ANTIBIOTIC ADSORPTION WITH MALT BAGASSE BIOCHAR OPTIMIZED BY CENTRAL COMPOSITE DESIGN

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ABSTRACT

The objective was to evaluate the adsorption capacity of malt bagasse (MB) biochar for the antibiotic levofloxacin (LEV) through a central composite design analysis. The influence of three variables, i.e., LEV initial concentration, MB biochar dosage, and solution pH were analyzed in 5 levels: -1, 0, +1, - α, and +α. The assays were performed in batch with a suspension of buffer solution, LEV, and MB biochar. The maximum adsorption capacity observed (1.108 mg g^{-1}) was at pH 4.51 (level -1), 7.9 mg L^{-1} of LEV initial concentration (level +1), and 4.02 g L^{-1} of MB biochar (level -1), which means that a higher LEV initial concentration, and a lower MB biochar dosage and solution pH increase the adsorption capacity. Through the analysis of the empirical model built with the significative regression coefficients ($p < 0.05$) and the Pareto diagram, it could be concluded that the influence order in LEV adsorption capacity was: LEV initial concentration > MB biochar dosage > solution pH. The results provided by this work highlight the use of a residue as an adsorbent and present adsorption as a promising complementary treatment to manage wastewater and/or water with pharmaceuticals.

Keywords: Micropollutants. Agro-industrial residue. Advanced tertiary treatment. Wastewater treatment.

1 INTRODUCTION

Micropollutants (MPs), also known as emerging contaminants, are a wide group of anthropogenic compounds, as well as natural substances, that are continuously being produced and released in the environment, e.g., pharmaceuticals, hormones, pesticides, personal care products, and microplastics [1]. The adverse effects of MPs in aquatic environments were already stated in organisms at various trophic levels [2]. MPs' low concentration and diversity hinder their detection and provide difficulties for water and wastewater treatment processes. That is why the entry routes of MPs into the ambient are mostly from domestic, hospital, and industrial wastewaters, as well as agricultural, aquaculture, and concentrated animal feeding operation run-offs [3]. Wastewater treatment plants (WWTPs) are not designed to treat such compounds, and their focus is the removal of usual nutrients [1]. There is a significant variability in removal efficiencies (12.5 - 100%) among WWTPs regarding MPs [3]. The research on advanced treatments regarding these environmentally persistent and recalcitrant compounds has been spurred in the literature.

Among these methods, adsorption with carbonaceous materials is an effective treatment for MPs. Adsorption is an advantageous process for MPs treatment since it does not produce transformation products, has a simple design, is easy to operate, has a low initial cost, and is not dependent on a hazardous substance's presence [5]. The adsorbent is responsible for 70% of the operational costs in an adsorption treatment [6]. Brazil stands out as a major contributor to the beer industry, and among the byproducts, malt bagasse (MB) accounts for 85% of the total output from the brewing process [7]. Using MB as a raw material for the conversion into biochar is a promising approach to managing the brewing industry residue and reducing costs associated with adsorbents.

In this scenario, the objective of this study was to evaluate the adsorption capacity of the MB biochar with an antibiotic, levofloxacin, as a promising treatment for wastewater and water contaminated with MPs. A central composite design approach was performed to verify the variable's influence on the response and to obtain the optimal conditions to achieve a higher adsorption capacity.

2 MATERIAL & METHODS

A central composite design (CCD) was performed to evaluate the ideal combination of variables to perform LEV adsorption. The solution pH (x1), LEV initial concentration (x2), and MB biochar dosage (x3) were the independent variables, and the adsorption capacity (y) was the response variable. The variables were studied in three levels: -1, 0, and 1, and two axial points: -α and +α, which enables the construction of a response surface model. In total, 17 experiments were carried out, with triplicates in the central point.

The suspension was composed of buffer solution (acetic acid-sodium acetate, pH 4; potassium phosphate-sodium hydroxide, pH 7; Kolthoff solution, pH 10; Clark-Lubs solution, pH 1.9; Ringer solution, pH 12) [8], LEV, and MB biochar at the determined conditions. The flasks containing 5 mL total volume were placed in a shaker (TE-430, Tecnal, Brazil) at 150 rpm, with the temperature at 25 ± 1 °C for 24 h. The assays were performed in the dark. LEV concentration was measured by a UV-vis spectrophotometer (Hach, DR 5000, USA) at 293 nm wavelength [9]. The significance of each variable was evaluated based on the analysis of variance (ANOVA) and p-value at a significance level of 95%, and the quality of the obtained model was evaluated by the coefficient of variation and by the confidence interval at Statistica 13.5 (StatSoft) software.

3 RESULTS & DISCUSSION

The results obtained by the CCD are presented in Table 1. The maximum adsorption capacity observed (1.108 mg g^{-1}) was at pH 4.51, 7.9 mg L^{-1} of LEV initial concentration, and 4.02 g L^{-1} of MB biochar, while the lowest (0.036 mg g^{-1}) was at pH 7.37, 0.4 mg L^{-1} of LEV, and 7.92 g L^{-1} of MB biochar (Table 1).

Table 1 Adsorption capacity reached for each condition on the CCD analysis.

Run	pH (x1)	LEV (mg L^{-1}) (x2)	MB biochar (g L^{-1}) (x3)	Adsorption capacity (mg g^{-1}) (y)
1	4.35	2.3	4.10	0.379
2	4.35	2.3	11.98	0.161
3	4.51	7.9	4.02	1.108
4	4.51	7.9	12.06	0.570
5	10.18	1.8	4.02	0.071
6	10.18	1.8	12.02	0.137
7	10.26	7.1	3.98	0.492
8	10.26	7.1	12.08	0.291
9	1.56	5.0	7.90	0.397
10	12.25	4.8	8.02	0.355
11	7.37	0.4	7.92	0.036
12	6.98	8.5	8.04	0.731
13	7.38	4.6	1.24	0.844
14	7.38	4.6	14.76	0.272
15	7.38	4.6	8.02	0.373
16	7.38	4.6	7.90	0.377
17	7.38	4.6	8.04	0.461

To analyse the influence of each variable in the response, the ANOVA table and the regression coefficients for the empirical model are presented (Table 2). The variables that showed statistical significance ($p < 0.05$) were x1, x2, and x3. Based on Table 2, only the linear coefficients were considered to build the model, as shown in Equation 1, since the quadratic and interaction variables were not significant ($p > 0.05$).

Table 2 CCD ANOVA table and regression coefficients.

Variable	SS	df	MS	F	p	Model		
						Coefficient	p	Confidence interval
Intercept						0.406 ± 0.064	0.000*	0.254 – 0.559
x1	0.123	1	0.123	9.829	0.016*	-0.095 ± 0.030	0.016*	-0.167 – -0.023
$x1^2$	0.004	1	0.004	0.314	0.592	-0.019 ± 0.033	0.594	-0.097 – 0.060
x2	0.608	1	0.608	48.477	0.000*	0.211 ± 0.030	0.000*	0.139 – 0.283
$x2^2$	0.003	1	0.003	0.232	0.645	-0.016 ± 0.033	0.646	-0.095 – 0.063
x3	0.251	1	0.241	20.042	0.003*	-0.136 ± 0.030	0.003*	-0.207 -0.064
$x3^2$	0.023	1	0.023	1.872	0.213	0.046 ± 0.033	0.212	-0.033 – 0.125
x1.x2	0.040	1	0.040	2.158	0.119	-0.070 ± 0.039	0.118	-0.164 – 0.023
x1.x3	0.048	1	0.048	3.843	0.091	0.077 ± 0.039	0.091	-0.016 – 0.171
x2.x3	0.043	1	0.043	3.433	0.106	-0.073 ± 0.039	0.106	-0.167 – 0.020
Error	0.088	7	0.012					
Total SS	1.244	16						
Model R^2							0.929	
Model R^2 Adj.							0.839	

SS: sum of squares; df: degrees of freedom; MS: mean sum of squares; *p-value < 0.05; coefficient ± standard deviation.

$$y = 0.406 - 0.095.x1 + 0.211.x2 - 0.136.x3 \quad (1)$$

Analyzing the model, the regression coefficients for pH (x1) and MB biochar (x3) were negative, while the coefficient for LEV initial concentration (x2) was positive (Table 2; Equation 1). This implies that a higher initial concentration, a lower biochar dosage, and a lower pH reflect a higher adsorption capacity. A similar conclusion can be achieved by analyzing the maximum and minimal adsorption capacities in Table 1. The Pareto diagram is shown to identify those with the greatest statistical significance (Figure 1). This plot graphically displays the standardized effects for each variable.

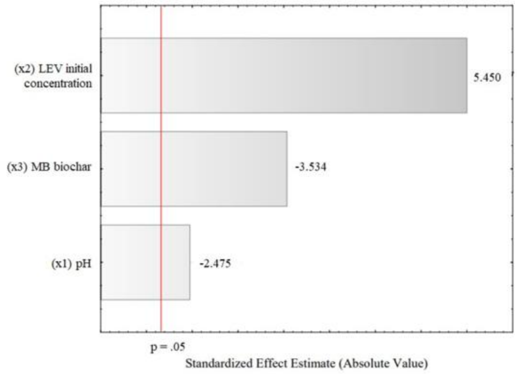

Figure 1 Pareto diagram of standardized effects.

According to Figure 1, the order of the variables that influenced the response was: LEV initial concentration > MB biochar > pH. The initial adsorbate concentration is expected to impact the adsorption capacity simply because if more adsorbate molecules are available in the media, the probability of them being adsorbed is higher. The same logic can be applied to the biochar dosage. A lower dosage enables a higher contact surface between the adsorbate and the adsorbent, enhancing adsorption. For pH, the behavior seen can be linked to the pKa of LEV. LEV has two dissociation constants (pKa 1 = 6.02, pKa 2 = 8.15). Thus, it may present three forms in aqueous media: i) cation, LEV^{+}; ii) anion, LEV^{-}; and iii) zwitterion, $LEV^{\pm}$. In pHs < 6.02, LEV mainly exists as LEV^{+}, while in pHs > 8.15, it is in LEV^{-} form. In between pHs 6.02 and 8.15, LEV has no charge ($LEV^{\pm}$) [10]. In this sense, LEV was dispersed as a cation in acidic conditions, mainly in its zwitterion form at pH 7, and was negative in basic conditions. Depending on the surface charge presented by the MB biochar, the adsorbent may favor the attraction of positive or negative molecules due to coulombic interactions. Since a lower pH is preferable in this scenario, the MB biochar may have a negative surface charge in acid solutions.

4 CONCLUSION

Malt bagasse (MB) biochar was employed in the adsorption of the antibiotic levofloxacin (LEV). The central composite analysis enabled the discrimination of the variables with a significant influence on the adsorption capacity. A higher LEV initial concentration, a lower MB biochar dosage, and acidic pH conditions achieved a higher response. The optimal point was 10 mg L^{-1} LEV initial concentration, 2 g L^{-1} MB biochar dosage, and pH 2.

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