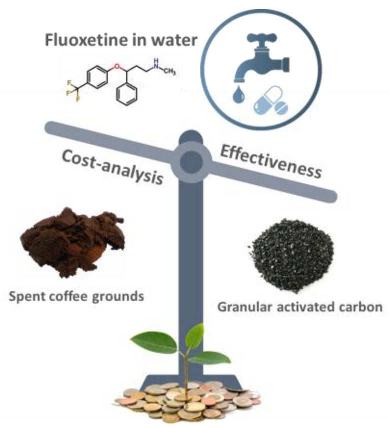

The goal of this study is to evaluate and to compare the effectiveness of spent coffee grounds (SCG), a waste-based biosorbent, and granular activated carbon (GAC) for the removal of fluoxetine, a widely consumed psychiatric pharmaceutical. Equilibrium measurements performed in batch experiments allowed to determine the adsorption capacity of the materials under evaluation. GAC had by far the highest adsorption capacity, 215.0 mg/g, while SCG showed a maximum uptake of 14.31 mg/g. The cost analysis performed revealed that SCG, although presenting lower adsorption capacity, is the most economically feasible adsorbent, with a cost of 0.77 € per gram of fluoxetine removed, that is quite lower when compared to that of GAC, 1.16 €/g. This study demonstrates that SCG is a waste-based biosorbent that may be successfully applied and be cost-effective for the removal of fluoxetine from water.

Introduction

Pharmaceuticals and their metabolites have been introduced in aquatic ecosystems, mainly from effluents of WWTP [1]. According to the Directive 2013/39 EU [2], there is an urgent need to evaluate new ways of reducing their input into the environment. The removal of pharmaceuticals by adsorption is one of most attractive techniques for the treatment of wastewater [3–5]. Although commercial adsorbents, such as activated carbon, provide high removal rates, their high cost is a drawback to their application in large scale systems. Thus, the search for alternative low-cost and biodegradable adsorbents is an urgent need. The use of wastes derived from agriculture has attracted the attention of the scientific community due to their abundance in nature, low price, good mechanical, chemical resistance and biodegradability. Spent coffee grounds (SCG), the solid residues obtained from the preparation of coffee, is an agro-based waste that has been used as low-cost biosorbent in wastewater treatment. The European Union is by far the biggest importer and consumer of coffee, where most of the SCG is currently being incinerated or disposed of in landfills [6]. The conversion of waste materials into adsorbents has, therefore, a double environmental benefit, including improved waste management and environmental protection. The goal of this study is to measure and compare the sorption capacity of activated carbon and spent coffee grounds, as well as to perform a cost analysis in order to select the most economical adsorbent.

Experimental

Fluoxetine-HCl (>98%) was purchased from Sigma-Aldrich. HPLC-grade acetonitrile (Fisher Chemical), phosphoric acid (85%, Merck) and ultra-pure water, obtained from a Milli-Q Millipore system, were used to prepare the mobile phase for fluoxetine quantification by ultra-high performance liquid chromatography (UHPLC). Granular activated carbon, supplied by MERCK, was ground with a mortar and pestle, sieved (< 1 mm) and dried at 105 ºC for 12 h. SCG was collected at a local coffee shop, dried and sieved through a 1 mm mesh in order to uniform particle size. The soluble materials of SCG were removed in contact with a 0.1 M NaOH solution for 3 h in an orbital incubator operating at 40 ºC and 100 rpm. After that, the SCG was washed repeatedly with deionized water and finally was dried during 24 h at 70 ºC. Different masses of SCG and GAC were added to amber Erlenmeyer flasks containing 50 mL of 5 mg/L fluoxetine-HCl solution. The suspensions were kept in an orbital incubator under moderate agitation, 170 rpm, at 25ºC, for the period of time needed to attain the equilibrium. Adsorbent doses between 0.01 and 0.1 g/L were used for GAC while adsorbent doses in the range of 0.1–1.5 g/L were used for SCG. After the equilibration time, samples were taken, filtered and analysed by UHPLC with diode array detection for the determination of fluoxetine-HCl concentration.

Adsorption isotherms

The amount of fluoxetine adsorbed in the equilibrium, q_e (mg/g) was calculated using Eq. (1):

$$q_e = \frac{(C_0 - C_e).V}{w} \quad \text{Eq. (1)}$$

where C_0 (mg/L) is the initial concentration of fluoxetine-HCl solution, C_e (mg/L) is the equilibrium concentration, V (L) is the volume of the fluoxetine-HCl solution and w (g) is the mass of sorbent.

The experimental data were fitted by the Langmuir and Sips isotherm models (Eqs. (2), and (3), respectively) in order to determine the equilibrium parameters of the systems. The models are as follows:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad \text{Eq. (2)}$$

where q_{max} represents the maximum adsorption capacity (mg/g) and K_L is a constant (L/mg).

$$q_e = \frac{q_{max} K_S {C_e}^{1/m}}{1 + K_S {C_e}^{1/m}} \quad \text{Eq. (3)}$$

where K_S is the affinity constant (L/g) and m is a parameter related with the heterogeneity of the system.

Results and discussion

The results obtained from the equilibrium adsorption experiments and the fittings with isotherm models are shown in Table 1 and Figure 1. According to R^2 values presented in Table 1, the Sips model is the one that best fits the adsorption isotherm onto SCG, while for GAC both models fit adequately the adsorption data. GAC was the adsorbent with the highest adsorption capacity, 215.0 mg/g, being fifteenfold the value determined for SCG, 14.31 mg/g. The highest value of the Sips coefficient, K_S, was attained for GAC, which points to a higher affinity of fluoxetine to this adsorbent in comparison with SCG. Although activated carbon is one of the most common and efficient adsorbent used for the removal of micropollutants, such as fluoxetine, its high cost is a significant disadvantage. Therefore, in the present work, an attempt is made to compare the cost of commercial activated carbon and spent coffee grounds, a waste-based biosorbent. The cost for the preparation of SCG biosorbent was calculated based on the performed pre-treatments (washing, heating and drying procedures). For GAC it was only considered its purchase cost. Taking into consideration the values of q_{max} obtained, the total costs were calculated for the removal of 1 g of fluoxetine hydrochloride from water (Figure 2).

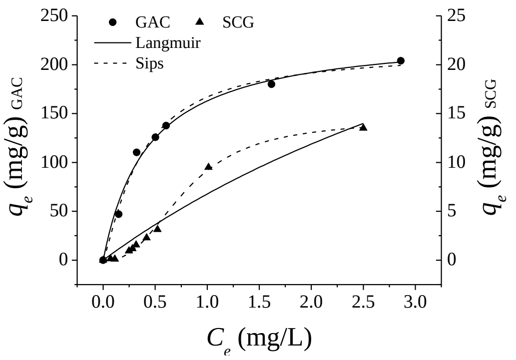

Figure 1. Adsorption of fluoxetine onto GAC and SCG (fittings by Langmuir and Sips isotherm models).

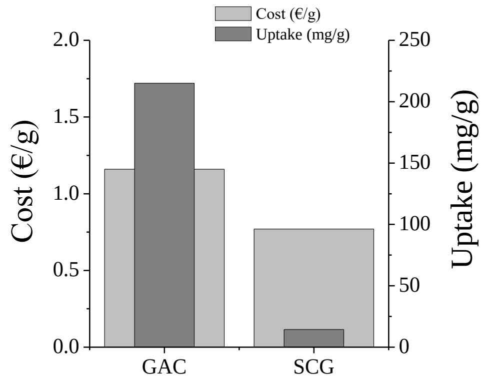

Figure 2. Adsorption capacity of GAC and SCG and respective cost for the removal of 1 g of fluoxetine from water.

The cost for the removal of 1 g of fluoxetine using GAC is 1.16 €, while SCG has a cost of 0.77 €/g. These results indicate that the costs associated with SCG are quite smaller when compared to that of commercial activated carbon.

Conclusions

This study demonstrates that SCG, a waste-based biosorbent, may be successfully applied and be cost-effective for the removal of fluoxetine from water. Adsorption technology employing wastes has a double environmental benefit, namely pollution mitigation and valorization of residues that otherwise would have to be disposed. The use of alternative biosorbents capable to compete with commercially available adsorbents is still an emerging field of research that requires further exploitation.

Table 1. Isotherm parameters obtained from the fitting to experimental results on the adsorption of fluoxetine onto GAC and SCG.

Adsorbent	Langmuir			Sips			
	q_{max}	K_L	R^2	q_{max}	K_S	m	R^2
GAC	233.5 ± 10.4	2.309 ± 0.304	0.988	215.0 ± 13.9	3.46 ± 1.21	1.24 ±0.21	0.989
SCG	48.30 ± 30.22	0.163 ± 0.132	0.931	14.31 ± 0.41	1.78 ± 0.24	2.54 ± 0.15	0.996

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