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Optimization of Cadmium Adsorption using Poultry Litter Biochar through Response Surface Methodology

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The objective of this study was to evaluate the ability of the poultry litter biochar (PLB) to adsorb cadmium (Cd^{2+}) in aqueous solutions under different experimental conditions including the following factors: Cd^{2+} concentration (5 - 45 mg L^{-1}), solution pH (3 - 7), contact time (2.5 - 2.5 h) and amount of adsorbent (0.5 - 2.5 g biochar) which were modeled by the response surface methodology (RSM). A Central composite design (CCD) was used for experimental runs to optimize the factors studied. Only the mass of the adsorbent and the initial concentration of Cd influenced significantly the process of adsorption of this ion by the PLB. The optimal experimental conditions were found combining a concentration of 45.0 mg L^{-1} of cadmium with 0.5 g of the adsorbent, which corresponds to a maximum adsorption of 1.59 mg g^{-1} of the studied metal.

1. Introduction

The main sources of heavy metal pollution in the environment come from human activities, such as agricultural activity. The application of organic fertilizers, phosphates and some pesticides contain in its composition heavy metals such as cadmium (Cd), zinc (Zn), copper (Cu) and lead (Pb) that contribute to the accumulation in the soil of these toxic potentials (Roberts, 2014). Cd is one of those elements with greater toxicity for humans, which can cause severe toxicity, even in low concentrations.
To remove heavy metal from aqueous solution, and/or soil, some common methods including precipitation, ion exchange, distillation, oxidation, reduction, filtration, electrochemical treatment, evaporation...etc were investigated, however, the sorption process has been used as an effective and economical way to remove heavy metal in recent decades (Babel and Kurniawan, 2003; Yaacoubi et al., 2014).
According to Saffari (2018a), commercial activated carbon has been one of the most common adsorbent materials and widely used in the removal of various pollutants, however the application of this carbon is very expensive (Babel and Kurniawan, 2003). Therefore, there is a growing interest in the use of various low-cost agricultural waste as a heavy metal adsorbent (Tito et al., 2011). One such waste is biochar, known as a product of pyrolysis and porous material, rich in carbon, containing a wide range of reactive functional groups on sorption surfaces, produced from various raw materials, such as biomass wood, animal manure, poultry litter, crop residues and solid residues (Kumar et al., 2011). According to Tan et al. (2015), the efficiency of removing pollutants from each biochar depends on its physical and chemical properties, which are considerably affected by the sources of biomass, pyrolysis time and temperature and pyrolysis conditions. Lima et al. (2017) showed that the physicochemical properties of the poultry litter biochar favored zinc adsorption on soil Argisol and Entisol. According to Chaves et al. (2020), the poultry litter biochar is a mesoporous material with an average pore size of approximately 15.5 nm and a surface area of 7.37 m^2 g^{-1}. The zero-charge point (ZCP) value showed the presence of negative charges on the surface of the biochar, generating a cation exchange capacity of 38.89 $cmol_c$ dm^{-3}. There is little information about the adsorption of cadmium by the poultry litter biochar, therefore, several tests and experimentation time are necessary to evaluate the main factors that influence the adsorption process of this heavy metal. To overcome these problems, the response surface methodology (RSM), an alternative method with a minimum number of tests,

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can be a suitable alternative. The (RSM) is a compilation of mathematical and statistical methods, helpful for fitting the models and analyse the problems in which independent parameters control the dependent parameter (s) (Saffari, 2018b). Therefore, the objective of this study was to evaluate the ability of poultry litter biochar to adsorb Cd^{2+} in aqueous solutions under different experimental conditions including Cd^{2+} concentration, solution pH, contact time, and amount of adsorbent, using the Central composite design (CCD) to optimize the factors studied under the RSM.

2. Material and methods

2.1 Preparation of the adsorbent (poultry litter biochar)

The biochar was produced from poultry litter at the Irrigation and Salinity Laboratory, Department of Agricultural Engineering, Federal University of Campina Grande, under slow pyrolysis at 350 °C for 3 hours, using a muffle furnace. After pyrolysis, the poultry litter biochar (PLB) was ground and sieved to obtain a particle size around 0.053 mm.

2.2 Preparation of adsorbate (Cadmium Solution, Cd^{2+})

The Cd^{2+} solution was prepared from a 1000 ppm stock solution. The desired concentration was obtained by diluting the stock solution with deionized water. The pH of the solution was adjusted with 0.1 mol L^{-1} of HCl or 0.1 mol L^{-1} of NaOH using a digital pH meter.

2.3 Experimental design

The response surface methodology involving central compound planning (CCP) was used in the present study. To assess the influence of operational parameters on the efficiency of Cd^{2+} adsorption (response Y), four factors (independent variables) were used: poultry litter biochar mass (X_1), pH of the initial solution (X_2), stirring time (X_3) and concentration of the Cd^{2+} solution (X_4), each one of the variables in five levels (−2, −1, 0, +1, +2) (Table 1-2). For the four variables, 30 experiments were carried out, including 16 experiments in cubic points, 8 experiments in axial points and 6 repetitions in central points. All experiments were derived from Eq. (1) (Jawad et al., 2015).

$$N = 2^n + 2n + n_c = 2^4 + 2(4) + 6 = 30 \qquad (1)$$

where N is the total number of experiments required and n is the number of independent variables.

For the data treatment, the statistical program Minitab Statistical Software version 18 was used to obtain the effects, coefficients and standard deviation of the coefficients, graphs of the standardized effects, Pareto graph, response surfaces and other statistical parameters of the adjusted models. The quality of the adjusted second order polynomial model was assessed by the coefficient of determination (R^2) and ANOVA.

2.4. Analytical procedure

The Cd^{2+} adsorption tests were conducted according to the CCP. The independent variables showed the following levels: PLB mass (0.5; 1.0; 1.5; 2.0 and 2.5 g), pH of the initial solution (3, 4, 5, 6 and 7), stirring time (2.5; 5.0; 7.5; 10.0 and 12.5 h) and concentration of the Cd^{2+} solution (5, 15, 25, 35 and 45 mg L^{-1}). Each test was performed in a 125 ml Erlenmeyer flask containing 25 ml of Cd solution shacked at 150 rpm/min at room temperature (25 °C) with PLB adsorbent. The combination of the PLB mass, the Cd^{2+} concentration, stirring time and the pH of the initial solution were defined by the CCP. After each stirring period, the samples were collected, filtered with filter paper (blue band, weight of 80 g/m²) and analysed by an Atomic Absorption Spectrophotometer. The amount of Cd^{2+} adsorbed by the PLB (q) was determined by Eq. (2).

$$q\ (mg\ g^{-1}) = \frac{(Ci - Cf)V}{m} \qquad (2)$$

where Ci and Cf are the initial and final equilibrium concentration of Cd^{2+} (mg L^{-1}), respectively. V the volume of the Cd^{2+} solution (L) and m the weight of the PLB adsorbent (g)

Table 1: Planning of central compound and observed and adjusted responses for Cd^{2+} adsorption by poultry litter biochar

Run	Code Levels				Independent variables				Response q (mg g^{-1})	
	X_1	X_2	X_3	X_4	m (g)	pH	t (h)	Ci (mg L^{-1})	Actual	Predicted
17	-2	0	0	0	0.5	5	7.5	25	1.1	1.02
1	-1	-1	-1	-1	1	4	5	15	0.36	0.39
9	-1	-1	-1	1	1	4	5	35	0.86	0.88
5	-1	-1	1	-1	1	4	10	15	0.37	0.40
13	-1	-1	1	1	1	4	10	35	0.86	0.88
3	-1	1	-1	-1	1	6	5	15	0.36	0.40
11	-1	1	-1	1	1	6	5	35	0.86	0.88
7	-1	1	1	-1	1	6	10	15	0.36	0.40
15	-1	1	1	1	1	6	10	35	0.86	0.88
19	0	-2	0	0	1.5	3	7.5	25	0.41	0.39
21	0	0	-2	0	1.5	5	2.5	25	0.41	0.39
23	0	0	0	-2	1.5	5	7.5	5	0.08	0.04
27	0	0	0	0	1.5	5	7.5	25	0.41	0.41
28	0	0	0	0	1.5	5	7.5	25	0.41	0.41
30	0	0	0	0	1.5	5	7.5	25	0.41	0.41
29	0	0	0	0	1.5	5	7.5	25	0.41	0.41
25	0	0	0	0	1.5	5	7.5	25	0.41	0.41
26	0	0	0	0	1.5	5	7.5	25	0.41	0.41
24	0	0	0	2	1.5	5	7.5	45	0.74	0.75
22	0	0	2	0	1.5	5	12.5	25	0.41	0.39
20	0	2	0	0	1.5	7	7.5	25	0.41	0.40
2	1	-1	-1	-1	2	4	5	15	0.18	0.18
10	1	-1	-1	1	2	4	5	35	0.43	0.41
6	1	-1	1	-1	2	4	10	15	0.18	0.18
14	1	-1	1	1	2	4	10	35	0.43	0.41
4	1	1	-1	-1	2	6	5	15	0.18	0.18
12	1	1	-1	1	2	6	5	35	0.43	0.41
8	1	1	1	-1	2	6	10	15	0.18	0.18
16	1	1	1	1	2	6	10	35	0.43	0.41
18	2	0	0	0	2.5	5	7.5	25	0.27	0.33

X_1 = poultry litter biochar mass, X_2 = pH of the initial solution, X_3 = stirring time X_4 = concentration of the Cd^{2+} solution, m = mass, t = time, Ci = initial concentration. The coded levels: +2, -2, +1, -1, and 0 correspond to the values of the independent variables, according to the expressions: Xmax; Xmin; [(Xmax + Xmin)/2] + [(Xmax-Xmin)/4]; [(Xmax + Xmin)/2] - [(Xmax-Xmin)/4] and (Xmax + Xmin)/2, respectively. X is the value of the independent variable.

3. Results and discussion

3.1 Model of the adsorption process and screening of significant factors

The observed and predicted results of Cd^{2+} adsorption by the PLB are shown in Table 1. Using the regression analysis, the coefficients for the developed response model (Cd^{2+} adsorption) and the empirical relationship between the Cd^{2+} adsorption capacity were calculated (q) and the process variables decoded, as shown in Eq. (3).

$$q\ (mg\ g^{-1}) = 0.440 - 0.764X_1 + 0.0199X_2 + 0.008X_3 + 0.03891X_4 + 0.2463X_1^2 - 0.00219X_2^2 - 0.00035X_3^2 - 0.000047X_4^2 + 0.0012X_1X_2 - 0.00050X_1X_3 - 0,01237X_1X_4 - 0.00025X_2X_3 + 0.000063X_2X_4 - 0.000025X_3X_4 \quad (3)$$

where q is the concentration of adsorbed Cd^{2+}, X_1, X_2, X_3 and X_4 are the independent variables, that is, PLB mass, pH of the initial solution, stirring time and concentration of the Cd^{2+} solution, respectively.

The choice of factors that significantly influenced Cd^{2+} adsorption was based on the Pareto graph and the normal probability of standardized effects. Analysing Figure 1A, it can be seen that all standardized effects that showed values greater than 2.13 (p = 0.05), which are located to the right of the dashed line, were significant. The factors whose effects were lower than 2.12 did not significantly influence Cd^{2+} adsorption. Standardized absolute values for the effects of each factor and interactions appear to the right of each bar. Figure 1B refers to the normalized probability distribution curve for standardized effects. All the factors and

interactions that were represented by square markers were significant and these are located outside the central line that crosses the zero value on the abscissa in a 50% probability. The effects positioned in that line were represented by a circular marker and correspond to the estimate of the errors of the effects, not being significant (Ci.Ci, pH.pH, t.t, m.t, t.Ci, pH.t, pH.Ci, m.pH, t and pH). Still, based on Figure 1, it can be inferred that the most important factors in the process of adsorption of Cd^{2+} by the poultry litter biochar were: Ci> m> m.m> m.Ci. The effect of the concentration of the solution and the mass of the adsorbent on the adsorption of this metal was also observed by other authors (Biswas et al., 2019; Iqbal et al., 2016).

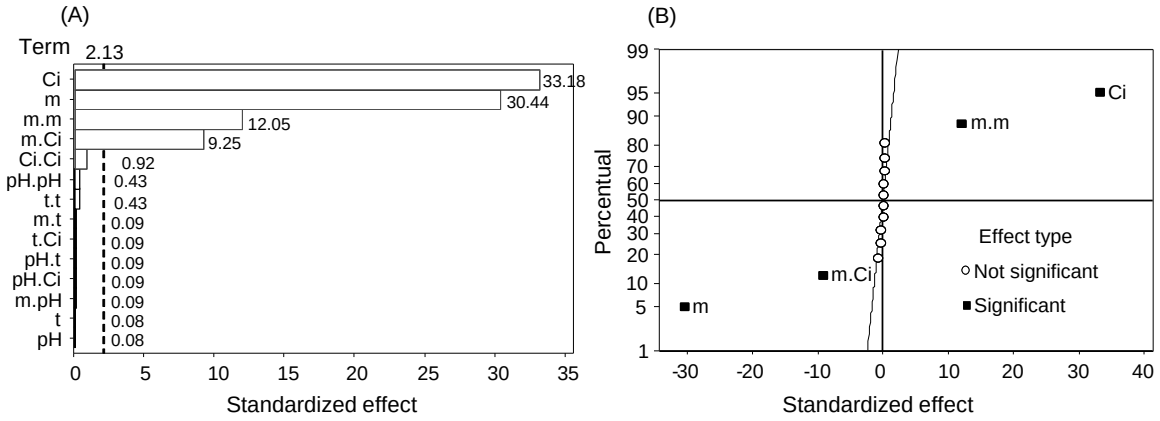

Figure 1: Pareto graph (A) and normal probability (B) of the standardized effects for the response q (mg g^{-1}) at p = 0.05

3.2 Analysis of variance

After defining the isolated and interaction effects that influenced the adsorption of Cd^{2+} by PLB, the analysis of variance (ANOVA) framework was conducted considering the following effects: Ci, m, m^2, Ci^2 and m.Ci, as shown in Table 2. Although the Ci^2 effect was not significant, it was included in the ANOVA to assess the statistical significance of the complete quadratic model, considering a 95% confidence interval.

Table 2: Analysis of variance (ANOVA) of central compound planning for the complete quadratic model predicted for Cd^{2+} adsorption using poultry litter biochar (PLB)

Source	Degrees of freedom	Sum of squares (Aj.)	Mean square (Aj.)	F value	Prob > F
Model	5	1.62627	0.325254	708.94	0.000
m	1	0.66334	0.663337	1445.84	0.000
Ci	1	0.78844	0.788437	1718.52	0.000
m*m	1	0.10973	0.109727	239.17	0.000
Ci*Ci	1	0.00049	0.000488	1.06	0.313
m*Ci	1	0.06126	0.061256	133.52	0.000
Residual	24	0.01101	0.000459		
Lack of fit	19	0.01101	0.000580		
Pure error	5	0.00000	0.000000		
Cor Total	29	1.63728			

Standard deviation = 0.021; R^2 = 0.99, adjusted R^2 = 0.99; predicted R^2 = 0.97

The significance of the coefficients was determined considering a P-value <0.05. As previously discussed, only the Ci^2 effect was not significant. Still in relation to Table 2, it can be seen that the generated quadratic model, its linear and quadratic coefficients and their interaction were significant. The amount of Cd^{2+} adsorbed by the PLB (q) can be determined by Eq. (4).

$$q\ (mg\ g^{-1}) = 0.5203 - 0.7684m + 0.03876Ci + 0.2484m^2 - 0.000041Ci^2 - 0.01238m.Ci \quad (4)$$

The suitability of the model was also confirmed by the F value (708.94) with a P-value <0.05 and by the analysis of the residuals (difference between the observed and predicted response values). This analysis identifies outliers (point outside the curve) and examines diagnostic plots, such as normal probability and

residual plots. The graph of the normal probability of the residue is illustrated in Figure 2A. The trend of the curve reveals that there is no change in the response and no major problem with normality, which was also confirmed by the Anderson-Darling (AD) test, which presented a P-value of 0.054. Figure 2B represents the residual value versus the predicted values for Cd^{2+} adsorption. The points on the graph are scattered at random with a constant range of residuals demonstrating that the variance of the original observations is constant. This also indicates that there are no requirements for transformations of the observed data.

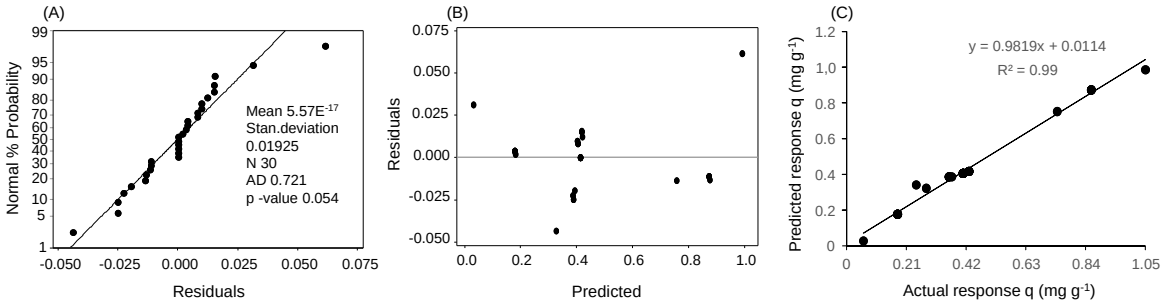

Figure 2: Plots of normal probability for Cd^{2+}adsorption efficiency (A), residual vs predicted values for Cd^{2+} adsorption (B) and comparison of the actual results of Cd^{2+} adsorption with the values predicted by the CCP model (C)

The model's adjustment efficiency was tested by comparing the actual values with the responses predicted by the model for Cd^{2+} adsorption through the multiple correlation coefficient (R^2), whose value corresponded to 0.9982 (Figure 2C). This value suggested that the regression is statistically significant and only 1.2% of the total variations are not explained by the model. The response surface regression, considering the factors adsorbent mass (m) and the initial concentration of Cd^{2+} (Ci), showed a predicted R^2 value (0.97) close to the adjusted R^2 (0.99), indicating that the model is highly significant.

3.3 Process optimization

The response surface methodology was used to evaluate the isolated and combined effect of the factors adsorbent mass (m) and initial concentration of Cd^{2+} on the adsorption of this metal. From the results of ANOVA, the effects of factors m and Ci in terms of the three-dimensional response surface and contour are represented in Figures 3A and 3B, respectively. The response model is represented by Eq. (4).

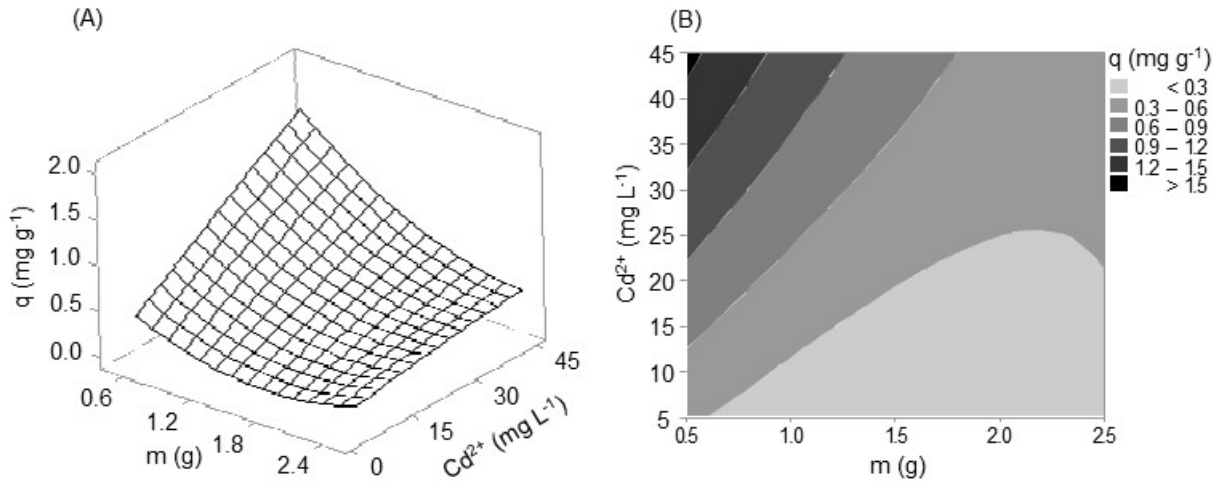

Figure 3: Response surface for Cd^{2+} adsorption (q) versus adsorbent mass (m) and initial concentration of Cd^{2+} (Ci) (A) and contour curves for q (mg g^{-1}) as a function of m versus Ci (B)

According to the highest F value (1718.52), the initial concentration of Cd^{2+} (Ci) had the greatest influence on the Cd^{2+} adsorption process (Table 2). Analysing Figure 3A, it is observed a tendency to increase the adsorption of Cd^{2+} with the increase in Ci and decrease with the increase in the adsorbent mass of the PLB (m). This result shows that the cadmium concentrations used in this study were not sufficient to completely

saturate the binding sites. The negative effect of the "m" factor on Cd^{2+} adsorption is probably due to the formation of aggregates, reducing the binding sites with the increase in PLB mass corroborating Iqbal et al. (2016) and Khalil et al. (2020). The greatest adsorption of the metal ion by PLB occurred in higher initial concentrations of Cd^{2+} regardless of the m range (Figure 3B) confirming the data in Figure 3A. Thus, the optimum operational condition was found at the initial metal ion concentration of 45.0 mg L^{-1} and mass of the adsorbent equal to 0.5 g, which corresponded to a maximum adsorption of 1.59 mg g^{-1} of the studied metal. This result is superior to that verified by Boni et al. (2018), whose maximum Cd^{+2} capacity was 0.8 mg g^{-1} using charcoal.

4. Conclusions

The adsorption of Cd^{2+} by the poultry litter biochar was studied and the optimal conditions were identified using the response surface methodology involving central compound planning. Among the studied factors, only the initial concentration (Ci) and the mass of the adsorbent (m) were significant in the adsorption process. The ideal conditions for maximum metallic ion adsorption were achieved by combining 45.0 mg L^{-1} of cadmium in the initial solution with 0.5 g of the adsorbent.

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