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Anionic dye removal from aqueous solutions using standard biochars – preliminary study

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Abstract

One of the most serious problems related to water pollution by the textile, plastics, leather and food industries, among others, is the emission of aqueous effluents containing dyes. The most commercially used dyes are resistant to biodegradation, photodegradation and the action of oxidizing agents. The presence of dyes in water bodies can significantly and adversely affect the photosynthesis of aquatic plants by reducing the penetration of sunlight. In addition, they can be toxic to certain forms of aquatic life. Treatment of aqueous effluents containing dyes can involve a variety of materials and techniques, of which adsorption stands out for its simplicity, low cost and efficiency. In this study, standard biochars derived from wheat straw (WSP), oil seed rape straw (OSR) and *Miscanthus* straw (MSP), obtained at two different pyrolytic temperatures (550 °C and 700 °C), were investigated as adsorptive materials for remazol black (RB) dye. Maximum adsorption capacities were obtained at a dosage of 5 g L^{-1} for most of the BCs, except for MSP550, for which the dosage of 10 g L^{-1} achieved the highest performance. pH effect indicated that most of the adsorptive functionalities of the BCs are favored at pH 5. The steps currently in progress refer to the experimental design for the optimization of adsorption parameters and will be added in the full paper.

Keywords: adsorption; anionic dye; biochar.

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1. Introduction

Many studies have demonstrated the excellent ability of different types of biochar to remove contaminants such as heavy metals and organic pollutants from aqueous solutions, some of which are comparable or even superior in this respect to commercial activated carbon [1–4].

The adsorption efficiency of a biochar is strongly influenced by its properties, which are generally linked to the raw material and the production process (mainly pyrolytic temperature and residence time). In addition, some parameters such as dosage, initial concentration, pH, contact time and temperature significantly affect the adsorption process [5].

In view of the above, this study proposes the application of the adsorption technique to evaluate the ability to remove the anionic dye remazol black B (RB) from aqueous solutions, using standard biochars derived from wheat straw (WSP), oil seed rape straw (OSR) and *Miscanthus* straw (MSP), obtained at two different pyrolytic temperatures (550 °C and 700 °C). The dosage and pH were highlighted in preliminary tests, which allowed evaluating the effect of these parameters on the adsorption of RB from aqueous solutions. This was important to define the levels in an ongoing study by a full factorial design, which results will be presented in the full paper.

2. Materials and methods

2.1. Biochars

The standard biochars were supplied by the UK Biochar Research Center (UKBRC, University of Edinburgh). They consist of biochars (BC) produced from oil seed rape straw, wheat straw and *Miscanthus* straw at two different temperatures, 550°C (OSR550, WSP550 and MSP550, respectively) and 700°C (OSR700, WSP700 and MSP700, respectively).

2.2. Synthetic solutions

All solutions were prepared with analytical grade reagents and high purity water, with a resistivity of 18.2 MΩ.cm, obtained by the Barnstead – Easypure system, model D7031 (Barnstead Thermolyne, Iowa, USA). The dye solutions used in the adsorption tests were prepared from the respective stock solutions of the dye: remazol black B (Sigma-Aldrich Co., San Luis, USA).

2.3. Adsorption experiments

The preliminary experiments were carried out using 100 mL beakers, stirring rate of 130 rpm at room temperature (25°C) for 24 h, after which, the mixture was centrifuged at 6,000 rpm for 15 min and the concentration of remaining dye in solution were subjected to quantification by UV-VIS spectroscopy (Pharmacia Biotech Ultrospec 3000, Upsala, Sweden). The spectra were recorded at λ_{max} = 597 nm. The calibration curve for remazol black was obtained using 6 points in a range of 0–100 mg L^{-1}.

The adsorption capacity (q) of each biochar were calculated according to Eq. (1):

$$q_t = \frac{(C_0 - C_t)\,V}{M} \qquad (1)$$

where q is the adsorption capacity of RB (mg g^{-1}), C_0 is the initial concentration of RB in solution (mg L^{-1}), C_t is the equilibrium concentration in solution (mg L^{-1}) at a given time t, V is the volume of the solution (L) and M is the mass of the biosorbent (g).

The extraction efficiency, R (%), will be determined using Eq. (2).

$$R(\%) = 100 \left[\frac{(C_0 - C_t)}{C_0}\right] \qquad (2)$$

where R is the efficiency of extraction or retention percentage, C_0 (mg L^{-1}) is the initial concentration of RB and C_t (mg L^{-1}) represents the concentration of RB at time t.

2.4. Effect of the dosage

Experiments were performed to evaluate the dosage effect of each biochar onto RB adsorption capacity using a 50 mg L^{-1} nominal RB initial concentration solution, with no pH adjustment, and varying the biochars’ dosages as follows: 1, 5, 10, 25, 50, 75 and 100 g L^{-1}. The solutions were then placed on an orbital shaker incubator (model BT 400, Biothec, Brazil) and continuously stirred (130 rpm) at room temperature (25 ± 2 °C) for a contact time of 24 h to allow sufficient time for RB sorption onto each biochar. After that, the supernatant was separated from each biochar by centrifugation at 6,000 rpm and the absorbance was measured by UV-VIS spectroscopy.

2.5. Effect of the pH

This effect was tested by adjusting the initial dye solutions to different pH values ranging from 3 to 12 using 0.1 mol L^{-1} HNO_3 and 0.1 mol L^{-1} NaOH solutions. A previous study [6] already determined that the pH at the point of zero charge (PZC) for the selected standard biochars were above 8.7, indicating that the anionic dye solution must be adjusted at pH < 8.7 to achieve a better performance, since the surface of the BCs are positively charged when $pH < pH_{PZC}$. The experiments were conducted using a 50 mg L^{-1} RB solution and the biochar dosage selected from the previous experiment. The same experimental procedure described in section 2.3 related to separation and time of mixture was also applied herein.

2.6. Characterization of the biochars

The BCs used in this study have been previously characterized by SEM and FT-IR analysis [6].

3. Results and discussion

3.1. Effect of the dosage

The tests were performed using a RB solution with an initial concentration of 47.95 mg L^{-1} (nominally 50 mg L^{-1}), prepared in a 100 mL volumetric flask and, at this stage, no pH adjustment. The removal percentage (R) and the adsorption capacities (q) were calculated and the results are displayed in Figure 1.

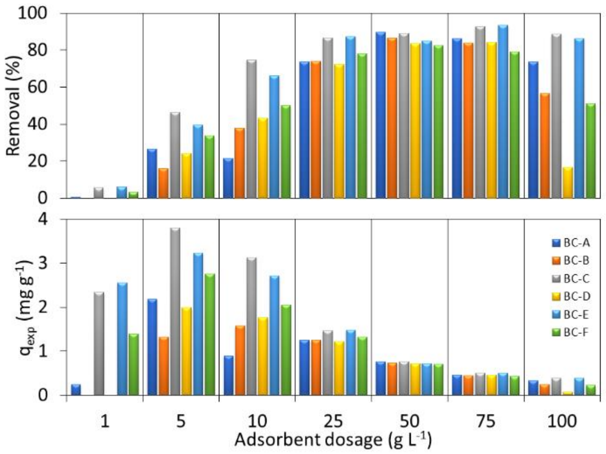

Fig. 1. Removal of RB and the adsorption capacities (q) of the standard BCs in different dosages. BC-A = MSP700. BC-B = MSP500, BC-C = WSP700, BC-D = WSP500, BC-E = OSR700, BC-F = OSR550.

The effect of the adsorbent dosage on the adsorption of RB indicated that the removal rate increases with higher dosages of BC. This increase was more accentuated in the initial points and remained almost steady for dosages higher than 25 g L^{-1}. The initial increase in the removal efficiency can be attributed to the number of adsorption sites available, which increased with the adsorbent dosage. After the sites got saturated, the amount of RB removal reached its maximum at 75 g L^{-1} for WSP550 (84.09%) and WSP700 (92.80%), at 50 g L^{-1} for OSR550 (82.68%) and 75 g L^{-1} for OSR700 (93.34%), at 50 g L^{-1} for MSP550 (86.75%) and MSP700 (89.80%). The measurements obtained for a higher dosage of 100 g L^{-1} were impaired, since the centrifugation process was not sufficient to separate the supernatant from the BC.

On the other hand, the adsorption capacity of the BCs (*q*) increased from 1 to 5 mg L^{-1}, but decreased with increasing adsorbent dosage. This can be attributed to the aggregation or overlapping of the BC adsorption sites, mainly due to the overcrowding of the BC particles, decreasing the total available surface area [7,8]. Generally, the maximum adsorption capacity was obtained at a dosage of 5 g L^{-1} for most of the BCs, except for MSP550, for which the maximum capacity was achieved at 10 g L^{-1} (1.58 mg g^{-1}). Among the tested BCs, WSP700 achieved the highest adsorption capacity (3.80 mg g^{-1}), followed by OSR700 (3.24 mg g^{-1}), OSR550 (2.76 mg g^{-1}), MSP700 (1.32 mg g^{-1}) and WSP550 (1.99 mg g^{-1}). The dosage of 1 g L^{-1} was insufficient to provide enough sites for RB adsorption, while higher dosages (> 25 g L^{-1}) presented lower adsorption capacities as a consequence of partial aggregation, which occurs when larger amount of BC is used, decreasing the active sites [9]. Based on these results, the effect of pH was measured by selecting a uniform dosage of 5 g L^{-1} for all BCs, except for MSP550, for which a dosage of 10 g L^{-1} was selected.

3.2. Effect of the pH

pH plays an important role in dye removal. The effect of solution pH was evaluated by varying the pH of the RB solutions from 3 to 12 (Figure 2).

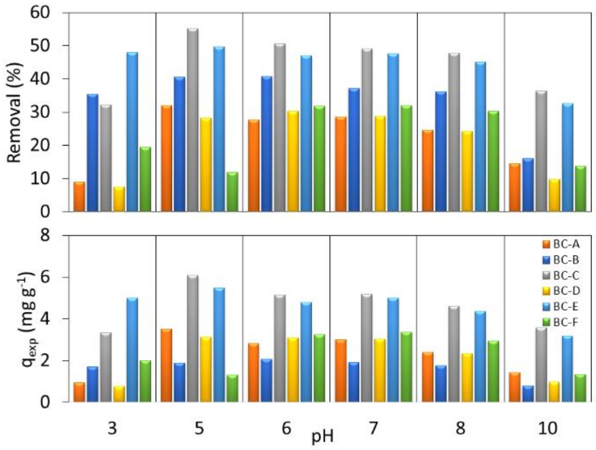

Fig. 2. Removal of RB (%) and the adsorption capacities (q) of the standard BCs in different pHs. BC-A = MSP700. BC-B = MSP500, BC-C = WSP700, BC-D = WSP500, BC-E = OSR700, BC-F = OSR550.

The results corroborated the previous theory that pH values over 8.7 (pH > pH_{PZC}) would compromise the removal of the anionic dye RB. The highest adsorption capacities were achieved for WSP700 (6.08 mg g^{-1}) and OSR700 (5.48 mg g^{-1}) at pH 5, followed by MSP700 also at pH 5 (3.52 mg g-1), WSP550 at pH 5, 6 and 8 (3.11 mg g-1, 3.09 mg g-1 and 3.02 mg g^{-1}, respectively), OSR550 at pH 6 and 8 (3.24 mg g-1 and 3.36 mg g^{-}

^{1}, respectively) and MSP550 at pH 6 (1.91 mg g^{-1}), although at pH 5 it had a similar performance (1.89 mg g-1). pH 5 could be selected for most of the BCs, except for OSR550, which responded best for pH 6 and 8. Reactive dye anions and BCs surfaces undergo electrostatic attraction that results in the enhancement of RB adsorption at lower pH values ($pH < pH_{PZC} = 8.7$) [10]. From these preliminary batch study, pH 5 was identified to be practical and optimum for RB adsorption onto all of the BCs, except OSR550, for which case, a pH value between 6 and 8 could be applied. This was taken into consideration when developing the experimental design.

4. Conclusions

The maximum adsorption capacity was obtained at a dosage of 5 g L^{-1} for most of the BCs, except for MSP550, for which the maximum capacity was achieved at 10 g L^{-1}. The pH effect showed that most of the BCs achieved the highest adsorption capacities at pH 5. The results, so far, empirically demonstrate the potential of WSP770 and OSR700 in the removal of RB from aqueous effluents. Further steps are design experiments for each of them. The results obtained reinforce the need to use alternative methods for industrial effluent treatment, aiming at the utilization of residues and adding value to the Brazilian agricultural productive chain.

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