

Removal of Cu(II) from Ethanol Fuel Using Mandarin Peel as Biosorbent

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Mandarin peels were investigated for the removal of copper ions from ethanol fuel. Infrared spectroscopy and thermogravimetric analysis were used for elucidating possible functional groups responsible for the adsorption of Cu(II) from ethanol. The influence of parameters such as the mass of the adsorbent, sample pH, stirring time, and initial copper(II) concentration was investigated using multivariate optimization strategies. The optimum conditions were a pH value of 7.0, a stirring time of 10.0 min, an initial copper(II) concentration of 6.0 mg L⁻¹, and an adsorbent mass of 95.0 mg. The sorption data were fitted satisfactorily to the Langmuir and Freundlich isotherm models. The mandarin peel presented a maximum adsorption capacity of 2.71 mg g⁻¹ and is low-cost, which makes it suitable for the removal of copper ions from ethanol fuel.

Keywords: Adsorption; Mandarin peel; Ethanol fuel; FAAS

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INTRODUCTION

The use of biofuels as a renewable energy source is one of the available methods to reduce air pollution and to limit global warming (Goldemberg *et al.* 2008). The most commonly used renewable fuel is bioethanol, which can be produced from various types of plants. Ethanol fuel is obtained in Brazil from the fermentation of sugar cane, and this process is now very well established. It is colorless, transparent, volatile, and miscible in water and various organic liquids and is usually sold in a hydrated form (95-96%) or anhydrous (greater than 99%) (ANP 2011).

The growing use of ethanol, whether as fuel or raw material for industries, justifies strict quality control of the alcohol sold, both wholesale and retail. The production of ethanol in Brazil is carried out by many distilleries scattered all over the country, a fact that complicates the standardization of the final product. Inorganic contaminants of fuel ethanol include: sulfate, chloride, potassium, sodium, iron, nickel, and copper. In Brazil, the National Agency of Petroleum, Natural Gas, and Biofuels (ANP) established specifications for anhydrous and hydrated ethanol fuel, such that the copper content must be less than 0.07 mg kg⁻¹. Detailed knowledge of the heavy metals present in the alcohol fuel is important because it can provide information about the best materials to use in the containers used to store and transport ethanol. The corrosion of such containers is the main source of contamination by metals (Pereira and Pasa 2005). The quantitative monitoring of metallic elements is of economic importance to the fuel industry as well as for automotive and environmental industries. Through efficient analytical control of the levels of metal ions, it is possible to manage the quality of

products offered to consumers. Poor fuel quality can cause direct damage to the consumer through automotive engine malfunction, increased consumption, and expenditure on maintenance. Therefore, it is important to study forms of metallic elements taken from the ethanol fuel (Alves *et al.* 2012; Almeida and Coelho 2012).

Adsorption methods, which are based on physical and chemical phenomena that occur when the adsorbate molecules accumulate on the adsorbent surface, have been successfully employed in metal adsorption processes (Demirbas 2008).

For an efficient adsorption process, it is necessary to choose an adsorbent with high adsorption capacity and high efficiency for removal of the adsorbate, which should be available in large quantities for a low cost (Sen Gupta and Bhattacharyya 2011). The adsorption capacity is determined by structural features and the opening of the pores of the adsorbent. Chemical modification of the material gives it a large surface area and pore size distribution appropriate for the adsorbate (Bailey *et al.* 1999; Beceiro-Gonzalez *et al.* 2000). Researchers have increasingly sought to use waste as an adsorbent (Demirbas 2008; Souza *et al.* 2012; Mosquetta *et al.* 2011), so the option of using mandarin peel for the removal of Cu(II) in hydrated ethanol fuel was investigated.

Mandarin (*Citrus reticulata*) is a citrus fruit also known as bergamot or tangerine. It is smaller, flatter, and easier to peel than an orange. Also, compared to the orange, buds of the mandarin are more easily separated, and the tree is more resistant to cold. *Citrus reticulata* has great commercial importance, is native to Asia, and is one of the most popular tangerines grown in Brazil, as well as worldwide (Pio *et al.* 2006; Saunt 2000).

The objective of the present work was to investigate the potential of the mandarin peel for removing Cu(II) ions from ethanol fuel. The maximum adsorption capacity and adsorption kinetics studies were evaluated.

EXPERIMENTAL

Instruments

The concentration of Cu(II) in the solutions before and after equilibrium was determined by flame atomic absorption spectrometry, using a Varian SpectrAA 220 instrument (Victoria, Australia) with an air-acetylene flame. A copper hollow cathode lamp from the same manufacturer was used as the radiation source ($\lambda = 324.7$ nm). Conventional values were used for the wavelength, slit width, and burner height.

A Gehaka PG1800 pH meter with combined glass electrode was used to set the pH of the samples and working solutions. The characterization of the material was done using a Shimadzu FT-IR (Fourier transform infrared) model 8300 (Kyoto, Japan) and thermogravimetric analyzer, the TGA 2950 from TA Instruments (New Castle, USA).

Adsorption experiments were carried out in 150 mL flasks containing adsorbent (*in natura* or treated with NaOH) and alcoholic solution of Cu(II). The flasks were shaken at room temperature on a TE-141 mechanical table (Tecnal, Piracicaba, Brazil).

Reagents and Solutions

All chemical reagents used in these studies were of analytical grade. All working solutions were prepared with ultra-pure water obtained from a Gehaka water purification system. All laboratory glassware was previously washed with neutral detergent, kept overnight in a 10% (v/v) nitric acid solution, and washed with deionized water. The working solutions used in this study were prepared through dilution of a 1000 mg L⁻¹

stock solution of copper (Carlo Erba, Italy) in ethanol fuel purchased at a gas station in the city of Catalão, GO, Brazil. The calibration curve was prepared through dilution of a 1000 mg L⁻¹ stock solution of copper (Carlo Erba, Italy) in ethyl alcohol P.A. The pH adjustment of the solutions was made with aliquots of 0.5 mol L⁻¹ HCl and 0.5 mol L⁻¹ NaOH.

Preparation and Characterization of Adsorbent

The mandarin peels used as adsorbent were obtained from a supermarket in Catalão City. After collecting the material, the peels were removed manually from the fruit and dried at 75 °C. After drying, the peels were crushed in a blender for household use and the powder was classified through a sieve shaker and separated into three particle sizes (20, 32, and 60 mesh).

The mandarin peel (25.0 g) of different grain sizes was shaken with deionized water (250 mL for 30 min), then filtered and oven dried at 75 °C for 24 h. This material is called *in natura* mandarin peel. The sieved biomass materials were stored in an airtight plastic container.

A 25.0 sample g of mandarin peel was soaked in 0.5 mol L⁻¹ NaOH (250 mL) for 30 min. The suspensions were then extensively washed with deionized distilled water to remove the excess NaOH and filtered thoroughly until a pH of 7 was reached. Finally, the resulting biomass was dried at 75 °C for 24 h. This material is called mandarin peel treated with NaOH.

For FT-IR analysis, the samples were mixed with KBr in a ratio of 1:100 (w/w) to produce tablets. The spectral range was from 4000 to 900 cm⁻¹, and 28 scans were taken at a resolution of 4 cm⁻¹. The purpose of using this procedure was to assess the main functional groups present in the material, especially with respect to the availability of the main groups involved in adsorption phenomena and to verify the changes undergone by the attack of NaOH on the surface of *in natura* mandarin peel. For thermogravimetric analysis, approximately 5 mg of adsorbent were heated from 20 to 600 °C at a heating rate of 20 °C min⁻¹ under an inert atmosphere of nitrogen.

Adsorption Studies

Adsorption studies were optimized using the multivariate method to determine the best conditions for Cu(II) adsorption. A two-level full factorial 2⁴ design with a central point and 18 runs in total was carried out, in duplicate, to determine the influence of the selected factors and their interactions. The variables studied were: mass of adsorbent (50 to 100 mg), sample pH (5 to 7), stirring time (30 to 60 min), and initial Cu(II) concentration (4 to 11 mol L⁻¹). In the study of the copper(II) adsorption on mandarin peel, the amount of Cu(II) adsorbed could depend on the mass of the adsorbent, the pH, the stirring time of the adsorbate and adsorbent, and the initial copper(II) concentration. The temperature was kept at 25 °C for all experiments. From the optimum conditions, an assessment was made to verify the influence of the initial Cu(II) concentration and mass of adsorbent on the Cu(II) adsorption. The removal efficiency was determined as the Q_e (uptake of metal per unit weight of sorbent) value obtained through the equation,

$$Q_e = \frac{(C_i - C_f) \times V}{m} \quad (1)$$

where C_i (mg L^{-1}) is the initial Cu(II) concentration, C_f (mg L^{-1}) is the final equilibrium Cu(II) concentration, V (L) is the volume of tested solutions, and m (g) is the mass of adsorbent.

Adsorption Isotherm

The experiments were carried out at room temperature, using 95 mg of adsorbent (35 to 60 mesh) and 20 mL of Cu(II) solution in concentrations of 0.5 to 20.0 mg L^{-1} Cu(II). The pH of the mixture was adjusted to 7.0, and the stirring time was 10 min. The mixture was filtrated and the copper was quantified by flame atomic absorption spectrometry.

RESULTS AND DISCUSSION

Characterization of Mandarin Peel

The FT-IR technique was used to study the main functional groups present in mandarin peel. This technique allows some important functional groups that are capable of adsorbing metal ions to be identified. Figure 1 shows the FT-IR spectra of the untreated and NaOH-treated mandarin peel.

The FT-IR spectrum of *in natura* mandarin peel presented a broad band centered at $3,400 \text{ cm}^{-1}$ (Fig. 1). The peak at $2,927 \text{ cm}^{-1}$ was assigned to the C–H stretching of methylcellulose (Gomez-Serrano *et al.* 1996). The FT-IR spectrum for the mandarin peel *in natura* and treated with NaOH presented almost the same profile, with peaks characteristic of lignocellulosic materials. The broad band in the region of $3,750$ to $3,000 \text{ cm}^{-1}$ is associated with stretching of the O–H and N–H groups present in proteins, fatty acids, carbohydrates (cellulose and hemicellulose), and lignin (Gomez-Serrano *et al.* 1996). The spectrum of mandarin peel treated with NaOH does not have any band at $1,750 \text{ cm}^{-1}$ that would have indicated the presence of ester. The peaks at $1,110$ and $1,059 \text{ cm}^{-1}$ are due to the C–O stretching, and are characteristic bands of cellulose and hemicellulose from lignocellulosic materials (Quessada *et al.* 2010).

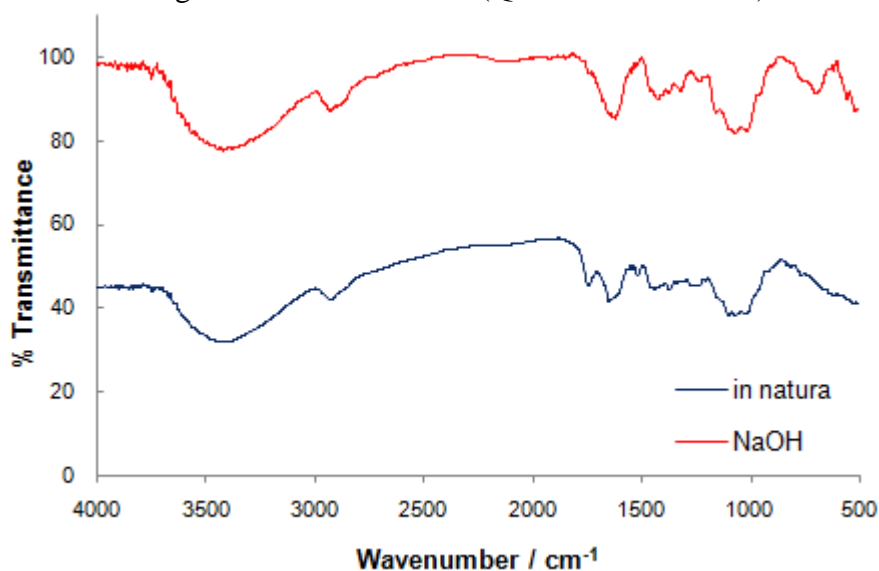


Fig. 1. FT-IR spectrum of mandarin peel (*in natura* and treated with NaOH)

The main differences between the two spectra are the increase in the bands at around 1,745 and 1,400 cm^{-1} due to an increased amount of hydroxyl groups and lignin content in the material modified with NaOH. The decrease in the peaks at 1,110 and 1,059 cm^{-1} is due to hydrolysis of some of the cellulose and hemicellulose present in the material modified with NaOH.

Mandarin peel can be classified as a lignocellulosic adsorbent, consisting mainly of cellulose, hemicellulose, and lignin. Functional groups present in these macromolecules have the ability to adsorb metal ions through ion exchange or complexation (Pagnanelli *et al.* 2003). It is important to note that biosorption of metals by biomass is not based solely on a single mechanism. Metal sequestration follows complex mechanisms including ion-exchange and complexation, and it is quite possible that at least some of these mechanisms are acting simultaneously to varying degrees.

Thermogravimetric analysis was used to characterize the decomposition stages and thermal stability of the mandarin peel. Figure 2 shows the curve obtained from the thermogravimetric analysis of *in natura* and treated with NaOH mandarin peels. The mass loss of *in natura* mandarin peel was 98.0%, and that of the mandarin peel treated with NaOH was 83.8%. This curve can be divided into four phases. The first phase, from 20 to 115 °C, was associated with the dehydration of the materials. The second phase, from 120 to 200 °C, was due to the decomposition of hemicellulose. The third phase, from 200 to 380 °C, was a result of the decomposition of cellulose, proteins, and carbohydrates. The phase from 380 to 540 °C occurred due to the decomposition of other constituents of the mandarin peel (Anwar and Rashid 2007). This thermogravimetric curve verifies the sample heterogeneity, since the intermediates formed are a mixture of several components.

Scanning electron microscopy studies performed by our research group with *M. oleifera* seeds, similar material to mandarin peel, show that the treatment with NaOH can increase the porosity of the material, making it more exposed to the adsorption of metal species (Marques *et al.* 2012). This change in the morphology of the material also results from the removal of some superficial structural components such as carbohydrates, proteins, and lignin.

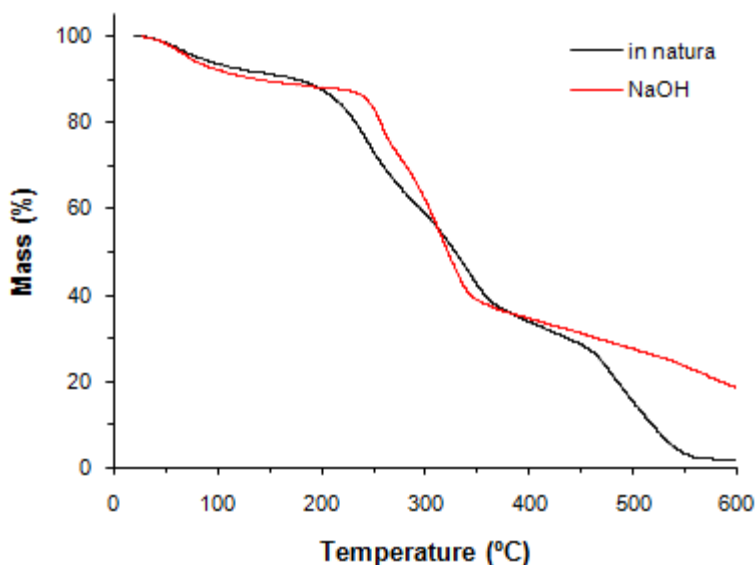


Fig. 2. Thermogravimetric curves of mandarin peel (*in natura* and treated with NaOH)

Adsorption Studies

After the chemical modification of mandarin peel using sodium hydroxide, the adsorption performance of the biosorbent was improved. Therefore, the solution at pH 6.0 was selected in order to avoid Cu(II) precipitation and so that the residue would present predominantly negative surface charges. It is important to emphasize that after chemical treatment, the biosorbent had improved adsorbent properties.

A multivariate optimization strategy was employed in order to achieve optimum levels of Cu(II) adsorption. A two-level full factorial 2^4 design was carried out, in duplicate, to determine the influence of the selected factors and their interactions, the results of which are shown in Table 1. An analysis of variance (ANOVA) and the significance level of p-values ($p > 0.05$) were used to obtain the effects, coefficients, standard deviation of coefficients, and other statistical parameters of the fitted models.

The selected factors were: mass of adsorbent (m), sample pH, stirring time (t), and initial Cu(II) concentration (C_o). A Pareto chart (Fig. 3) was plotted to observe the influence of the factors and their interactions in the system. An effect was considered significant when it was above the standard error at a 95% confidence level ($p > 0.05$), which is denoted by the vertical line on the graph.

Table 1. Conditions for Cu(II) Adsorption and Analytical Response for the Study of Multivariate Optimization Using Mandarin Peel Treated with NaOH and Determination by FAAS

Experiments	pH	t (min)	m (mg)	C_o (mol L ⁻¹)	Q_e (mg g ⁻¹)
1	5	30	50.0	4.0	0.05
2	7	30	50.0	4.0	0.09
3	5	60	50.0	4.0	0.04
4	7	60	50.0	4.0	0.07
5	5	30	100.0	4.0	0.02
6	7	30	100.0	4.0	0.06
7	5	60	100.0	4.0	0.03
8	7	60	100.0	4.0	0.04
9	5	30	50.0	11.0	0.31
10	7	30	50.0	11.0	0.31
11	5	60	50.0	11.0	0.31
12	7	60	50.0	11.0	0.39
13	5	30	100.0	11.0	0.16
14	7	30	100.0	11.0	0.19
15	5	60	100.0	11.0	0.17
16	7	60	100.0	11.0	0.13
17	6	45	75.0	7.5	0.09
18	6	45	75.0	7.5	0.09

As can be observed, the mass of adsorbent, the initial copper(II) concentration, and the interaction between the factors mass of adsorbent and initial copper(II) concentration were found to be significant (Fig. 3). The initial copper(II) concentration showed a positive influence, indicating that an increase in the initial concentration led to a higher analytical signal. The mass of adsorbent showed a negative influence, indicating that a decrease in mass of the adsorbent led to a higher analytical signal. The sample pH showed a positive influence, indicating that an increase in the pH led to a higher analytical signal. At higher pH values (between 5 and 8), fewer competing hydrogen ions and more ligands with negative charges were exposed, resulting in greater Cu(II)

sorption. However, at pH values higher than 7.0, precipitation of the solution occurred, which led to a reduction in the sorption capacity. Therefore, the initial pH of the sample was adjusted to 7.0 (Bianchin *et al.* 2009).

Since the variable time of contact did not affect Cu(II) adsorption, a study varying the stirring time from 0 to 30 min revealed that the maximum adsorption had been reached within 10 min.

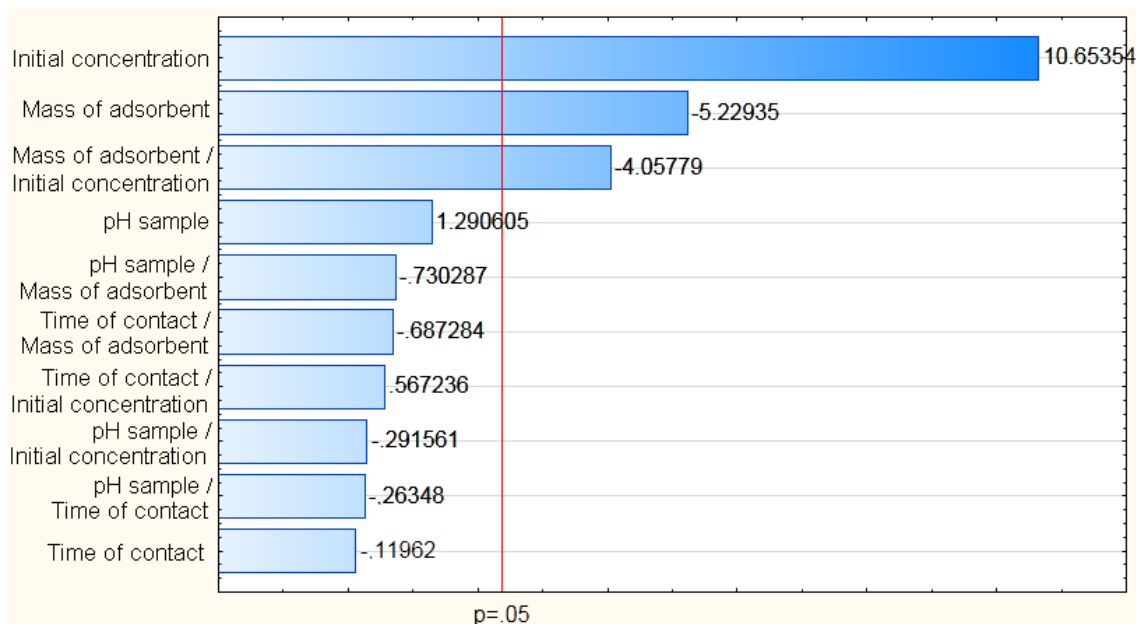


Fig. 3. Pareto chart obtained from the optimization study of the variables, with their significance, for the Cu(II) adsorption using mandarin peel treated with NaOH and determined by FAAS

The results obtained for the full factorial study indicated that the variables mass of adsorbent and initial copper(II) concentration required final optimization. Therefore, the aforementioned variables were optimized using a central composite design (CCD). The optimization was carried out using response surface methodology in order to obtain the critical values through application of the CCD. Table 2 shows the design matrix used to construct the response surface and the Q_e values obtained.

Table 2. Values Used for the Construction of the Response Surface Using Central Composite Design

Experiments	m (mg)	C_0 (mol L ⁻¹)	Q_e (mg g ⁻¹)
1	50.0	4.00	0.53
2	50.0	11.00	0.16
3	100.0	4.00	0.21
4	100.0	11.00	0.30
5	39.6	7.50	0.27
6	110.4	7.50	0.14
7	75.0	2.60	0.21
8	75.0	12.40	0.75
9	75.0	7.50	0.07
10	75.0	7.50	0.07

The response data were used to generate response surfaces for the system studied (Fig. 4). The maximum point was obtained for surface response and the critical values for the factors adopted in further experiments were: initial copper(II) concentration of 6.0 mg L⁻¹ and mass of adsorbent of 95.0 mg.

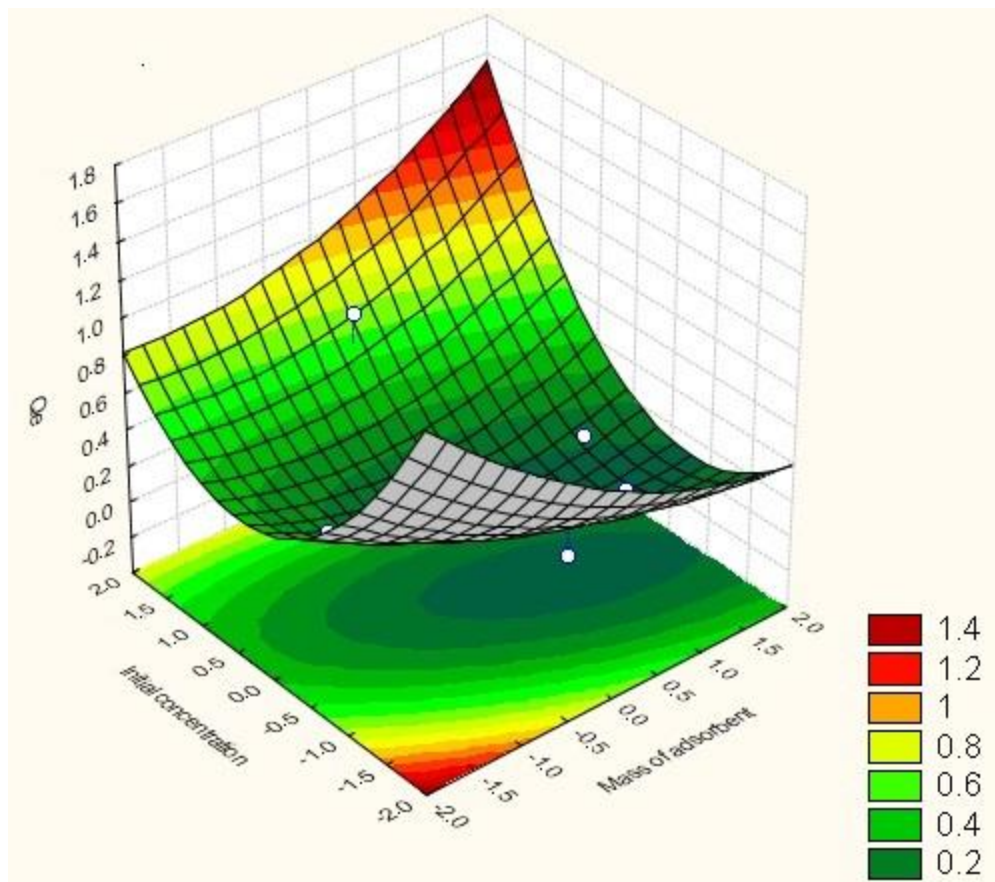


Fig. 4. Response surface for optimization using central composite design

Thus, as a result of the optimization procedures, the following working conditions were selected: adsorbent mass of 95.0 mg, stirring time of 10 min, sample pH of 7.0, and initial Cu(II) concentration of 6.0 mol L⁻¹.

Adsorption Isotherm

An important physicochemical aspect in terms of the evaluation of sorption processes is the sorption equilibrium. Two models were considered. The Langmuir isotherm model assumes monolayer adsorption onto an adsorbent surface containing a finite number of identical sites and without interaction between adsorbed molecules. The Freundlich model describes adsorption onto an energetically heterogeneous surface not limited by the monolayer capacity.

The linearized Langmuir (Alleoni *et al.* 1998) and Freundlich (Falone and Vieira 2004) isotherms are the most commonly employed models to describe adsorption equilibrium. These equations are given below:

$$\text{Linearized Langmuir isotherm: } \frac{C_f}{Q_e} = \frac{1}{Q_{max} b} + \frac{C_f}{Q_{max}} \quad (2)$$

where C_f is the supernatant concentration after the equilibrium of the system (mg L^{-1}), b is the Langmuir affinity constant (L mg^{-1}), and Q_{max} is the maximum adsorption capacity of the material (mg g^{-1}), assuming a monolayer of adsorbate up-taken by the adsorbent,

$$\text{Linearized Freundlich isotherm: } \log Q_e = \log K_f + \frac{1}{n} \log C_f \quad (3)$$

where K_f is the Freundlich constant related to adsorption capacity and n is the Freundlich exponent.

Figure 5 shows Freundlich (6A) and Langmuir (6B) isotherm plots for the sorption copper ions onto mandarin peel.

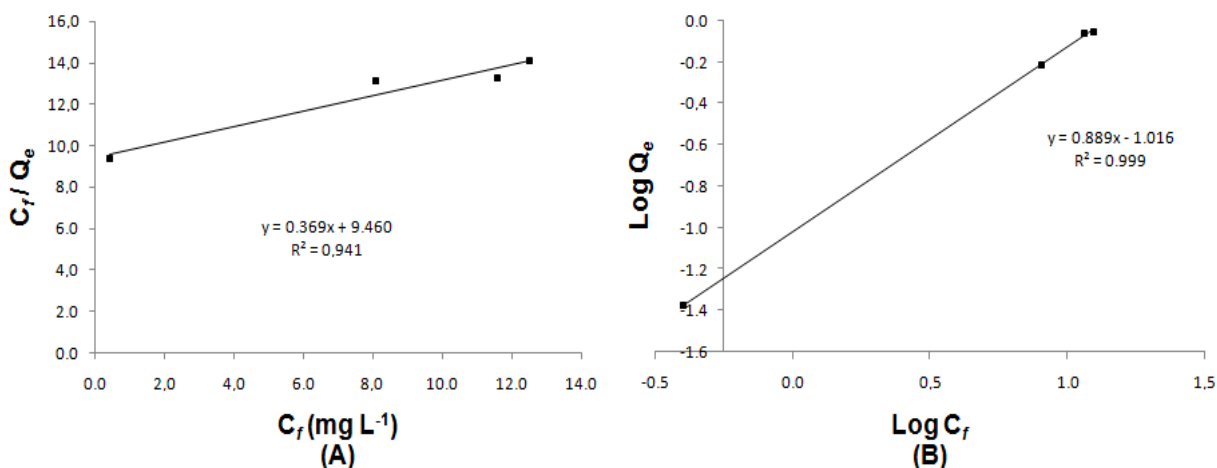


Fig. 5. Freundlich (A) and Langmuir (B) isotherm plots for the sorption of copper ions onto mandarin peel

Figure 6A was plotted according to Eq. 3, and the fitted values of n , K_f , and R^2 were 1.106, 0.089 L mg^{-1} , and 0.941, respectively. Figure 6B was plotted according to Eq. 2. The correlation coefficient obtained was 0.999, and the calculated value of q_{max} was 2.71 mg g^{-1} .

In Table 3, the values of the parameters of these isotherm models are presented. It can be observed that in the isotherm study, the experimental data for the adsorption of Cu(II) ions onto mandarin peel provided good fits to the two isotherm models. Comparing the Langmuir and Freundlich models, mandarin peel demonstrated a good removal capacity for Cu(II).

Table 3. Parameters of Fitted Langmuir and Freundlich Isotherms for Cu(II) Adsorption in Mandarin Peel Treated with NaOH

Langmuir				Freundlich			
Q_{max} (mg g^{-1})	b (L mg^{-1})	R^2	R_L	n	$1/n$	K_f (L mg^{-1})	R^2
2.71	0.016	0.999	1.000	1.106	0.904	0.089	0.941

Comparison with Other Adsorbents

The lack of studies involving removal of Cu(II) from an alcoholic medium hampers comparison of the method with other adsorbents. As the material used in this work is a natural material, a comparison of the values of natural adsorbent materials can be seen in Table 4. The data of chitosan microspheres, although a synthetic material, was used to show that removal of Cu(II) in an alcoholic medium is less than the removal of Cu(II) in an aqueous medium.

Although some materials exhibit capacity close to or better than that of mandarin peel (Prado *et al.* 2011), this material yielded the development of a rapid and simple methodology. Combined with their low cost and ease of purchase and considering the satisfactory experimental results, mandarin peel can be considered as an effective adsorbent for copper ions removal from alcoholic medium and has the advantage that it does not need to be previously subjected to chemical or thermal treatment. The data obtained in this work can be judged as satisfactory, since an alcoholic medium was used. This work showed that mandarin peel demonstrated good removal capacity for Cu(II) in the presence of interfering ions (Na(I), Fe(III), Ni(II)), compared to reports related to other adsorbents. Moreover, mandarin peel offers advantages such as low cost, high efficiency, and minimized chemical sludge. It can therefore be used in remediation techniques.

Table 4. Comparison with Other Adsorbents

Adsorbent	Medium	Maximum adsorption capacity (mg g ⁻¹)	Reference
Chitosan microspheres	Alcoholic	45.1	Prado <i>et al.</i> 2011
Chitosan microspheres	Aqueous	144.9	Du <i>et al.</i> 2009
Cassava waste / HNO ₃	Aqueous	85.2	Horsfall <i>et al.</i> 2003
Cassava waste	Aqueous	71.3	Horsfall <i>et al.</i> 2003
Wheat bran	Aqueous	15.0	Farajzadeh & Monji 2004
Grape stalk wastes	Aqueous	9.6	Villaescusa <i>et al.</i> 2004
Mandarin peel	Alcoholic	2.71	This work

CONCLUSIONS

1. Mandarin peel is a low cost and readily available adsorbent for the removal of Cu(II) from ethanol fuel. The mandarin peel presented a maximum adsorption capacity of 2.71 mg g⁻¹.
2. The adsorption of Cu(II) is dependent on its stirring time, pH of solution, and mass of adsorbent. Maximum removal of Cu(II) was obtained with the stirring time of 10 min, pH of 7.0, and mass of adsorbent of 95.0 mg.

3. Isothermal data of Cu(II) adsorption on the biosorbent can be modeled by Langmuir and Freundlich isotherms.
4. The ions Na(I), Ni(II), and Fe(III), controlled by Brazilian legislation, show no significant interference in the adsorption of Cu(II).
5. The results show that this low-cost biosorbent can be used effectively for the removal of Cu(II) ions from ethanol fuel.

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