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APPLICATION OF BOILER ASH FROM THE SUGAR-ALCOHOL INDUSTRY AS AN ADSORBENT FOR PARACETAMOL REMOVAL

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ABSTRACT

Water contamination by pharmaceuticals is a growing environmental concern due to overuse and improper disposal. In Brazil, non-steroidal anti-inflammatory drugs (NSAIDs) account for approximately 45% by mass of marketed pharmaceuticals. After use, these compounds are discharged into wastewater systems requiring effective bioremediation strategies and alternatives to conventional processes. One option is the adsorption using non-traditional adsorbents due to their low cost and efficiency. The use of sugarcane bagasse ash has been explored in the literature (in natura or produced in the laboratory), but there is a lack of studies exploring real industrial wastes. The aim of this work was to evaluate the use of sugarcane bagasse ash from industrial boilers in the bioremediation of water contaminated with paracetamol by means of adsorption. For this purpose, a factorial design 2^3 was performed varying the diameter of the ash particles (100-300 µm), the amount of material used (1-3%) and the pH of the solution (5-11), in order to identify conditions of higher paracetamol removal. The best conditions in the range studied were 300 µm, 3% of biomass and pH 5, achieving a paracetamol removal of 75.22%. These results contribute to the development of a process for paracetamol removal using a low-cost adsorbent.

Keywords: Boiler ash. Biosorption. Paracetamol. Agro-industrial waste.

1 INTRODUCTION

Inadequate waste disposal has led to the accumulation of micropollutants in water resources, increasing worldwide concerns about drinking water scarcity, alteration of environmental dynamics and the risks of toxicity[1]. The presence of pharmaceutical waste in water is due to the high excretion of these products by the human body and the improper disposal of medicines, which pass directly through the water treatment and replenishment system[2;3]. In Brazil, non-steroidal anti-inflammatory drugs (NSAIDs) account for approximately 45% by mass of all the total marketed drugs, including paracetamol.

Paracetamol is very popular, administered for its analgesic and antipyretic properties, widely prescribed, sold without a prescription, and often associated with self-medication[4,5]. Furthermore, the impact of the long-term accumulation of this drug is of concern, as up to 9% of administered paracetamol is excreted in its original form[6]. Conventional water treatment processes are not sufficient to remove this drug residues[7]. An alternative is to use the adsorption method, which can be carried out in a batch or fixed-bed column containing a porous adsorbent. The complete adsorption sequence can be demonstrated in three steps: external diffusion, intraparticle diffusion and surface reaction[8]. Adsorption is based on mass transfer, which is influenced by the adsorbent porosity, surface area, pore volume and surface functional group coverage of the adsorbent[9;10]. Potential adsorbents can be domestic or industrial wastes, agricultural products or residues, and other materials[9].

In this context, non-traditional adsorbents have emerged as a cheaper, more advantageous and effective option, with high adsorption capacity and specificity for different pollutants. The use of agro-industrial wastes as adsorbents for pharmaceutical products has been studied in the literature. Various agricultural residues can potentially be used to decontaminate effluents[10]. Sugarcane bagasse is a byproduct of sugarcane processing and for every ton of sugarcane processed, 120 kg of bagasse is produced[11], which is burned in the boiler to cogenerate electricity. After burning, wet bagasse ash is generated and disposed of. However, due to the large amount of ashes generated, the valorization of this waste represents an important strategy to develop a circular economy and contribute to the sustainability of biorefineries. The adsorption of emerging pollutants in sugarcane bagasse ash has been explored in the literature[12-15], but these works generally use bagasse in natura or ash produced in the laboratory, leaving the real waste poorly explored. In this sense, the aim of this work was to evaluate the use of sugarcane bagasse ash from industrial boilers in the bioremediation of water aiming at the removal of paracetamol.

2 MATERIAL & METHODS

The biomass used in this work consisted of wet sugarcane bagasse ash provided by a local sugarcane mill from São Paulo state that co-produce sugar, ethanol and electricity. The biomass was dried in a kiln at 60ºC for 48 hours and stored in a dry place at room temperature. It was then fragmented and sieved into 3 different diameters. The experimental design, shown in Table 1, consisted of 2^3 factorial points and a triplicate at the central point, totaling 11 experiments to verify the influence of the factors studied on the removal of paracetamol from the solution. The range of values of pH and particle diameter were based on preliminary tests, assuming the values of 5, 8 and 11 and 0-100 µm, 101-200 µm and 201-300 µm, respectively. The biomass values were based on the literature, assuming values of 1, 2 and 3% ($m\cdot v^{-1}$)[16;17].

The initial paracetamol solution was prepared at a concentration of 20 mg·L^{-1}, according to the average values of paracetamol in wastewater observed in recent studies[10; 18]. Paracetamol was used in its powdered form (Valdequímica brand), adding deionized water until the desired concentration was obtained. The experimental tests were carried out in triplicate according to the experimental design. The suspensions of paracetamol solution and adsorbent were shaken (approximately 150 rpm) for 120 minutes at room temperature (approximately 24 ºC) and then filtered through a syringe filter. The resulting solution was quantified by UV-Vis spectrometry, at a wavelength of 700 nm, according to the previously assembled calibration curve, determining the remaining concentrations of the drug. The statistical analysis of the experimental design was performed in the Protimiza Experimental Design software.

3 RESULTS & DISCUSSION

The results of removal efficiency obtained from the experimental design using boiler ash and paracetamol solutions are presented in Table 1. The highest removal efficiency was obtained in experiment 4, with 75.22% paracetamol removal. The lowest removal efficiency was observed in experiment 5, with 14.11%.

The organic residues emerge as a viable alternative treatment to remove pharmaceuticals. In a study using bibliometric analyses, it was observed that among the biomasses studied, those from herbaceous and agricultural sources presented the highest adsorption capacity for paracetamol, but obtained the lowest average removal compared to other drugs, with a removal value of 72.3%[19]. In another work, the results indicated that it was possible to obtain 95% of removal under pH 6 and 5 g·L^{-1} of solid adsorbent. However, it was a granular activated carbon[20].

Table 1 Experimental design matrix of paracetamol removal using sugarcane bagasse boiler ash. Where variable levels (-1, 0, +1) are X_1: 0-100 µm, 101-200 µm, 201-300 µm; X_2: 1%, 2%, 3%; and X_3: 5, 8, 11.

Experiment	(X_1) Particle diameter (µm)	(X_2) Biomass quantity (%)	(X_3) pH value	% Removal Efficiency
1	(-1)	(-1)	(-1)	20.46 ± 2.94
2	(+1)	(-1)	(-1)	38.12 ± 3.12
3	(-1)	(+1)	(-1)	44.07 ± 5.00
4	(+1)	(+1)	(-1)	75.22 ± 5.23
5	(-1)	(-1)	(+1)	14.11 ± 5.89
6	(+1)	(-1)	(+1)	30.53 ± 0.61
7	(-1)	(+1)	(+1)	27.22 ± 8.00
8	(+1)	(+1)	(+1)	45.44 ± 6.81
9	0	0	0	41.29 ± 6.30
10	0	0	0	44.23 ± 11.73
11	0	0	0	44.77 ± 12.28

The Pareto chart based on the adsorption tests (Figure 1) shows that all individual variables (X_1 – particle diameter, X_2 – biomass quantity and X_3 – pH) were significant in the experiment with 95% confidence level.

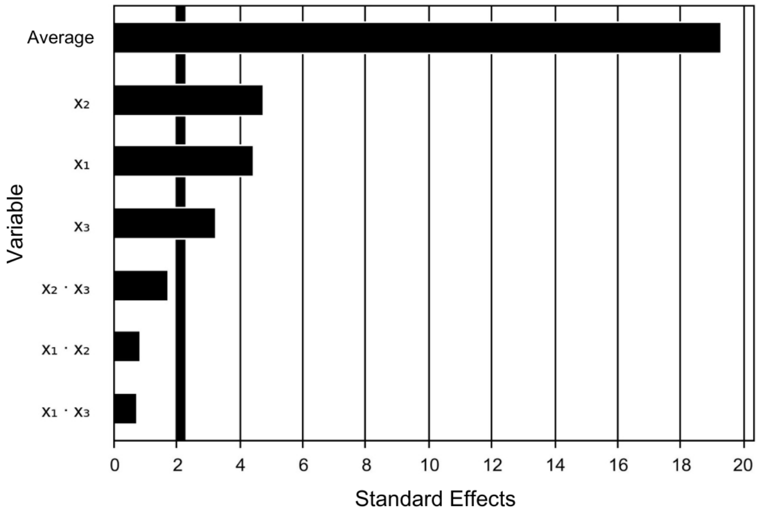

Figure 1 Pareto chart

The variables X_1 and X_2 had a positive effect, while variable X_3 had a negative effect, as can be seen in the adjustment model represented by Equation 1. As a result, the best conditions in the studied range were a diameter of 201-300 µm, an amount of biomass of 3% (m·v^{-1}) and a pH 5. However, the optimum test conditions could not be determined, given the absence of a maximum point or curvature in the surface analysis (Figure 2), which could be studied in the future by extending the study range.

$$Removal\_Efficiency\ (\%) = 38.68 + 10.43\, X_1 + 11.09\, X_2 - 7.57\, X_3 \qquad (1)$$

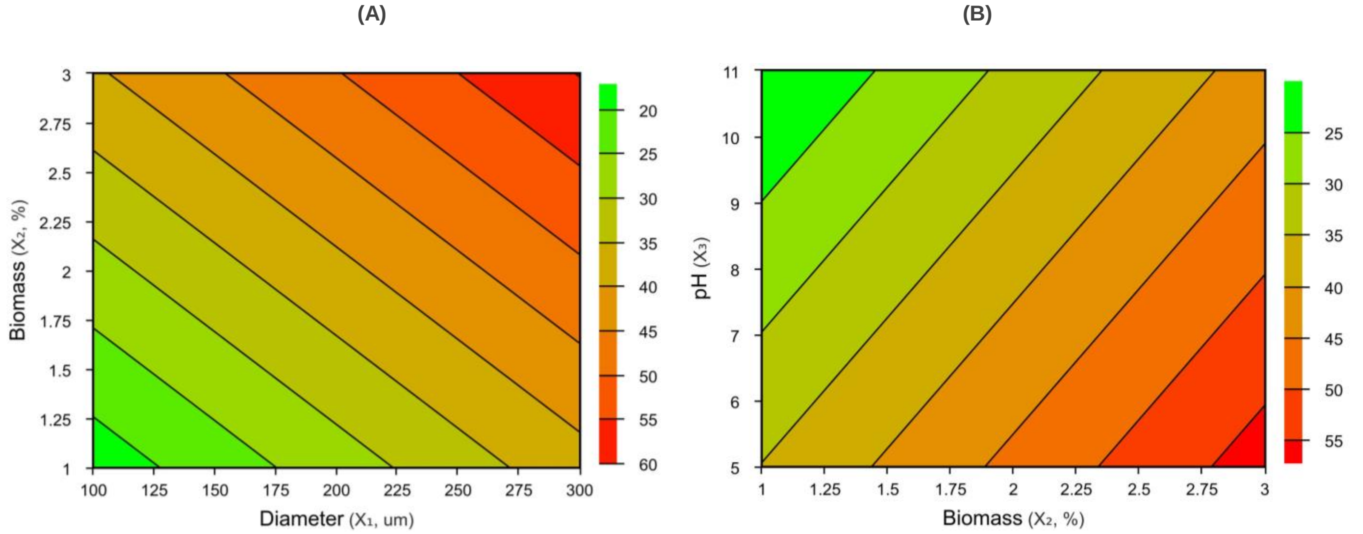

Figure 2 Experimental design response surface of influence of diameter and biomass (A) and pH and Biomass (B) on the paracetamol removal

4 CONCLUSION

The biosorption tests demonstrated a removal efficiency using boiler ash as adsorbent of pharmaceutical paracetamol, showing a maximum of 75.22% removal. Therefore, these results demonstrate that a real agro-industrial waste can be an efficient biomass adsorbent, requiring further studies to obtain the best removal conditions.

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