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Methylene blue biosorption by bone meal using experimental design

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Abstract

This study aims at expanding the knowledge on the applicability of bone meal powder (BMP), and assess its potential as an adsorbent material for methylene blue (MB) removal, a toxic textile dye. BMP is a low-cost material still little studied for the adsorption of contaminants in aqueous media. In this work, we employed the 2^k experimental design (k = 3) to systematically explore the most important process parameters, which were pH of the MB solution, initial MB concentration in solution and biosorbent dosage (mass of biosorbent/volume of contaminated solutions).

Keywords: adsorption; dyes; factorial design; low-cost biosorbents.

1. Introduction

Finding effective ways of removing dyes from effluents is crucial. The most common methods for removing dyes from industrial effluents are biological oxidation (activated sludge), flocculation, chemical precipitation, filtration, ozonation and adsorption. The adsorption process finds extensive industrial applicability, because it associates low cost and high removal rates. Furthermore, in some cases, recovery of the dye without losing its chemical identity is a possibility, as it is a non-destructive process [1–3].

Various types of biosorbents, including yeasts [4–6], algae [7,8], alginate [4,6] and agricultural crops residues, such as sugarcane bagasse ash and husks [9] can be used as low-grade biosorbents [10].

The use of bone meal powder (BMP) for the treatment of aqueous solutions containing methylene blue (MB) has not yet been thoroughly investigated. It is a low-cost, abundant and natural material that has considerable adsorptive capacity. BMP is obtained from industrial meat processing residues and is composed of 65-70% inorganic substances, mainly hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) [11,12].

This study aimed to evaluate the potential of BMP as an adsorbent material for the removal of MB dye from synthetic aqueous solutions. Therefore, synthetic aqueous solutions containing the MB dye were submitted to treatment via biosorption with BMP, using an experimental design to optimize the following parameters: MB's initial concentration in solution, pH of the solution and dosage of the BMP biosorbent.

2. Materials and methods

2.1. Biosorbent

Bone meal (Fênix - Indústria e Comércio de Fertilizantes LTDA-ME, Cidade Cedral, Brazil) was grounded and sieved to obtain particle sizes between 0.297-0.125 mm. Subsequently, they were stored in sealed polyethylene flasks in the laboratory for later use. This material was previously characterized by scanning electron microscopy and electron diffraction spectroscopy [13].

2.2. Synthetic solutions

All solutions were prepared with analytical grade reagents and distilled water. The MB solutions used in the adsorption assays were prepared from the respective stock solutions of the MB dye (Merck, Darmstadt, Germany).

2.3. Adsorption tests

The experiments were performed in batch mode, using known MB concentrations in contact with the biosorbent. Erlenmeyer flasks containing MB solutions and the biosorbent were shaken at 130 rpm at controlled temperature (25 ± 2 °C) in an orbital shaking BT 400 incubator (Biothec, Piracicaba, Brazil). Appropriate masses of BMP were suspended in 50 mL containing MB. Contact time was kept at 24 h. After shaking, the supernatant was separated from the biosorbent by centrifugation at 6,000 rpm for 15 min. First, preliminary experiments were conducted with an adsorbent mass/solution (*M*) of 2 g L^{-1}, initial MB concentration (C_0) of 50 mg L^{-1} and pH 8. Secondly, from these results, a factorial experimental design was proposed, in which *M*, $[MB]_0$, and pH were further investigated. The quantitative determination of MB was performed on a Pharmacia Biotech Ultrospec 3000 UV UV-VIS spectrophotometer (Uppsala, Sweden). The absorption spectrum was recorded by measuring the absorbance at λ_{max} = 668 nm, corresponding to the maximum absorption of MB by UV-VIS. The MB calibration curve was obtained using solutions of different concentrations of MB, in a range from 0 to 20 mg L^{-1} (9 points: 0/0.05/0.5/1/2.5/5/10/15 and 20 mg L^{-1}). The amount of MB adsorbed by the biomaterial was calculated using equation Eq. (1).

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

where q is the adsorption capacity of MB (µg g^{-1}), C_0 is the initial concentration of MB 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 removal percentage, R (%), was determined using Eq. (2).

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

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

2.4. 2^k factorial experimental design

The adsorption experiments were performed based on the equation $n = 2^k$, where n is the total number of experiments and k is the number of variables. To determine the importance of each process variable in terms of maximizing MB removal, a complete factorial design was set up considering the initial concentration of the MB solution (C_0), the pH of this solution and the dosage of the BMP biosorbent (M). The matrix of the complete factorial design of each test with their respective real and coded values is shown in Table 1. In summary, the effect of the variables was evaluated through factorial design 2^3, in triplicate (total of 24 experiments), according to the lower and upper levels of each parameter, represented by (-1) and (+1), respectively. Experimental design and statistical analysis were performed in RStudio [14] with the PID package [15]. Analysis of Variance (ANOVA) of the data was performed with a confidence level of 95% to evaluate the interactions of the independent variables and the main effects on the percentage of MB removal and adsorption capacity.

Table 1. Two-level full factorial experimental design matrix.

Test	*M* (g L^{-1})	pH	C_0 (mg L^{-1})
1	1 (-1)	5 (-1)	25 (-1)
2	4 (+1)	5 (-1)	25 (-1)
3	1 (-1)	11 (+1)	25 (-1)
4	4 (+1)	11 (+1)	25 (-1)
5	1 (-1)	5 (-1)	100 (+1)
6	4 (+1)	5 (-1)	100 (+1)
7	1 (-1)	11 (+1)	100 (+1)
8	4 (+1)	11 (+1)	100 (+1)

Eq. 3 was used to calculate the coded values of the variables, where *var* is the selected variable.

$$\text{coded var} = \frac{var\ (real) - center\ (real)}{\frac{range\ (real)}{2}} \qquad (3)$$

3. Results and discussion

3.1. Experimental design

The exploratory results indicated an adsorption capacity of 23.97 ± 0.14 mg L^{-1}, with a removal of

95.89 ± 0.56 % (M = 2 g L^{-1}; pH = 8; $[MB]_0$ = 50 mg L^{-1}). To search for higher adsorption capacities and removal rates, further experiments were conducted and a factorial experimental design was employed. To provide a better model, the exploratory results were included and named N_0. The response (adsorption capacity) obtained for each experiment is shown in Table 2.

Table 2. Design matrix for MB removal by BMP.

Run	A	B	C	X_A	X_B	X_C	y_1 (mg g^{-1})	y_2 (%)
N_0	2	8	50	-0.3	0	-0.33	24	96
N_1	1	5	25	-1	-1	-1	18	74
N_2	4	5	25	+1	-1	-1	5	87
N_3	1	11	25	-1	+1	-1	18	73
N_4	4	11	25	+1	+1	-1	5	85
N_5	1	5	100	-1	-1	+1	30	30
N_6	4	5	100	+1	-1	+1	13	50
N_7	1	11	100	-1	+1	+1	45	45
N_8	4	11	100	+1	+1	+1	11	44

The model equation represents the role of each variable process and estimates variations in the experimental range. Eq. (4) shows the estimated model.

$$Y_{1,model} = 18.82 - 9.87A + 1.64B + 6.25C - 2.02A:B - 3.16A:C + 1.72B:C - 2.04A:B:C \quad (4)$$

3.2 Statistical analysis

The Pareto chart is shown in Figure 1(a), revealing the significant effects of the independent variables A and C, followed by the interactions A:C, A:B:C and A:B. B (pH) alone was found to play a minor role on the process, although its interactions were more striking as regards the empirical model. A (dosage) was found to negatively act on adsorption capacity, conversely to C (C_0). These effects are illustrated in Figure 1(b) in the contour plot, which also shows the low interaction of these terms.

The Pareto plot indicated that, to increase adsorption capacity, the adsorbent dosage is required to be decreased and the initial MB concentration is required to increase. The contour plot suggested the same behavior, in which higher values are found in the upper left corner of Figure 1(b). The observed curvatures are indications that the interactions of these variables play a role in the process. In real world values, to search optimized experimental conditions, one should design experiments with lower values of M (< 1 g L^{-1}) and higher C_0 (> 75 mg L^{-1}).

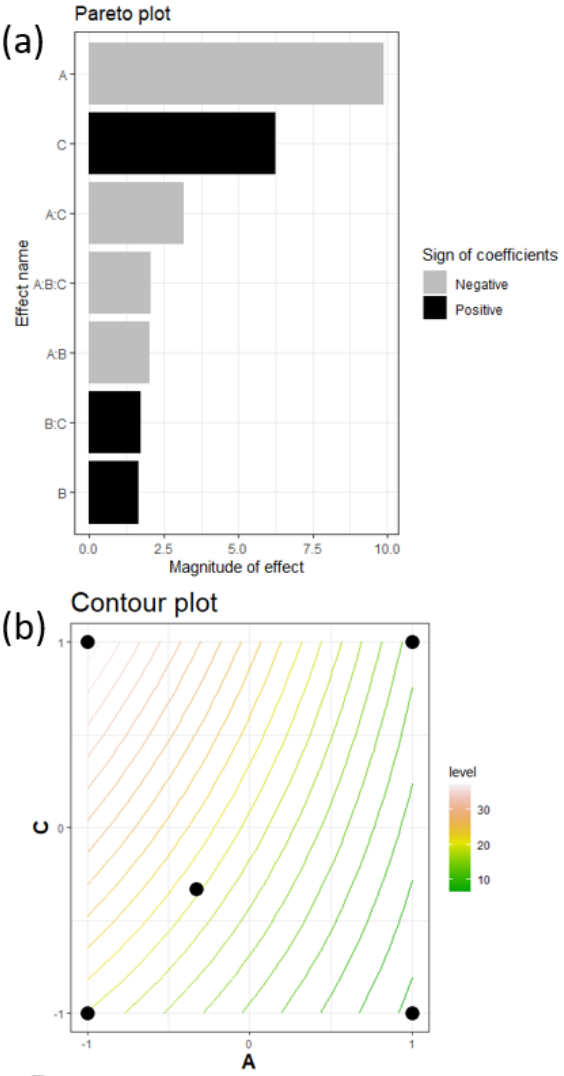

Fig. 1. (a) Pareto plot from the adsorption capacity of BMP on the removal of MB (all effects labeled); (b) Contour plot of the main interaction (A:C) regarding MB adsorption of MB by the BMP

4. Conclusions

N_0 (M = 2 g L^{-1}; pH = 8; $[MB]_0$ = 50 mg L^{-1}) showed the best performance based on the MB removal (R = 96%). Nevertheless, when adsorption capacity is the response of interest, the best experimental conditions were achieved by N7 (M = 1 g L^{-1}; pH = 11; $[MB]_0$ = 100 mg L^{-1}), with 45 mg g^{-1}. The results so far empirically demonstrate the potential of BMP to remove this contaminant from aqueous effluents. Further steps are designing experiments with lower values of M (< 1 g L^{-1}) and

higher C_0 (> 100 mg L^{-1}). The results obtained reinforce the need to use alternative methods of effluent treatment, aiming at the use of residues and adding value to the Brazilian agricultural supply chain.

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5. References

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