Removal of Cu^{2+} ions from aqueous solutions using modified stalk of Ricinus communis L. in a batch and fixed bed column: Optimization using statistical design methods

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RESUMO – This work investigates the ability of modified stalk of Ricinus communis L., an agricultural biomaterial, to remove Cu ions from aqueous solution in a batch and fixed-bed column. Batch biosorption experiments indicated that the aximum adsorption capacity calculated by Langmuir model (q_{max}) was 131.04 mg/g for for MMB. Three significant variables (bed height, flow and initial concentration) were selected for further optimization via response surface methodology (RSM) based on Box–Behnken model. A statistically quadratic model was constructed on basis of which the three-dimensional response surfaces were plotted.

1. INTRODUÇÃO

Recently, a progressive increase in industrialization and urbanization has substantially enhanced the aquatic environmental pollution by the discharge of industrial effluents containing various pollutants. Among these, the toxic metals produced and consumed by various industrial sectors such as mining, textiles, painting, electroplating, refining and pesticides generate a huge volume of toxic wastewater contaminated with highly toxic metals. Among these metals, copper, mainly from smelting and electroplating industries, is one of the most widespread contaminants and has been a major issue because of its systemic effects such as hemolysis, liver and kidney damage, and fever with influenza syndrome (GANG XIAO, et al. 2013).The discharge of copper wastewater is strictly regulated. Some general techniques for heavy metals removal are ion exchange, nanofiltration, precipitation an activated carbon adsorption. Most of these methods have some limitations for industrial applications, such as high capital and operating costs, incomplete metal ion removal and secondary pollution as hydroxide or concentrated effluents (MELO, *et al.* 2013). Among the various techniques, adsorption from waste is very popular due to its low cost and simplicity.

Biosorption is an efficient and economical method that can be used for the removal of heavy metals from wastewaters. The majority of recent biosorption studies were conducted with low-cost agricultural waste, such as , sugar cane bagasse (SOUSA *et al.* 2009), cashew bagasse (MOREIRA *et al.* 2009), coconut shell (NETO et al.

2012) and all of them have been identified as potential biosorbents for toxic metal removal..

The present study, focuses on adsorption of Cu^{2+} ions from aqueous solutions and fixed-bed using modified stalk of Ricinus communis L.(MMB) as an adsorbent.

2. MATERIALS AND METHODS

2.1 Materials

Analytical-grade chemicals and ultrapure water (Millipore Direct Q3 Water Purification System) were used to prepare the solutions. Stock solutions of Cu^{2+} (500 $mg.L^{-1}$) was prepared with $Cu(NO_3)_2.3H_2O$, (Merck, São Paulo, Brazil). The acetate buffer was prepared with sodium acetate and glacial acetic acid. NaOH (0.10 $mol.L^{-1}$) and HCl (0.10 $mol.L^{-1}$) solutions were used for pH adjustments.

2.2 Alkaline treatments

MMB was treated with different concentrations of NaOH (5, 10 and 15% w / v) for 4 h at 60 °C, then washed with deionized water until neutral, and dried at 60 °C.

2.3 Adsorption performance evaluation of MMB

The adsorption ability of MMB was evaluated by the batch adsorption experiments.0.05 g MMA was added to conical flasks containing 50 ml Cu^{2+} solution with determined concentration from 20 to 500 mg/L. The mixture was shaken in a reciprocal shaker (200 rpm) at 28ºC for 2 h. The final concentration was measured by an Atomic Absorption Spectrophotometer (933 plus, GBC, Sydney, Australia). The adsorption capacity of Cu^{2+} was determined by mass balance calculation

$$q_e = \frac{(C_o - C_e)}{W} V \quad \text{(Eq. 1)}$$

where: q_e is the equilibrium adsorption capacity (mg of metal/g adsorbent), C_o is the initial concentration of the metal ion ($mg.L^{-1}$), C_e is the equilibrium concentration of metal ion ($mg.L^{-1}$), V is the volume of the solution (L), and W is the mass of adsorbent (g). Control experiments were carried out in the absence of adsorbent to check for any adsorption on the walls of the flasks.

2.3 Optimization by response surface methodology (RSM): Fixed-bed experiments

An adsorption column (30 cm height and 1.0 cm diameter) was manufactured. The experiments design was used to choose the important factors with affect the Cu^{2+} adsorption efficiency. The three factors, including initial Cu^{2+} concentration, bed height and liquid flow rate, were studied at three coded levels and a set of 15 experiments (3 central points) were conducted using the Box–Behnken design (Table 1)(BOX, *et al.* 1978).

Table 1 – Coded factors and Box-Behnken design matrix with results

Code	Factor (unit)	(-)	0	(+)
A	Liquid flow rate (mL/min)	1	2	3
B	Bed Height (cm)	5	7.5	10
C	Initial Cu^{2+} conc. (mg/L)	100	200	300

Run	Coded Factors			Response
	A	B	C	$q_{Cu(II)}$
1	–	–	0	13.34
2	+	–	0	14.17
3	–	+	0	*
4	+	+	0	16.88
5	–	0	–	8.82
6	+	0	–	*
7	–	0	+	15.45
8	+	0	+	12.20
9	0	–	–	5.04
10	0	+	–	10.61
11	0	–	+	13.06
12	0	+	+	29.38
13	0	0	0	16.53
14	0	0	0	16.27
15	0	0	0	16.67

* Misleading experiments. Not included in the model.

Minitab statistical software (version 16) was used to design and analyze the experiments. The results obtained were fit to a second-order polynomial model. The analysis of variance (ANOVA) was performed at a significance level of $p < 0.01$. The model fitted to the experimental data could be described by the following equation:

$$q_{Cu(II)} = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2$$

where $q_{Cu(II)}$ represents the response, namely Cu(II) adsorption capacity, β_0 is the offset term, β_i, β_{ij}, β_{ii} are the regression coefficients of the first-order main effects, the interaction effects and the second-order main effects, respectively.

Surface plots were constructed to observe the regions were the response is maximized. The Minitab Response Optimizer tool was used to show what set of variables leads to maximum adsorption. Graphical representation in form of an optimization plot was used to visualize the optimum point.

3. RESULTS AND DISCUSSION

3.1 Influence of alkaline treatments

The most effective removal of metal ions occurred at a concentration of 15%, with adsorption capacities 28.52 mg/g for Cu^{2+}. This process, smaller hydrates of the sodium hydroxide dipole penetrate into the cellulose crystalline regions and destroy the strong intermolecular. Thus, the increase in adsorption capacity on MMB submitted to alkaline treatment can be attributed to the formation of cellulose type II, which has more hydroxyl group available to react with the metal. The fibers modified with 15% (w/v) sodium hydroxide were used for subsequent experiments.

3.2 Adsorption performance of MMB

In order to evaluate the application potential of MMB as an adsorbent a series of batch adsorption experiments the results were shown in Fig. 1.

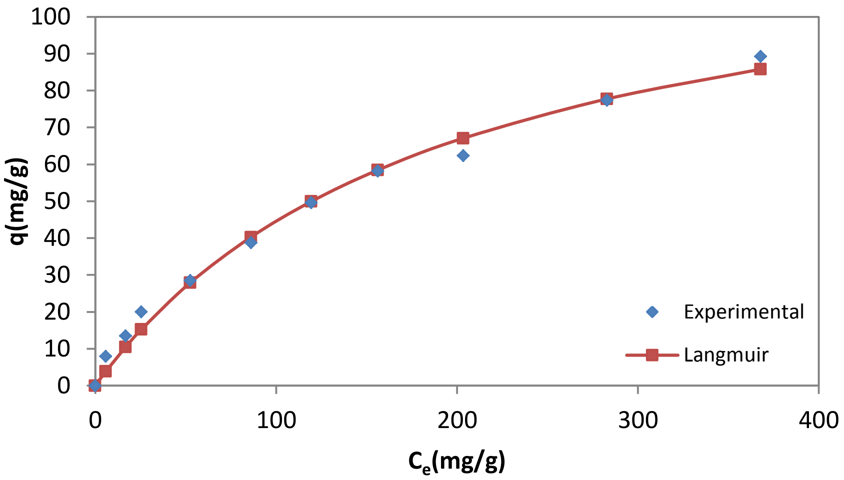


Figure 1. Adsorption capacity of MMB

As can be seen from Fig. 1, MMB similar Langmuir adsorption equilibrium relationship. The maximum adsorption capacity calculated by Langmuir model (q_{max}) was 131.04 mg/g for for MMB.

3.3 Results of the response surface design

The Box-Behnken design was used to determine the optimum levels of the three factors in the column biosorption of Cu^{2+} by MMB. The analysis of variance (ANOVA) results are shown at table 2. The ANOVA results indicate the significance of the model (P = 0.001) indicating that there are a relationship between the factors and the response. The determination coefficient at 99% of confidence level was 0.9873 which demonstrates the high correlation between the observed and predicted values while the rest (1.27%) was explained by the residues.

In table 2 the sum of squares is used to estimate the factor effects and F-ratios are defined as the ratio of the respective mean square effect and the mean square error. Since $F_{0.01,1,3}$ = 34.12, all effects presenting F higher than 34.12 are statistically significant. The non-significant lack of fit (F = 27.61, did not exceed 34.12) explain that the quadratic model is valid for the present work.

It can be observed that each main factor, interaction factor and second order factor have one degree of freedom, leaving 3 degrees to determination of error. The number of degrees of freedom in a model is equal $n - 1$, where n is the number of experiments performed. A traditional Box-Behnken design performed without replicates and with three central points have 14 degrees of freedom. Since the determination of each factor uses only one degree of freedom, it would remain 5 degrees to determination of total error. In this case, $F_{0.01,1,5}$ = 16.26 and it would be more likely that an effect would be considered of statistical significance. But it can be seen at table 2 that at a confidence level of 99% the only factor not statistically significant was A^2. Thus, the exclusion of two experimental points in the dataset did not invalidate the model.

Table 2 – Analysis of Variance (ANOVA) for the quadratic model

Source	Sum of squares	DF	Mean square	*F*	*P*
Regression	384.59	9	42.73	104.38	0.001[a]
A	50.56	1	50.56	123.50	0.002
B	155.45	1	155.45	379.71	0.000
C	201.62	1	201.62	492.51	0.000
AB	35.56	1	35.56	86.86	0.003
AC	14.88	1	14.88	36.34	0.009
BC	28.94	1	28.94	70.69	0.004
A^2	10.09	1	10.09	24.66	0.016
B^2	49.30	1	49.30	120.45	0.002
C^2	95.00	1	95.00	232.05	0.001
Lack of Fit	1.15	1	1.15	27.61	0.034[b]
Pure Error	0.08	2	0.04		

$F = MS_{FACTOR}/MS_{ERROR}$; $R^2 = 0.9968$, $R^2adj = 0.9873$

[a] Significant under 99% level of confidence.

[b] Not significant relative to the pure error due to noise.

The second order model for Cu^{2+} adsorption capacity in terms of coded factors is as follows:

$$q_{Cu(II)} = \underset{(\pm 0.37)}{16.49} - \underset{(\pm 0.39)}{4.35A} + \underset{(\pm 0.29)}{5.69B} + \underset{(\pm 0.29)}{6.48C} - \underset{(\pm 0.49)}{4.55AB} + \underset{(\pm 0.49)}{2.95AC} + \underset{(\pm 0.32)}{2.69BC} + \underset{(\pm 0.46)}{5.07B^2} - \underset{(\pm 0.46)}{7.03{*}C^2}$$

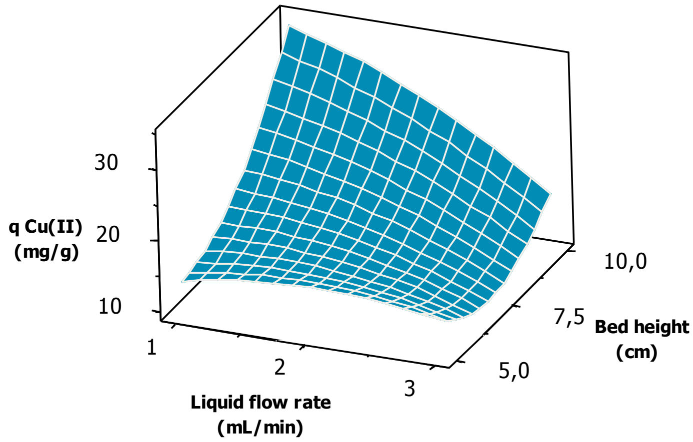
where *A*, *B* and *C* are the coded values of the studied variables, liquid flow rate, bed height and initial Cu(II) concentration, respectively. Note that the factor A^2 is not shown at the model as it is insignificant at the level of confidence of 99%.

The main effects (*A*, *B* and *C*) represent deviations of the average between high and low levels for each of them. In case of variable *A* (liquid flow rate), a change in the variable from low to high level results in 8.70 mg/g decrease in the adsorption capacity. If a variation from low to high level is made for *B* (bed height) and *C* (initial Cu(II) concentration), increases of, respectively, 11.38 and 12.96 mg/g in the adsorption capacity are observed.

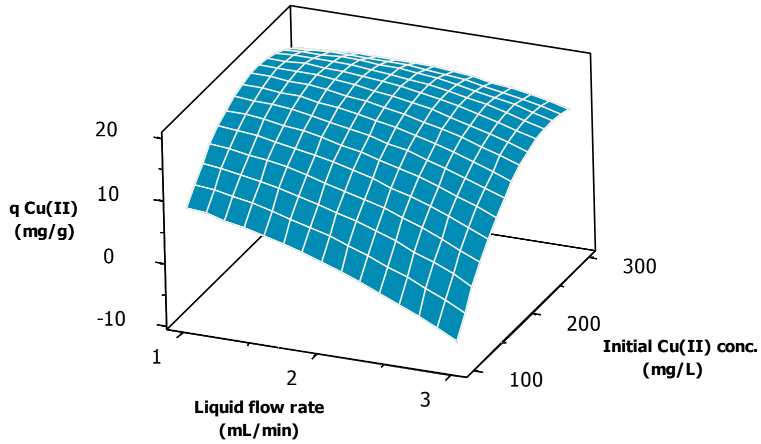
The interaction effects (*AB*, *AC*, and *BC*) represent the difference in deviations of the average between high and low levels of a factor, while maintaining a second factor in low level an after in high level. In case of *AB* (interaction between liquid flow rate and bed height), a difference between the change in variable A from low to high level while maintaining variable B at low level and after at high level gives a decrease in total adsorption capacity of 9.10 mg/g. It means that an increase in variable *A* provokes a higher decrease in response when variable *B* is at its higher level. The same interpretation can be made to the other interaction effects. The increase in variable *A* provokes a higher increase in response when variable *C* is at its higher level. A difference of 5.90 mg/g in the adsorption capacity. The same manner an increase in variable *B* leads to an adsorption capacity 5.38 mg/g higher when variable *C* is at high level.

The second order terms (B^2 and C^2) represent the curvature of the model. The higher the β value the higher the curvature. The signal indicates the concavity of surface. A positive signal denotes the existence of a minimum and a negative signal the existence of a maximum. It means that at some point while varying variable *B* from low to high level the adsorption capacity comes to a minimum, and then begins to increase again. The same happens with variable *C*. At some point a maximum is achieved, and then the adsorption capacity begins to decrease.

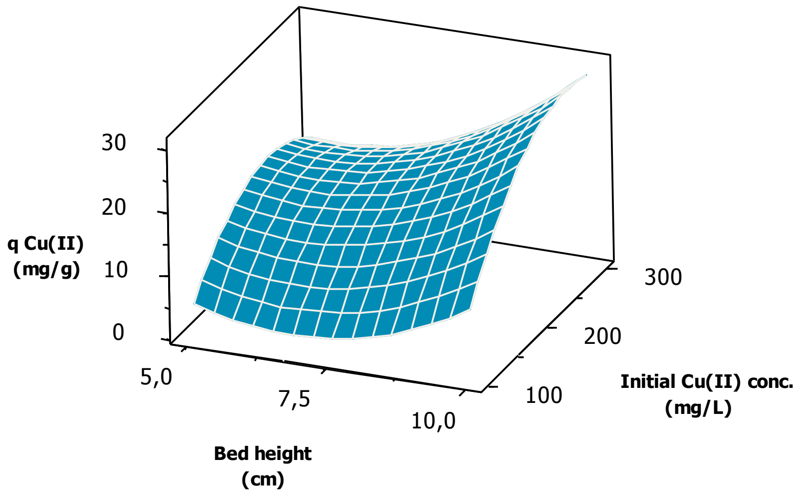
The three-dimensional response surfaces were plotted based on the fitted regression model as presented in Figure 2.



(a) Effect of liquid flow rate and bed height on Cu(II) adsorption



(b) Effect of liquid flow rate and initial Cu(II) concentration on Cu(II) adsorption



(c) Effect of bed height and initial Cu(II) concentration on Cu(II) adsorption

Figure 2. Response surface plots for Cu(II) adsorption capacity. Hold values (Liquid flow rate: 2 mL/min; Bed height: 7.5 cm; Initial Cu(II) conc.: 200 mg/L).

As can be seen in figure 1(a), when bed height is higher than 7.5 cm, the liquid flow rate has a negative effect on Cu^{2+} adsorption capacity, while when it is lower than 7.5 cm the liquid flow rate almost do not influence the response. Bed height has a positive effect on response, with higher effect when liquid flow rate is 1mL/min.

Figure 1(b) illustrates the effect of liquid flow rate and initial Cu^{2+} concentration on response. We can observe that the liquid flow rate influences the response negatively, but this effect is more pronounced when initial Cu^{2+} concentration is low. Initial Cu^{2+} concentration have a positive effect on response.

From figure 1(c) we can see that both bed height and initial Cu^{2+} concentration have a positive effect on response. This phenomenon could be explained as: for the lower bed height there was not adequate binding sites for toxic heavy under higher initial Cu^{2+} concentration; when the bed height was greater, the active adsorption sites were enough and the higher initial concentration meant larger mass transfer driving force (FUTALAN *et al*. 2011)

The optimization plot for the quadratic model is presented in figure 3.

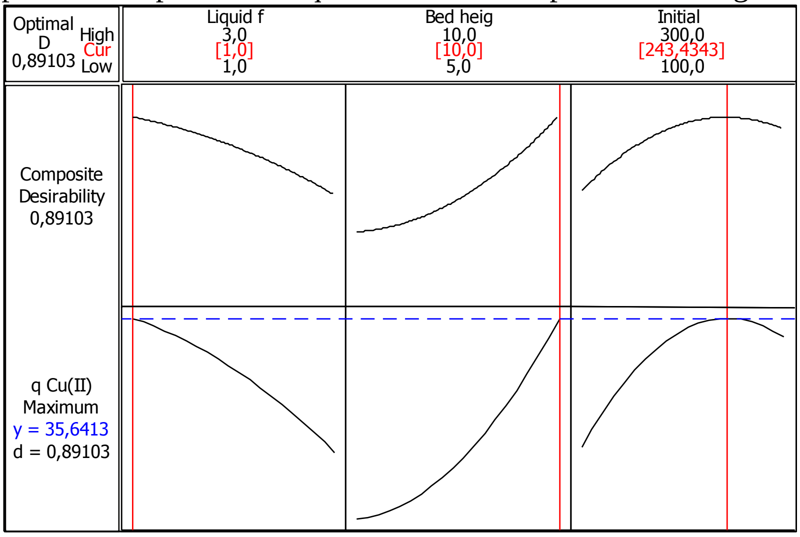


Figure 3. Optimization plot for the model.

The optimization plot shows the effect of each factor (columns) on the responses or composite desirability (rows). The vertical red lines on the graph represent the current factor settings. The numbers displayed at the top of a column show the current factor level settings (in red). The horizontal blue lines and numbers represent the responses for the current factor level. The composite desirability, *d*, is a factor to express how close of the target value is the predicted response. The optimization tool was performed setting a target value of 40.00 mg/g. This value is arbitrary and affects only the value of *d*, but the optimum experimental conditions remain the same. The optimization plot indicates that by maintaining the liquid flow rate at 1 mL/min, using a bed height of 10 cm and an initial Cu2+ concentration of 243.43 mg/L the maximum adsorption capacity for the designed system can be achieved, q_{Cu2+} = 35.64 mg/g. Further experiments may be performed to confirm the validity of this statement.

CONCLUSÕES

The copper adsorption process was optimized using Box–Behnken design. A significant quadratic regression model was established with the small error. The optimization plot indicates that by maintaining the liquid flow rate at 1 mL/min, bed height of 10 cm and initial Cu^{2+} concentration of 243.43 mg/L the maximum adsorption capacity for the designed system can be achieved, q_{Cu2+} = 35.64 mg/g. MMB showed high adsorption capacity for giving is to be a promising adsorbent for industrial applications of heavy metals wastewater treatment.

REFERENCIAS

BOX, G. E.; HUNTER, W. G.; HUNTER, J. S. *in Statistics for Experiments*, Wiley, New York, 1978.

FUTALAN, C.M., KAN, C.C., DALIDA, M.L., PASCUA, C., WAN, M.W., Fixed-bed column studies on the removal of copper using chitosan immobilized on bentonite. *Carbohydr. Polym*. 83, 697–704, 2011.

MELO, D. Q.; GOMES, E. C. C.; RAULINO, G. S. C.; LONGHINOTTI, E.; NASCIMENTO, R. F . Adsorption equilibria of Cu^{2+}, Zn^{2+}, and Cd^{2+} on EDTA-functionalized silica *J. Chem. Eng. Data*, 58; 798-806, 2013.

MOREIRA, S. A.; SOUSA, F. W.; OLIVEIRA, A. G.; BRITO, E. S.; NASCIMENTO, R. F. Remoção de metais de solução aquosa usando bagaço de caju *Quim. Nova*. 32, 1717-1722, 2009.

NETO,V. O. S.; CARVALHO, T. V.; HONORATO, S. B.; GOMES, C. L.; FREITAS, F. C.; SILVA, M. A. A.; FREIRE, P. T. C.; NASCIMENTO, R. F. Coconut bagasse treated by thioureia/ammonia solution for cadmium removal: kinetics and adsorption equilibrium *Bioresources*, 7, 1504-1524, 2012.

SOUSA, F. W.; SILVA, M. J. B.; OLIVEIRA, I. R. N.; OLIVEIRA, A. G.; CAVALCANTE, R. M.; FECHINE, P. B. A.; SOUSA NETO, V. O.; DE KEUKELEIRE, D.; NASCIMENTO, R. F. Evaluation of a low-cost adsorbent for removal of toxic metal ions from wastewater of an electroplating factory *J. Environ. Manage*.89, 1-5.2009.

XIAO, G.; ZHANG, X.; SU, H.; TAN, T. Plate column biosorption of Cu(II) on membrane-type biosorbent (MBS) of Penicillium biomass: Optimization using statistical design methods *Bioresource Technol*, 143, 490–498, 2013.