Adsorption of Cu(II) on *Araucaria angustifolia* wastes: Determination of the optimal conditions by statistic design of experiments

Eder C. Lima [a,*], Betina Royer [a], Júlio C.P. Vaghetti [a], Jorge L. Brasil [a],
Nathalia M. Simon [a], Araci A. dos Santos Jr. [a], Flavio A. Pavan [a],
Silvio L.P. Dias [a], Edílson V. Benvenutti [a], Edson Antônio da Silva [b]

[a] *Instituto de Química, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves 9500, Caixa Postal 15003,
CEP 91501-970, Porto Alegre,RS, Brazil*
[b] *Escola de Engenharia Química, Universidade do Oeste do Paraná, Rua da Faculdade 2550, Toledo,PR, Brazil*

Abstract

Wastes of *Araucaria angustifolia* (named pinhão) natural (PW) and also loaded with Congo red (CRP) were tested as low-cost adsorbents for Cu(II) removal from aqueous solutions. In order to reduce the total number of experiments to achieve the best conditions of the batch adsorption procedure, three sets of statistical designs of experiments were carried-out for each adsorbent. Initially, a full 2^4 factorial design for each adsorbent with two central points (18 experiments) were performed, to optimize the following factors: mass of adsorbent (m), pH, time of contact (t) and initial metallic ion concentration (Co). These results indicated that almost all the main factors and its interactions were significant. It was verified for both adsorbents, that a mass of 30.0 mg leaded to higher Cu(II) uptake and that the best pH for Cu(II) adsorption was 5.6. In order to continue the batch adsorption optimization of the systems, a central composite surface analysis design with two factors (Co, t) containing 13 experiments, divided in to four cube points, four axial points and five centre points was carried-out for each adsorbent. By performing these two sets of statistical design of experiments, the best conditions for Cu(II) uptake using pinhão wastes (PW) and pinhão wastes loaded with Congo red (CRP) using batch adsorption system, where: $m = 30.0$ mg of adsorbent; pH 5.6; $t = 2.5$ h. After optimizing the batch adsorption system by statistical design of experiments, isotherms for Cu(II) uptake using PW and CRP were performed. These isotherms fitted to the linear Langmuir and Freundlich models. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

The industrial activity is responsible to generate a large volume hazardous containing effluents [1,2]. These hazardous effluents need to be treated before being delivered into the environment. Adsorption procedure is one of the most employed treatment procedures for removal of heavy metals from industrial effluents. Activated carbon has been widely employed as the most popular adsorbent for the effluents treatment [3]. Besides its extensive use, activated carbon of high quality remains costly [4]. Due to the high costs of the adsorbents, there is an increas-ing interest in the obtainment of low-costs adsorbents, which are able to remove metallic ions from liquid effluents [4,5]. These adsorbents should be available in large amounts (at least at the proximity of the effluent treatment plant) presenting low costs.

The *Araucaria angustifolia* syn. *Araucaria brasiliensis* is a tall tree (30–52 m) of the genus *Araucaria* [6], which occu-pies large areas in the south and southeast of Brazil and east of Argentina [6]. The flowering of the *A. angustifolia* produces a bunch of seeds, which is named pinha. Each one of these presents a diameter of 10–25 cm and contains about 700–1200 scales with about 150 seeds weighing up to 4.7 kg [6]. The seeds are named pinhão, which contains a resistant coat that involves it [7]. The pinhão is cooked in water and it is largely consumed in Brazil. The coat of the pinhão seed is usually discarded on the garbage, and it takes so much time to being decomposed. There

* Corresponding author. Tel.: +55 51 3316 7175; fax: +55 51 3316 7304.
E-mail addresses: ederlima@iq.ufrgs.br, profederlima@gmail.com
(E.C. Lima).

is estimation that Brazil generates about 10 t of pinhão wastes per year.

Due to the need to find new and inexpensive adsorbents for metal removal, and also to diminish the large amounts of pinhão wastes, in this work is presented an application of the use of pinhão wastes (PW) as well as pinhão wastes loaded with Congo red (CRP) as low-cost adsorbents for removal of copper(II) from aqueous samples using batch adsorption system. In addition, to reduce the total number of experiments to achieve the optimal conditions of batch adsorption system statistical designs of experiments were employed.

The design determines which factors have important effects on a response as well as how the effect of one factor varies with the level of the other factors [8–15]. The determination of factor interactions could only be attained using statistical designs of experiments [8–10], since it can not be observed when the system optimization was carried-out by varying just one factor at the time and fixing the others. Response surface methods are often employed after a screening of important factors, usually by performing a previous factorial design, which indicated a curvature [13,14]. This statistical design is used to examine the relationship between one or more response variables and a set of quantitative experimental factors. After that, it is necessary to find the factor settings that optimize the response.

Although statistical design of experiments has largely been employed in the optimization of industrial process [8–10] or in analytical works [11], it has been scarcely applied to adsorption process [12–15]. In this way, there is a demand for more applications of statistical design of experiments applied to adsorption studies.

2. Experimental

2.1. Reagents and solutions

Doubly distilled water was throughout employed.

A 5000 mg l^{-1} copper(II) stock solution was prepared dissolving 9.8228 g of CuSO$_4$·5H$_2$O (Vetec, Rio de Janeiro, RJ, Brazil) in water and completing the final volume to 500.0 ml. Working Cu(II) solutions from 10.00 to 1000.0 mg l^{-1} were prepared from suitable serial dilution of the stock solution. The pH adjustments of the solutions were made with aliquots of 1.0 mol l^{-1} of HCl and NaOH, utilizing a pH/mV hand-held meter handylab 1 Schott (Mainz, Germany) provided with combined glass electrode model Blue-Line 23.

Congo red (see Scheme 1) furnished by Aldrich (St. Louis, MO, United States) was used as received without previous purification. Solution of 1.00 g l^{-1} of the dye was obtained by dissolving 200.0 mg of it in 200.0 ml of water.

2.2. Adsorbents preparation and characterization

Pinhão was acquired at local market in Porto Alegre, RS, Brazil. The weight of each seed varied between 7 and 9 g. The seed coats correspond to approximately 22% of the seed. About 2 kg of pinhão were cooked in a 10 l glass beaker for 2 h, and then the seed was separated from the coat. The brown aqueous
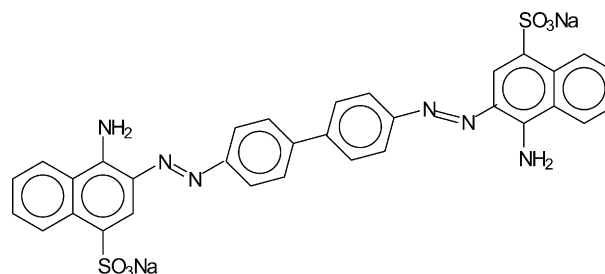
Scheme 1. Congo red structural formula.

solution resulted from the pinhão cooking containing oxidized phenols [7] was discarded. Afterwards, the pinhão wastes were again heated to boil for two more hours, in order to remove the water soluble phenolic compounds [7], and avoiding releases of these compounds to the water solutions. Subsequently, the pinhão wastes were washed with distilled water, dried at 70 °C in an air-supplied oven for 8 h. After that, the pinhão wastes were grounded in a disk-mill and subsequently sieved. The part of adsorbent (PW) with diameter of particles ≤250 μm was used. The apparent density of the powder pinhão wastes was 1.18 g cm^{-3}, and it presented an intense brown coloration that was assigned to tannins [7] which must be the main organic compounds responsible for biosorption of copper(II).

For loading the pinhão wastes with Congo red (CRP), 200.0 ml of 1.0 g l^{-1} of Congo red solution at pH 2.0 were added to 5.0 g of dried pinhão wastes placed in an 500 ml Erlenmeyer flask. The slurry was magnetically stirred for 24 h. Afterwards, the slurry was filtrated in a sintered glass funnel, and the solid phase was thoroughly washed with water and then with cold ethanol, until no more dye was leached-out from the solid phase. Subsequently, the material was dried at 70 °C in an air-supplied oven for 8 h, yielding a reddish tint product. (Fig. 1).

Pinhão wastes (PW) was characterized by FTIR using a Shimadzu FTIR, model 8300 (Kyoto, Japan). The spectrum was obtained with a resolution of 4 cm^{-1}, with 100 cumulative scans.

Pinhão wastes loaded with Congo red (CRP) was characterized by visible spectra of solid samples using a Cary 5G UV–vis NIR spectrophotometer using the diffuse reflectance accessory. The spectrum of the CRP immobilized on the sorbent surface was obtained by subtracting the spectrum of CRP sorbent by the PW pure sorbent (blank).

2.3. Determination of Cu(II)

Copper(II) was measured by using a Perkin-Elmer (Boston, MA, United States) Flame atomic Absorption Spectrometer model Analyst 200 (FAAS) using air–acetylene (10:2.5 l min^{-1}) flame under optimized conditions. Hollow cathode lamp of Cu(II) of the same manufacturer, was used as radiation source ($\lambda = 324.7$ nm).

2.4. Copper(II) batch adsorption procedure

An aliquot of 20.00 ml of 10.00–1000.0 mg l^{-1} Cu(II) was added to a conical plastic tube (117 mm height, 30 mm diameter) containing 30.0–50.0 mg of PW and CRP. The flasks were
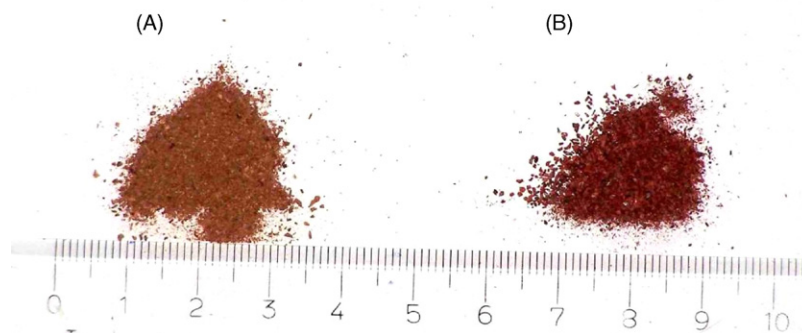
Fig. 1. Pictures of: (A) PW; (B) CRP after extensive washing with water.

capped, in placed horizontally in a Tecnal shaker model TE-240 (Piracicaba, SP, Brazil), and the system was agitated for 1–4 h. Afterwards, in order to separate the adsorbent from the aqueous solution the flasks were centrifuged using Fanem centrifuge (São Paulo, SP, Brazil) and aliquots of 1–5 ml the supernatant were properly diluted to 25.0–100.0 ml in calibrated flasks using water. The copper(II) final concentrations were determined by FAAS, after multiplying the measured concentration value found in the solution after the adsorption procedure, by the proper dilution factor.

The amount of Cu(II) adsorbed by the adsorbents was given by the Eq. (1).

$$q = \frac{Co - Ce}{m} V \qquad (1)$$

where q is the amount of metallic ion adsorbed by the adsorbent (mg g^{-1}), Co the initial Cu(II) concentration put in contact with the adsorbent (mg l^{-1}), Ce the Cu(II) concentrations (mg l^{-1}) after the batch adsorption procedure, m is the mass of adsorbent (g) and V the volume of metallic ion put in contact with the adsorbent (l).

2.5. Statistical design of experiments

2.5.1. Full factorial design

For studying the copper(II) biosorption on PW and CRP, the amount of adsorbed metallic ion (q) could depend on the mass of adsorbent (m), acidity of the medium (pH), the time of contact (t) between the adsorbate and adsorbent, and initial copper(II) concentration (Co). Others variables such as, speed of agitation was kept at 150 strikes per minute; temperature was kept at 25 °C. A full 2^4 factorial design employed was given in Table 1. The factor levels were coded as −1 (low), 0 (central point) and 1 (high) [8,9]. For treatment of datum, the Minitab Statistical Software release 14.12.0 was employed throughout in order to obtain the effects, coefficients, standard deviation of coefficients, and other statistical parameters of the fitted models, besides of the statistical plots (pareto, normal probability of the residues, main effects and surface plots).

2.5.2. Central composite response surface design

In this work, after performing a screening of the factors with the factorial design for the both adsorbents, two indepen-

dent response surface analysis statistical procedure [8–10] were employed sequentially, in order to achieve the highest amount of copper(II) adsorbed by the two adsorbents. The experimental set was carried out according to Tables 2 and 3.

2.6. Isotherm modeling

The linearized Langmuir [17] and Freundlich [17] isotherms are the most employed models to describe the adsorption equilibrium. These equations of isotherms were given below:

linearized Langmuir isotherm, $\quad \dfrac{Ce}{q} = \dfrac{1}{bQ_{max}} + \dfrac{Ce}{Q_{max}} \qquad (2)$

where Ce is the supernatant concentration after the equilibrium of the system (mg l^{-1}), b the Langmuir affinity constant

Table 1
Optimization of Cu(II) adsorption on pinhão wastes (PW) and pinhão wastes loaded with Congo red (CRP)

Experiments	m	pH	t	Co	PW q (mg/g)	CRP q (mg/g)
1	−1	−1	−1	−1	0.172	0.444
2	1	−1	−1	−1	0.198	0.347
3	−1	1	−1	−1	5.107	9.203
4	1	1	−1	−1	3.353	5.735
5	−1	−1	1	−1	0.000	0.425
6	1	−1	1	−1	0.000	0.360
7	−1	1	1	−1	5.179	9.088
8	1	1	1	−1	3.984	6.452
9	−1	−1	−1	1	1.060	3.593
10	1	−1	−1	1	0.496	5.576
11	−1	1	−1	1	9.237	12.740
12	1	1	−1	1	6.235	8.854
13	−1	−1	1	1	0.705	7.145
14	1	−1	1	1	0.558	6.343
15	−1	1	1	1	10.006	12.030
16	1	1	1	1	7.032	8.416
17	0	0	0	0	3.846	4.315
18	0	0	0	0	3.785	4.476

Factors	Levels		
	−1	0	1
m (mg)	30.0	40.0	50.0
pH	2.0	3.8	5.6
t (h)	1.0	2.5	4.0
Co (mg l^{-1})	10.0	15.0	20.0

Full 2^4 factorial design containing two central points.

Table 2

Optimization of Cu(II) biosorption on pinhão wastes (PW) and pinhão wastes loaded with Congo red (CRP)

Experiments	Co	t	PW q (mg/g)	CRP q (mg/g)
1	−1	−1	13.254	32.563
2	1	−1	25.254	54.028
3	−1	1	17.563	33.060
4	1	1	28.542	54.254
5	−1	0	16.587	32.328
6	1	0	25.524	53.236
7	0	−1	21.254	41.547
8	0	1	20.254	41.900
9	0	0	21.238	40.773
10	0	0	20.452	41.368
11	0	0	20.654	42.080
12	0	0	20.142	41.367
13	0	0	21.032	40.254

Factors	Levels		
	−1	0	1
Co (mg l^{-1})	100	200	300
t (h)	2.0	3.0	4.0

Central composite surface design (13 experiments with 2 factors (Co, t)). The pH was fixed at 5.6 and the amount of adsorbent was fixed at 30.0 mg.

($1 \,\mathrm{mg}^{-1}$), and Q_{max} the maximum adsorption capacity of the material (mg g^{-1}) assuming a monolayer of adsorbate uptaken by the adsorbent.

$$\text{linearized Freundlich isotherm,} \quad \log q = \log K_F + \frac{1}{n} \log Ce \quad (3)$$

where K_F is the Freundlich constant related with adsorption capacity and n is the Freundlich exponent.

In addition, the models were evaluated by the error function, which measure the differences of the amount of metallic ion uptaken by the adsorbent predicted by the models (Langmuir and Freundlich) and the actual q measured experimentally.

$$\text{error function,} \quad F_{error} = \sum_{i}^{p} \left(\frac{q_{i \,\text{Model}} - q_{i \,\text{experimental}}}{q_{i \,\text{experimental}}} \right)^2 \quad (4)$$

Where $q_{i \,\text{model}}$ is each value of q predicted by the fitted model and $q_{i \,\text{experimental}}$ is each value of q measured experimentally, and P the number of experiments performed.

3. Results and discussion

3.1. Adsorbents characterization

In Fig. 2 was shown the FTIR absorption spectrum of pinhão wastes. The absorption bands at 3400, and 2920 cm^{-1} were assigned to O–H bonds of macromolecular association, and –CH2– bonds, respectively [18,19]. The sharp intense peak observed at 1620 cm^{-1} was assigned to C=C ring stretch of aromatic rings [19]. From these results, it can be inferred that pinhão wastes is rich on tannins, as already reported [7].

In order to characterize pinhão wastes loaded with Congo red (CRP) adsorbent, visible spectra with diffuse reflectance

Table 3

Factorial fits: q vs. m; pH; t; Co; estimated effects and coefficients for q (coded units)

Term	Effect	Coef	SE Coef	P
PW				
Constant		3.3326	0.01078	0.002
m	−1.2012	−0.6006	0.01078	0.011
pH	5.8680	2.9340	0.01078	0.002
t	0.2007	0.1004	0.01078	0.068
Co	2.1670	1.0835	0.01078	0.006
$m \times$ pH	−1.0300	−0.5150	0.01078	0.013
$m \times$ t	0.1223	0.0611	0.01078	0.111
$m \times$ Co	−0.4705	−0.2352	0.01078	0.029
pH $\times t$	0.3665	0.1833	0.01078	0.037
pH $\times$ Co	1.5548	0.7774	0.01078	0.009
$t \times$ Co	0.1175	0.0588	0.01078	0.116
$m \times$ pH $\times t$	0.0245	0.0122	0.01078	0.460
$m \times$ pH $\times$ Co	−0.2862	−0.1431	0.01078	0.048
$m \times$ t $\times$ Co	−0.0110	−0.0055	0.01078	0.700
pH $\times t \times$ Co	0.0983	0.0491	0.01078	0.138
$m \times$ pH $\times$ t $\times$ Co	−0.1217	−0.0609	0.01078	0.112
Ct pt		0.4829	0.03235	0.043
S	0.0431335			
R^2	1.0000			
CRP				
Constant		6.047	0.02839	0.003
m	−1.573	−0.786	0.02839	0.023
pH	6.036	3.018	0.02839	0.006
t	0.471	0.235	0.02839	0.076
Co	4.080	2.040	0.02839	0.009
$m \times$ pH	−1.8279	−0.914	0.02839	0.020
$m \times$ t	−0.206	−0.103	0.02839	0.171
$m \times$ Co	−0.006	−0.003	0.02839	0.928
pH $\times t$	−0.607	−0.304	0.02839	0.059
pH $\times$ Co	−1.190	−0.595	0.02839	0.030
$t \times$ Co	0.322	0.161	0.02839	0.111
$m \times$ pH $\times t$	0.482	0.241	0.02839	0.075
$m \times$ pH $\times$ Co	−0.343	−0.171	0.02839	0.105
$m \times$ t $\times$ Co	−0.422	−0.211	0.02839	0.085
pH $\times t \times$ Co	−0.759	−0.380	0.02839	0.047
$m \times$ pH $\times$ t $\times$ Co	0.282	0.141	0.02839	0.126
Ct pt		−1.652	0.08516	0.033
S	0.113543			
R^2	0.9999			

Full 2^4 factorial design for optimization of Cu(II) uptake by pinhão wastes (PW) and pinhão wastes loaded with Congo red (CRP). The effects and coefficients are given in coded units. Coef: Coefficient, SE Coef: Standard error of coefficient, P: probability, Ct pt: central point, S: standard error, R^2: square correlation factor.

was obtained from the CRP, pinhão wastes and the dye Congo red solids (Fig. 3). In order to simplify the visualization of this figure, the spectrum of the CRP was subtracted from the pinhão wastes (blank). As can be seen the CRP presents an absorption band at 550 nm, which is similar to the band of the Congo red dye alone. This information corroborates that the Congo red dye was strongly adsorbed on the pinhão wastes after extensive washing with water (see Fig. 1).

3.2. Screening of factors for copper(II) uptake by PW and CRP

Metallic ion uptake by a adsorbent in a batch system usually depends on several factors, such as, mass of the adsorbent (m),
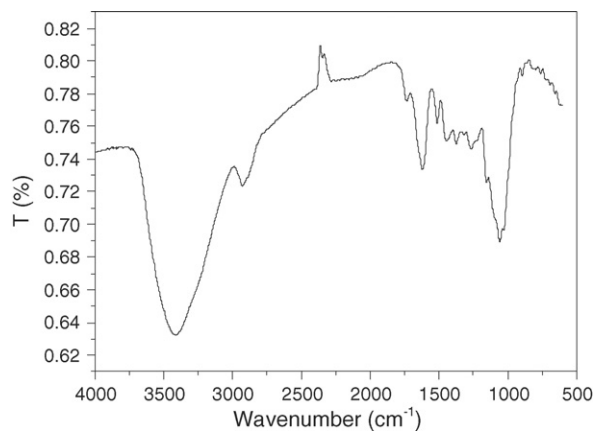
Fig. 2. FTIR spectrum of pinhão wastes.

Table 4
Parameters of fitted Langmuir and Freundlich isotherms for Cu(II) uptake in PW and CRP as adsorbents

	Adsorbent	
	PW	CR
Langmuir isotherm		
Q_{max}	32.2	68.6
b	0.0210	0.0423
R^2	0.9951	0.9988
F_{error}	0.3702	0.9647
Freundlich isotherm		
K_F	5.19	16.6
n	3.64	4.55
R^2	0.9642	0.9815
F_{error}	0.0699	0.0517

Q_{max} is expressed as $mg\,g^{-1}$; b as $l\,mg^{-1}$; K_F as $mg\,g^{-1}\,(mg\,l^{-1})^{-1/n}$; n dimensionless.

acidity of medium (pH), time of contact between the metallic ion and the adsorbent (t), initial metallic ion concentration (Co), speed of shaking, etc. The optimization of all those variables using the univariate procedure is very tedious, because any variable (factor) is optimized, by varying just one factor by the time and fixing the others. Then, the best value achieved by this procedure is fixed and other factors will be varied by the time. The disadvantage of this univariate procedure is that the best condition could not be attained, because the interactions among all the factors are neglected, and also it is not known if the set of other variables which were kept fixed during the experiments were set at other levels, the results would lead to the same optimization. In addition the total number of experiments to be carried-out in the univariate procedure is much higher when compared with statistical design of experiments [8–10].

In this work, the factors screened were, adsorbent mass (m), pH, initial Cu(II) concentrations (Co), and time of contact between the adsorbent and Cu(II) (t) for best metallic ion uptake using a batch adsorption system. The experiments of Table 1 ($n = 18$, for each adsorbent) were carried-out, obtaining the metallic ion uptake (q) in mg of Cu(II) per gram of pinhão wastes (PW) and pinhão wastes loaded with Congo red (CRP). The definitions of the factors and the levels used in the
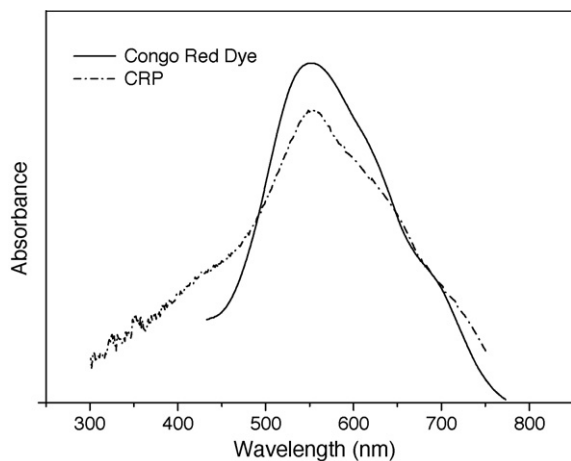

Fig. 3. Visible spectra of reflectance diffuse of solid samples of CRP and Congo red dye.

complete design were presented in Table 1. Main, interaction effect, coefficients of the model, and standard deviation of each coefficient, and probability for the full 2^4 factorial designs were presented on Table 4. As can be seen, almost all main factors and its interaction were significant at a 5% of probability level ($P < 0.05$). All the effects and interactions that presented probability lower than 0.05 were significant. The central point carried out in duplicate was useful to obtain the standard error of the coefficients. The probability results showed that the central point was significant in the chosen models, $P = 0.043$ and 0.033 for PW and CRP, respectively, at 5% of probability level. It means that it was detected a curvature of the factors when the levels were changed from the lower level ($-$) to the higher level ($+$), passing through the central point (0). There should be a curvature of the responses, and a surface analysis design should be carried-out in order to achieve a better comprehension of the adsorption systems. In addition, the fit models presented square correlation coefficients (R^2) of 1.0000 and 0.9999, for PW and CRP adsorbents, respectively, fitting very well the statistical models.

For pinhão wastes (PW) the Cu(II) uptake could be expressed as the following equation:

$$q_{PW} = 3.3326 - 0.6006m + 2.9340pH + 1.0835Co$$
$$- 0.5150m \times pH - 0.2352m \times Co + 0.1833pH$$
$$\times t + 0.7774pH \times Co - 0.1431m \times pH$$
$$\times Co \ (R^2 = 1.0000) \tag{5}$$

For pinhão wastes loaded with Congo red (CRP) the Cu(II) adsorption could be expressed as the following equation:

$$q_{CRP} = 6.047 - 0.786m + 3.018pH + 2.040Co - 0.914m$$
$$\times pH - 0.595pH \times Co - 0.380\,pH \times t$$
$$\times Co \ (R^2 = 0.9999) \tag{6}$$

Being the values of the factors coded and its levels valid only to the levels described on Table 1. The positive values of effects meant that an increase in their levels leaded to an increase in
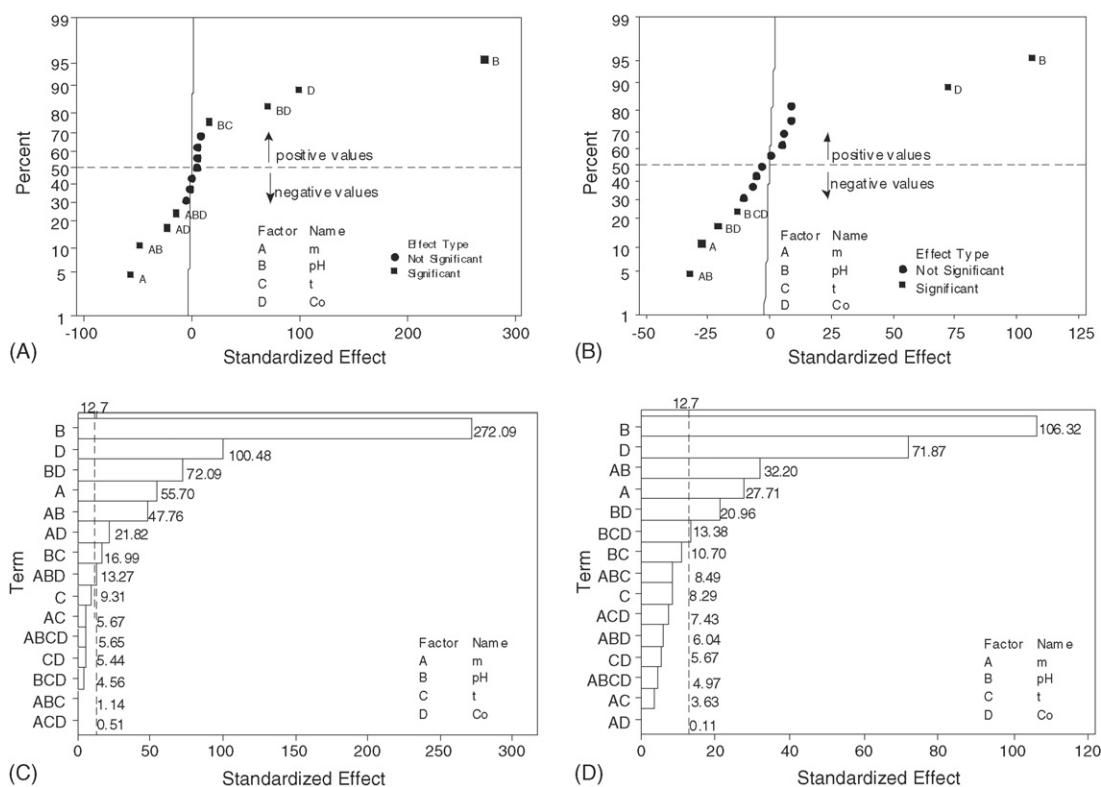
Fig. 4. Normal probability plot of standardized effects at $P = 0.05$: (A) PW adsorbent; (B) CRP adsorbent and Pareto plot of standardized effects at $P = 0.05$; (C) PW adsorbent; (D) CRP adsorbent.

the metallic ion uptake by the adsorbents (q), on the other hand, the negative values of the effects, leaded to a diminution of the response (q), when their levels were increased.

It should be highlighted that, the amount of Cu(II) adsorbed by CRP was higher than the amount adsorbed by the PW adsorbent. All the coefficients obtained for CRP adsorbents presented higher values when compared with PW. Although the system was not already completely optimized until this point, it can be inferred that pinhão wastes loaded with Congo red lead to a remarkable increase in the amount of metallic ion uptaken (see Tables 1 and 4, and Eqs. (5) and (6)).

In order to better evaluate each factor and its interactions, in Fig. 4A and B were presented the normal probability plot of standardized effects for PW and CRP, respectively. These graphs could be divided in two regions, the region with percent below to 50%, where the factors and their interactions presented negative coefficients (PW: m, $m \times$ pH, $m \times$ Co, $m \times$ pH $\times$ Co; CRP: $m \times$ pH, m, pH $\times$ Co, pH $\times t \times$ Co) and the region with percent above 50%, where the factors presented positive coefficients (PW: pH, Co, pH $\times$ Co, pH $\times t \times$ Co; CRP: pH, Co). All these factors and interactions, which were represented as a square were significant figures, and they were out of the central line that crosses the zero value at the abscissa at the 50%. The effects positioned in this line were represented by a circle and correspond to the estimate of errors of the effects, being not significant.

In Fig. 4C and D were presented the Pareto Chart of standardized effects at $P = 0.05$, for PW and CRP, respectively. All

the standardized effects were in absolute values (to verify which were positives and negatives, see Fig. 4A and B). All the values that presented an absolute value higher than 12.7 ($P = 0.05$), which were located at right of the dash line, were significant. The absolute standardized value of the effect of each factor and its interaction appeared at the right of each bar.

Analyzing the graphs of Fig. 4 and the values of Table 4 it can be inferred that the pH was the most important variable of the overall adsorption procedure of both adsorbents. The positive value of its coefficient, meant that the Cu(II) uptake by PW and CRP were favored at pH 5.6. The decrease in the pH leaded to a remarkable decrease of Cu(II) uptake by the both adsorbents, because the functional groups (phenolic groups present on the fiber, amino and azo groups of CRP) of the adsorbents could have been protonated hindering the metallic ion uptake. Taking into account that Cu(II) at higher concentrations could precipitate at pH higher than 6.0 [17], in this work the pH of Cu(II) solution was fixed at 5.6.

The second important factor for overall optimization of the batch system was the initial concentration of the metallic ion. An increase of the initial concentration leads to an increase in the metal uptake, until the saturation of the adsorbent. This factor was further optimized in the surface response analysis design, by increasing this level to higher values. The third important factor to the overall optimization of the adsorption processes were different for PW and CRP, however in both situations the interactions of two factors were more significant than the main factor (m) alone. Only the achievement of this result, justifies

the use of the statistical design of experiments over the conventional univariate process of optimization of the system. This information would not be acquired in a univariate optimization of the adsorption system. For PW, the interaction of two factors pH × Co was more significant than the main factor m. The positive value of the coefficient of this interaction meant that an increase in the pH associated with an increase in the Co leaded to an increase in the response (q). This synergistic effect would not be detected in a univariate optimization of the system. For CRP, the interaction $m \times pH$ was more significant than the main factor m. The negative value of the coefficient of this interaction meant that a diminution of the mass of CRP adsorbent associated with a decrease in pH of the solution, leaded to a diminution of the amount of metallic ion adsorbed. Also, this antagonistic effect would not be perceived in the univariate optimization of the system.

The fourth important factor for the overall optimization of the batch biosorption procedure was the mass of both adsorbents. As early observed [13], the adsorption experiments were carried-out in a batch system using conical plastic tubes (117 mm height, 30 mm diameter) the amount of adsorbent was limited to the conical plastic tube dimension for performing the experiments. This justifies, that low adsorbent mass leaded to highest metallic ion uptake (negative coefficient value). In order to minimize problems of non-homogeneity of the adsorbent for small

amounts, in the further experiments the adsorbent amount was fixed to 30.0 mg.

The decreasing order, from the fifth to the last, in the ranking of the overall optimization of the biosorption systems, in absolute values were $m \times pH > m \times Co > pH \times t > m \times pH \times t$ for PW and $pH \times t > pH \times t \times Co$ for CRP.

3.3. Surface analysis

After performing a screening of factors using a full 2^4 factorial design, a central composite response surface design (containing 13 experiments, divided in four cube points, four axial points and five central points) were carried out according to experiments described in Table 2, in order to achieve the highest amount of Cu(II) uptaken by PW and CRP adsorbents. The levels of the chosen factors were set based on the previous factorial design described above, increasing the initial Cu(II) concentration up to 300.0 mg l^{-1}; varying the contact time up to 4.0 h and fixing the mass of adsorbent in 30.0 mg and the pH at 5.6.

In Fig. 5 were shown the contour plots of the response (q) for time of contact between the adsorbate and adsorbents and also the surface plots, for the optimization of Cu(II) biosorption on PW and CRP used as adsorbents. As can be seen, the highest Cu(II) uptake by the both adsorbents occurred for times of contact higher than 2.5 h and for higher metallic ion concentration.
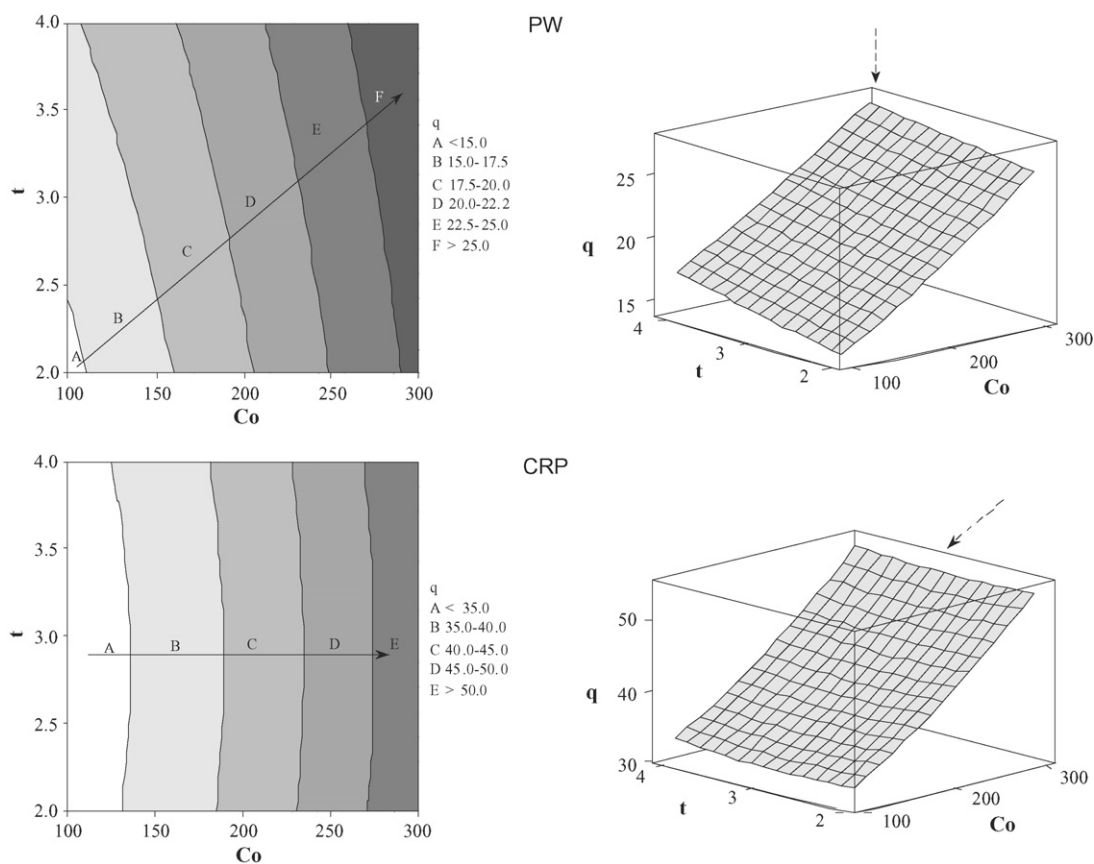

Fig. 5. Contour plot of q for PW and CRP adsorbents, t vs. Co. The regions of the contour plot are divided in several regions, where the response q is expressed in mg/g. The arrows indicate the increasing in the q at the several regions. Co is expressed in mg l^{-1} and t is expressed in hours. Surface plots for Cu(II) uptake by PW and CRP adsorbents. The arrows indicate the maximum responses (q).
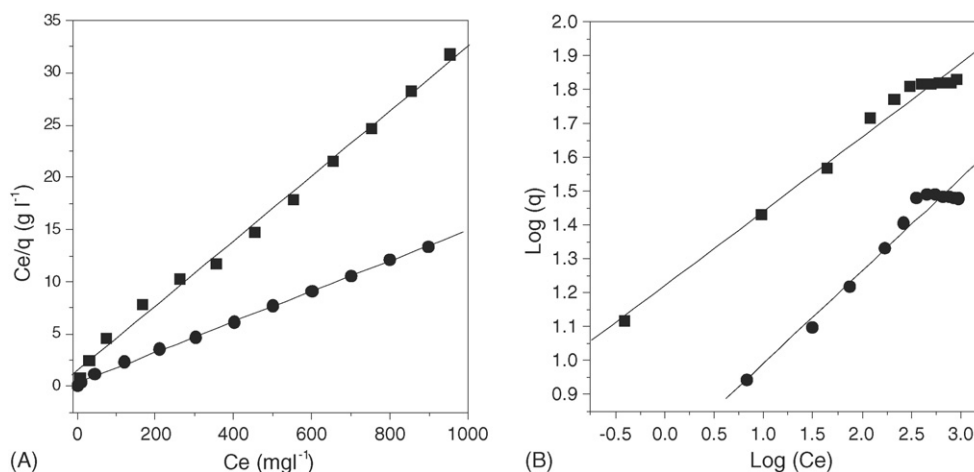
Fig. 6. Isotherms of Cu(II) adsorption on PW and CRP as adsorbents: (A) linearized Langmuir isotherms; (B) linearized Freundlich isotherms. (●) PW, (■) CRP.

It also can be noted that the saturation of the both adsorbents did not occurred when the initial concentration employed was $300.0 \, mg \, l^{-1}$.

Base on the two set of statistical design of experiments for the PW and CRP as adsorbents, it could establish the following conditions:

- The adsorbent masses of PW and CRP should be 30.0 mg;
- The ideal pH for obtaining the maximum amount of Cu(II) uptaken by the adsorbents was 5.6;
- The ideal time of contact between the adsorbents and adsorbate was at least 2.5 h to guarantee the equilibration;
- The saturation of the adsorbents did not occurred when the initial concentration of Cu(II) was up to $300.0 \, mg \, l^{-1}$. In order to obtain the maximum amount of the metallic ion uptaken by the adsorbents, isotherm curves should be obtained, using the best conditions optimized by the factorial design of experiments;
- The amount of Cu(II) uptaken by CRP is higher than that adsorbed by PW. The amino and azo groups presented on the Congo red which is loaded on the pinhão wastes should be responsible for this enhancement of the biosorption capacity.

The total number of experiments carried-out to get all this information was only 31 for each adsorbent studied (1st factorial design – 18 experiments, 2nd response surface analysis – 13 experiments).

3.4. Adsorption Isotherms for Cu(II) uptake on PW and CRP

In Table 4 were presented the values of the parameters of these models of isotherms. In order to evaluate which model was best fitted, the error function was measured. How lower is the error function, lower will be the difference of the q calculated by the model from the experimental q measured. For both adsorbents (PW and CRP), the Freundlich isotherm presented lower error function, even though the R^2 values of Langmuir model were better than the Freundlich ones. Therefore it can be inferred that just analyzing the R^2 of the fitting is not the unique parameter that should be take into account to verify the best fitting of isotherm model. In addition, by analyzing this table, it can also be inferred that the Congo red adsorbed in pinhão wastes increased the amount of Cu(II) adsorbed by more than two times using the Langmuir maximum adsorption (Q_{max}) or more than three times using the Freundlich maximum capacity (K_F), confirming the data of statistical design of experiments performed earlier.

In Fig. 6 are shown the linearized Langmuir and Freundlich isotherms. As can be seen, the both models were suitably fitted.

3.5. Comparison of pinhão wastes as adsorbent for Cu(II) uptake with other adsorbents

In Table 5 was presented a comparison of several adsorbents employed for Cu(II) uptaken. As can be seen from Table 5, the adsorbents employed in this work (PW and CRP) presented higher adsorption capacity when compared with several different adsorbents. It was verified that pinhão wastes (PW) presented adsorption capacity compared with carrots residues, and granular activated carbon. The modified pinhão wastes (CRP) presented adsorption capacity close to pulp of cactus, which was chemically modified [21].

3.6. Stability of the Congo red adsorbed on pinhão wastes

In order to verify if CRP adsorbent leached-out any dye amount after contact with effluents, 20.0 ml of solutions with pH ranging from 2.0 to 5.6 were kept in contact with the adsorbent for 6 h. After that, visible spectra were recorded of the liquid phase. No dye visible band were verified in the electronic spectra, indicating that the Congo red adsorbed on pinhão wastes did not leached out during the batch adsorption experiments. This result also confirms that pinhão wastes could be used for Congo red removal from aqueous effluents, and after the saturation of the biosorbent, it could be simply washed with water and reused for Cu(II) removal from aqueous solution.

Table 5
Comparison of different biosorbents for Cu(II) adsorption

Adsorbent	Characteristic	q_{max} (mg g^{-1})	Reference
Granular activated carbon	Commercial available	38	[4]
Activated carbon fibrous	Oxidized with nitric acid	30	[4]
Olive pomace	Grounded and sieved	4.26	[16]
Mandarin peel	Washed with water, dried and grounded, sieved	83.2	[18]
Wheat bran	Treated with acid	15.0	[20]
Wheat shell	Washed with water, dried, grounded	8.26	[21]
Cork	50–100 μm	20.9	[22]
Pulp of cactus	Oxidized, washed and dried under vacuum	67.6	[23]
Carrot residues	Dried at 60 °C, grounded in a mill	32.74	[24]
Olive mill residues	Dried at atmospheric environment for 1 year, grounded and sieved	13.5	[25]
Olive mill residues	Organic polymeric fraction	47.7	[26]
Marine alga	*Ecklonia maxima*	93.46	[27]
Pine sawdust	Washed with water and sieved	2.46	[28]
Grape stalks	Washed with water, dried and grounded	10.10	[29]
Yohimbe bark	Washed with water, dried and grounded	9.53	[29]
Cork bark	Washed with water, dried and grounded	3.00	[29]
Pine bark	Washed with water, dried and grounded, sieved	9.47	[29]
Cone biomass of tree	*Thuja orientalis*	19.23	[30]
Rice husk	Rice husk modified with carboxylic acids	29.0	[31]
Wheat bran	Lignocellulosic substrat extracted from wheat bran	12.58	[32]
Pinhão wastes	Treatment with water boiling, dried, and grounded	32.2	This work
Pinhão wastes	Loaded with Congo red	68.6	This work

3.7. Desorption experiments

Desorption experiments of Cu(II) ions loaded on PW and CRP were carried-out by placing 30.0 mg of loaded Cu(II) PW and CRP adsorbents with 20.0 ml of 0.1 mol l^{-1} HCl and keeping the contact for 6 h. After that, the liquid phase was analyzed in order to measure how much of the metallic ion could be removed from the adsorbents. For PW the desorption process was limited to 35%, and for CRP the desorption process was limited to 55%. Although it could seem not a good result, for the reutilization of the adsorbent, the pinhão wastes is available in large amounts in Brazil and present no commercial value.

4. Conclusion

Two sets of statistical design of experiments were successfully employed for optimizing the best conditions to attaining the maximum amount of Cu(II) uptaken by PW and CRP, used as adsorbents. These two statistical designs of experiments leaded to the following conditions: $m = 30.0$ mg of adsorbent; pH 5.6; $t = 2.5$ h.

After optimizing, the conditions, isotherms of the metallic ion adsorbed on PW and CRP were carried-out. These isotherms were suitably fitted to Langmuir and Freundlich isotherm models.

The pinhão wastes with Congo red increased the amount of Cu(II) uptaken by more than two times using the Langmuir maximum adsorption (Q_{max}) or more than three times using the Freundlich maximum capacity (K_F), confirming the data of statistical design of experiments performed earlier.

This paper also brings an ecological correct application of a pinhão wastes loaded with an Congo red for Cu(II) uptake from aqueous solution. Therefore pinhão wastes could be employed for removal of dyes from aqueous solution, and afterwards, instead of this residue be only disposed in a landfill, it could be employed for successful removal of Cu(II) from aqueous solution.

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