Assessment of Cadmium and Lead Adsorption in Organic and Conventional Coffee

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Many metals are toxic in human organism, as is the case of cadmium and lead. Therefore, the metal levels in food need to be controlled. In coffee, metals may present risks when they are extracted from the powder to be consumed as beverage. A flow injection analysis (FIA) system is proposed, with atomic absorption detection, to metal adsorption studies in coffee powder. Kinetic study, best isotherms and time, and mass influences were determined. They allowed analyzing the high lead and cadmium adsorption percentage in organic and conventional ground coffee. Metal adsorption occurs in multilayers, following Freundlich's model, and the kinetic model obeyed is the pseudo-second order. The cadmium adsorption suffered higher temperature influence, while the lead retention suffered higher mass influence. This study indicates that the majority of these toxic agents will be retained in the powder and will not be consumed by man, avoiding possible deleterious effects.

Keywords Cadmium, lead, coffee, adsorption

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Introduction

Coffee was discovered at around the third century A.D. by an Ethiopian pastor. Since that, it was widely disseminated.[1] Nowadays, coffee is one of the most consumed beverages worldwide. Due to its strong participation in the global economic market, it is important to maintain the quality during the crop stage, as well as in the final product. Two different types of coffee management can be considered: organic and conventional. The organic coffee has to be produced in crops that will not use pesticides and chemical fertilizers. The different management types will have influence on the grain composition and on the beverage quality.[2]

Some studies were developed aiming at establishing a relationship between the coffee compounds and their managements. In the context of mineral compound evaluation, Schmidt *et al.*,[3] proved the existence of chromium (Cr), cobalt (Co), nickel (Ni), lead (Pb), cadmium (Cd), copper (Cu), zinc (Zn) and manganese (Mn) in coffee samples from different soils from Paraná State, Brazil.

Many metals play important roles in human organism. Others, however, such as lead and cadmium, do not have this role, being rather toxic. Lead may alter metabolism in several body systems, including nervous, circulatory, endocrinal, renal, reproductive and gastrointestinal.[4] Cadmium might be accumulated in tissues, affecting neurological, reproductive, cardiovascular, gastrointestinal, hepatic and renal systems.[5] The metal levels in food need to be controlled due to their toxicity.

When coffee beverage is prepared, metals can be drawn from the powder and ingested, causing adverse effects. On the other hand, the powder coffee has adsorptive properties, as demonstrated by Azouaou *et al.*[6] They determined the cadmium adsorption rate as ranging from 40 to 80% in ground coffee. This result can be beneficial in decreasing the toxic metal availability in the beverage. Not much is known about the metal amount passing into the drink. Therefore, the metal adsorption study in the ground coffee is relevant. The adsorption process consists in the substance binding to the solid surface, occurring by physical or chemical forces.[7] Therefore, if there is a strong cadmium or lead adsorption on coffee powder, these will not pass to the beverage, avoiding their intake.

In this present work, a flow injection analysis (FIA) system is proposed, with atomic absorption detection, to metal adsorption studies in coffee powder. The studied analytes were cadmium and lead in organic and conventional roasted coffee (BCS-OKO Guarantee Master Certificate No. POCO-7569/07.08/14291-BR).

The adsorption studies in solid materials (coffee powder), of species present in aqueous solution (*e.g.* Cd^{+2}, Pb^{+2}), are frequently time consuming and include the preparing of suspensions, pre-defining of time agitation, filtration and determination of the analytes in the supernatant steps. In this work, the sample (suspension) was inserted in the FIA system, which had an on-line filtering unity,[8] and the detection technique used was thermo-spray flame furnace atomic absorption spectrometry (TS-FF-AAS).[9] However, the isotherms adsorption

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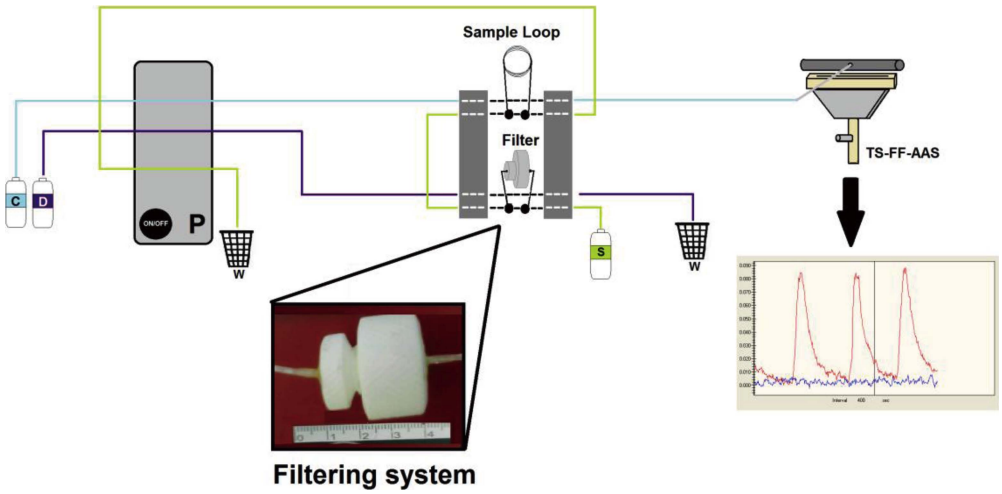

Fig. 1 FIA-TS-FF-AAS Module. S. Sample, W. Waste, P. Peristaltic pump, C. Carrier solution/ carrier stream, HNO_3 0.1% (v/v), D. Filter washing solution, distilled water.

of low concentration analytes was obtained by the TS-FF-AAS technique, being it faster due to the on-line filtering FIA system.

Material and Methods

Solutions and reagents

The reagents used in this work were: cadmium solution 1000 mg L^{-1} (Titrisol Merck, Germany), for 5, 10, 12, 15, 20, 22, and 25 µg L^{-1} standards. Lead solution 1000 mg L^{-1} (Titrisol Merck, Germany), for 50, 100, 200, 300, 400, 500, 600, and 700 µg L^{-1} standards. All solutions were prepared using deionized water (Milli-Q system, Millipore, Quantum EX, USA).

For FIA system, the carrier was nitric acid 0.1%. It was prepared using stock solution (Fmaia, Brazil). For washing, the filtration system used distilled water.

Samples

Organic and conventional powder coffee provided by the Poço Fundo Small Producers' Association, Poço Fundo, Minas Gerais, Brazil, were the samples used in the experiments. The organic coffee was certified (BCS-OKO Guarantee Master Certificate No. POCO-7569/07.08/14291-BR) and its fertilizations were made with bran castor micro-nutrients. The conventional coffee used NPK 20-05-20 fertilizer.

FIA-TS-FF-AAS System

For the metal determination, the TS-FF-AAS method[9] with an atomic-absorption spectrometer (Shimadzu AASS-6800, Germany) and the sample introduction by FIA system were used. The flame flow, consisting of air/acetylene, was 1.0 L min^{-1}. The background signal correction was made with deuterium lamp. For the cadmium hollow cathode lamp (VHG Labs, USA), it was used the 228.8 nm wavelength and 8 mA current, for the lead one (Analytikjena, Germany), 217 nm and 10 mA, respectively.

For the Thermal Spray (TS) system, the nickel metal tube (J&J Ethen, 52070, Aachen, Germany), 100 mm length, containing 8 holes of 1.5 mm diameter each and a 2.0 mm perpendicular hole were used. The samples were introduced into the tube through a ceramic capillary (Friatec, Mannhein, Germany).[9]

Figure 1 shows the FIA-TS-FF-AAS module. In the sampling position, the sample was aspirated through the filter system and filled up the loop (8 cm length, which corresponds to 40 µL). At the same time, the carrier (with 1.2 mL min^{-1} flow rate) was introduced into the nickel tube to maintain the base line. In the analysis step, the sample was introduced into the carrier stream and conducted up to the detector. Meanwhile, the filter was washed with distilled water in a countercurrent flow. The figure also shows the filtering system, consisted of a Teflon® holder[10] with coffee paper filter (Melitta® paper filter) fixed with rubber sealing ring.

Theory and Experimental

Kinetic study of adsorption

To study the adsorption kinetics, 25 g of coffee powder were weighed and transferred to a 1 L Erlenmeyer. Later, 500 mL of metal standard solution was added. For the cadmium experiment, a solution of 20 mg L^{-1} was used, for lead, a 500 mg L^{-1}. The flask was taken to shaker table (LE 203 Labor Müszeripari Müvek, Hungary). Aliquots of 5 mL were withdrawn every 10 min during the first half hour and every 30 min thereafter. The data were treated according to the pseudo-first order model (Eq. (1)) and pseudo-second-order (Eq. (2)).[11]

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t. \quad (1)$$

Where Q_e is the adsorbed amount per gram of adsorbent (mg g^{-1}), Q_t is Q_e in time t, k_1 is the pseudo-first order velocity constant (min^{-1}).

$$\frac{1}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (2)$$

Where k_2 is the pseudo-second order velocity constant (g mg^{-1} min^{-1}).

Adsorption isotherms

For the lead and cadmium adsorption experiments, 20 mL (exactly determined volumes) of the standard solutions were

introduced in tubes with 1.0 g of organic or conventional powdered coffee. The tubes were brought to stir for 10 min, and then the supernatant was removed and analyzed.

The adsorption percentage was evaluated. For the calculations, the same formulas employed by Porpino and Barreto[12] were used. The lead and cadmium adsorbed amount per adsorbate gram, Q_e, was calculated using Eq. (3).

$$Q_e = \frac{(C_i - C_e)V_l}{M_c \cdot 1000}. \quad (3)$$

Where M_c is the weight of coffee sample in mg.

The adsorbed lead and cadmium percentages (%) were calculated by the Eq. (4).

$$\%Ads = \frac{(C_i - C_e)\cdot 100}{C_i}. \quad (4)$$

Where Q_e is the quantity of adsorbed lead and cadmium in the equilibrium per adsorbate gram/mg g^{-1}, C_i is the initial concentration for lead or cadmium solution/mg L^{-1}, C_e is the lead or cadmium concentration which remains into the solution after reaches the balance/mg L^{-1}, and V_t is the total volume of used solution/mL.

Following data were treated according to the linear Langmuir isotherm Eq. (5) and Freundlich Eq. (6).[13]

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{1}{K_L} C_e \quad (5)$$

Where Q_m is a constant related to the adsorption energy/L mg^{-1}, K_L is the Langmuir constant, which gives the theoretical adsorptive capacity in the monolayer/L g^{-1}, Ce is the adsorbate concentration in equilibrium/mg L^{-1};

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (6)$$

Where K_F is the Freundlich constant/mg g^{-1}, n is an empirical parameter.[12]

Metal adsorption evaluation in usual conditions of beverage preparation

The coffee brew is traditionally obtained from aqueous suspensions containing coffee powder and boiling water. However, some variations regarding powder amount and water temperature are common to different regions where it is prepared. Thus, the influence of these two parameters related to the metal adsorption efficiency in powder coffee was evaluated in this study. The Doehlert matrix, a chemometric tool, was used to a better investigation of these variables. This consists of a multivariate tool, that allows to evaluate the variable effects, as well as the interactions among them. It also allows obtaining equations for response surface construction with graphic display of results.[14]

The Doehlert matrix allows experiments exploring more levels to the more important variable and less to the less important variable.[14] As it was expected that the temperature exerted more influence than the mass, the former was studied in five levels, and the second in three. Experiments are listed in Table 1.

The samples were weighed and transferred to tubes with lid. After that, 20 mL of standard solution were added in the proposed temperature (20 mg L^{-1} for cadmium and 500 mg L^{-1} for lead). The solutions were heated on hot plate (Marconi, MA038, Brazil), and the temperature was monitored with a mercury thermometer (Incoterm, L265/07, Brazil), with a precision of 0.1°C. After reaching the desired temperature, the samples were placed on the shaker table, equipped with a tank which contained water at the analysis temperature to ensure isothermal conditions for the experiments. The samples were shaken for 10 min. Then, 5 mL were removed for analysis. Data were analyzed with Statistica 7 program (Statsoft, Tulsa, USA).

Table 1 Experiments using Doehlert matrix

Experiment	Experimental variables	
	Mass/g	Temperature/°C
1	1.000	61.0
2	1.000	61.0
3	1.000	61.0
4	1.000	96.0
5	1.750	78.5
6	1.000	26.0
7	0.250	43.5
8	0.250	78.5
9	1.750	43.5

Results and Discussion

Kinetic Study

Before performing the experiments for isotherms construction, the necessary time for reaching the adsorption equilibrium was determined. The results for the cadmium in conventional coffee are showed in Fig. 2.

In Fig. 2A, it is possible to analyze the metal amount, in mg, which is adsorbed per coffee powder gram. Therefore, as time passes, a greater metal amount is adsorbed to stabilize at a ratio of 80% adsorption after 20 min.

The pseudo-first and pseudo-second order kinetic models were used to infer about the adsorption mechanism, as chemical reactions and mass transferences. For example, physical adsorption occurs instantaneously, so the kinetics is controlled mainly by the mass transfer resistance.[15] They are also used to define the time necessary for the metal adsorption on the adsorbent. The best definition of the kinetic model is by determining the highest correlation coefficient (R^2), and the proximity of the calculated and experimental Q_e value.[12]

The pseudo-first and -second order models' linear forms are shown in Figs. 2B and 2C. For the pseudo-first order, the theoretical Q_e was 5.48×10^{-4} mg g^{-1} and the correlation coefficient (R^2) was 0.9860. For the pseudo-second order, the theoretical Q_e was 3.33×10^{-7} mg g^{-1} and R^2 was 0.9983. The second model was the one that had best described the adsorption process in coffee powder, because it had highest R^2, and closer proximity between theoretical and experimental Q_e ($Q_e = 3.47 \times 10^{-7}$ mg g^{-1}).

The adsorption process in organic coffee followed the same profile as the conventional one, that is, there was also an increased adsorption in time 0 to 20 min, reaching 80% adsorption percentage, then becoming constant.

For the kinetic model, the adsorption in organic coffee followed the pseudo-second order, this being the one with the greatest R^2 (0.997) and greater proximity from the theoretical ($Q_e = 3.33 \times 10^{-7}$ mg g^{-1}) to the experimental ($Q_e = 3.00 \times 10^{-7}$ mg g^{-1}).

By comparing the cadmium adsorption on two types of coffee,

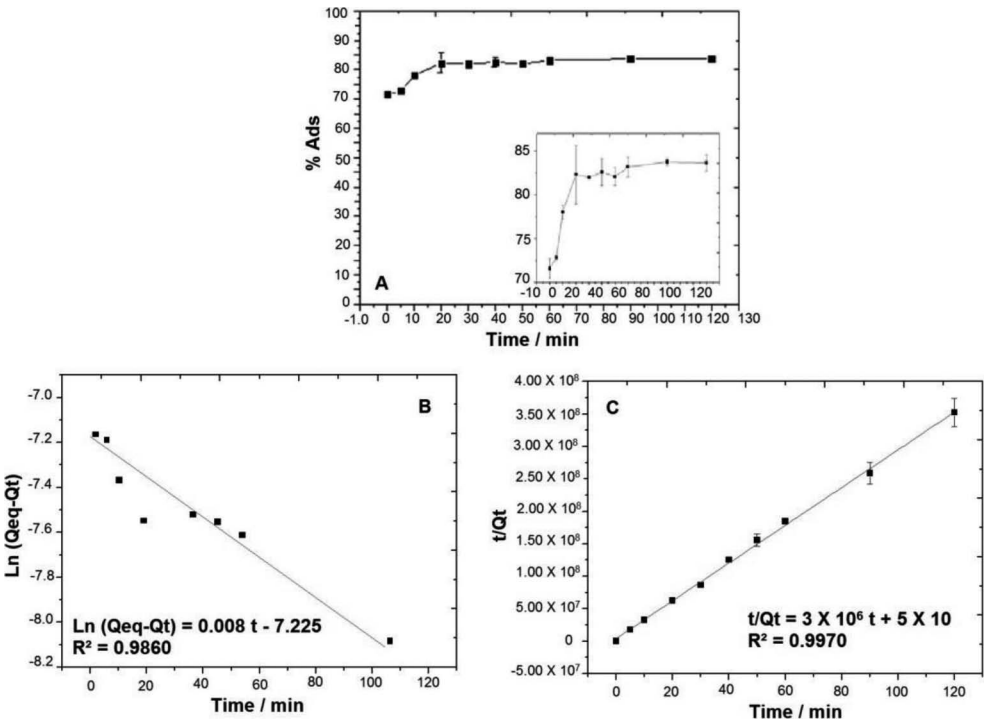

Fig. 2 A. Cadmium adsorption in function of contact time in conventional coffee, B. Kinetic model of cadmium removal in conventional coffee, pseudo-first order, C. Pseudo-second order. Q_{eq}. The adsorbed amount per gram of adsorbent in the balance/mg g^{-1}.

one realized that the adsorption occurred in large proportions (80%) and in a short time, which was advantageous, since the coffee preparation time usually does not exceed 10 min. The kinetic profile was followed by pseudo-second order, indicating that the adsorption was multilayer and was probably controlled by mass transfer, being faster in conventional coffee, due to its higher k (2.25×106 g mg^{-1} min^{-1}, in conventional coffee, *versus* 1.8×106 g mg^{-1} min^{-1}, in organic coffee). Figure 3 presents the lead results in conventional coffee.

Figure 3A shows the lead adsorption kinetics for conventional coffee. During the whole experiment, the adsorption percentage was 70 to 80%, so the process was little time dependent.

The linear forms of pseudo-first (B) and pseudo-second order (C) models for the lead adsorption, in conventional coffee, are shown in Figs. 3B and 3C. For the pseudo-first order the theoretical Q_e was 0.0382 mg g^{-1} and the R^2 was 0.1933. For the pseudo-second order the theoretical Q_e was 0.0063 mg g^{-1} and R^2 was 0.9917. It was observed that the pseudo-second-order R^2 was the largest, so this was the followed model. It was notable that the theoretical Q_e was closest to the experimental in this model, indicating the highest correlation.

The lead kinetic adsorption in organic coffee followed the same profile as the adsorption in conventional coffee, *i.e.*, in the course of time, the adsorption varied from 75 to 85%. The kinetic adsorption model adopted was the pseudo-second order, this being the one with the greatest R^2 (0.9862) and greater proximity from the theoretical Q_e ($Q_e = 5.51 \times 10^{-7}$ mg g^{-1}) to the experimental ($Q_e = 7.14 \times 10^{-6}$ mg g^{-1}).

For both types of coffee, one had an advantageous lead adsorption (in the range of 70 to 80%) and little time-dependency. This is advantageous, in the case of coffee brew preparation, once the adsorption is high, regardless of its preparation time. The same kinetic profile was followed, the pseudo-second order. The adsorption process occurred faster in the conventional coffee, due to its higher k (22.72 g mg^{-1} min^{-1}, in conventional coffee, against –16450.1 g mg^{-1} min^{-1}, in organic coffee).

The high adsorption of both metals in different coffee powder types is consistent with what was observed in other coffee parts, as the bark. Reis *et al.*[16] proved that the coffee dried bark was capable of adsorbing lead and cadmium (from 60 to 80%). Azouaou *et al.*[6] proved good cadmium adsorption in untreated coffee grounds.

Isotherms

After setting the adsorption time, in order to infer which best described the adsorption process, one studied Langmuir and Freundlich's isotherms. The cadmium adsorption isotherms, in conventional coffee, are presented in Figs. 4A and 4B.

Isotherms are used to determine how the adsorption process occurs, and can be described by two main models, Langmuir and Freundlich. For Langmuir's, the adsorbent surface is uniform with identical adsorption sites, according to the energy. This model is based on the hypothesis of adsorbed molecule motion by the adsorbent surface. Therefore, as more molecules are adsorbed, there is a uniform distribution, forming a monolayer which covers the entire surface.[13] As for Freundlich's, the multilayer adsorption is the model which best describes the adsorption.[11]

By analyzing the calculated constants for cadmium adsorption isotherms, in conventional coffee: Langmuir's constants were Q_m = –139.96 L mg^{-1}, $K_L = -9.43 \times 10^{-5}$ and R^2 = 0.8397; Freundlich's constants were K_F = 97.03, n = 0.4103 and R_2 = 0.9753. It can be observed that the Freundlich's model was what best described the process, for it was that having the highest correlation coefficient. The n value less than 1 corroborated to this model, since it indicates that the process was favorable.[17]

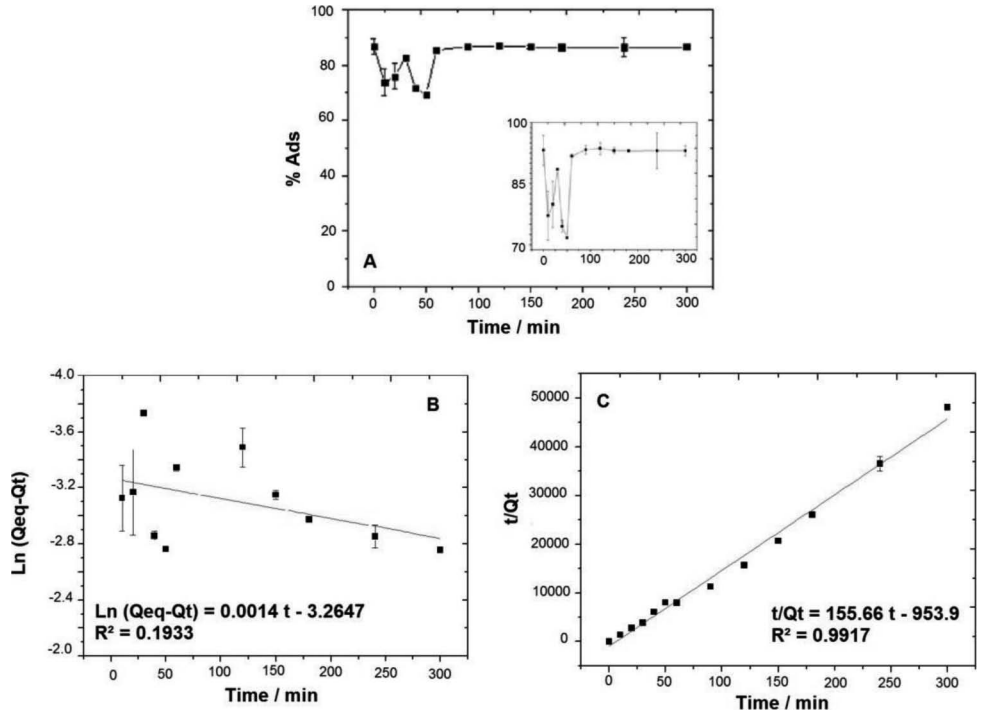

Fig. 3 A. Lead adsorption in function of contact time in conventional coffee, B. Kinetic models of lead removal in conventional coffee, pseudo-first order, C. Pseudo-second order.

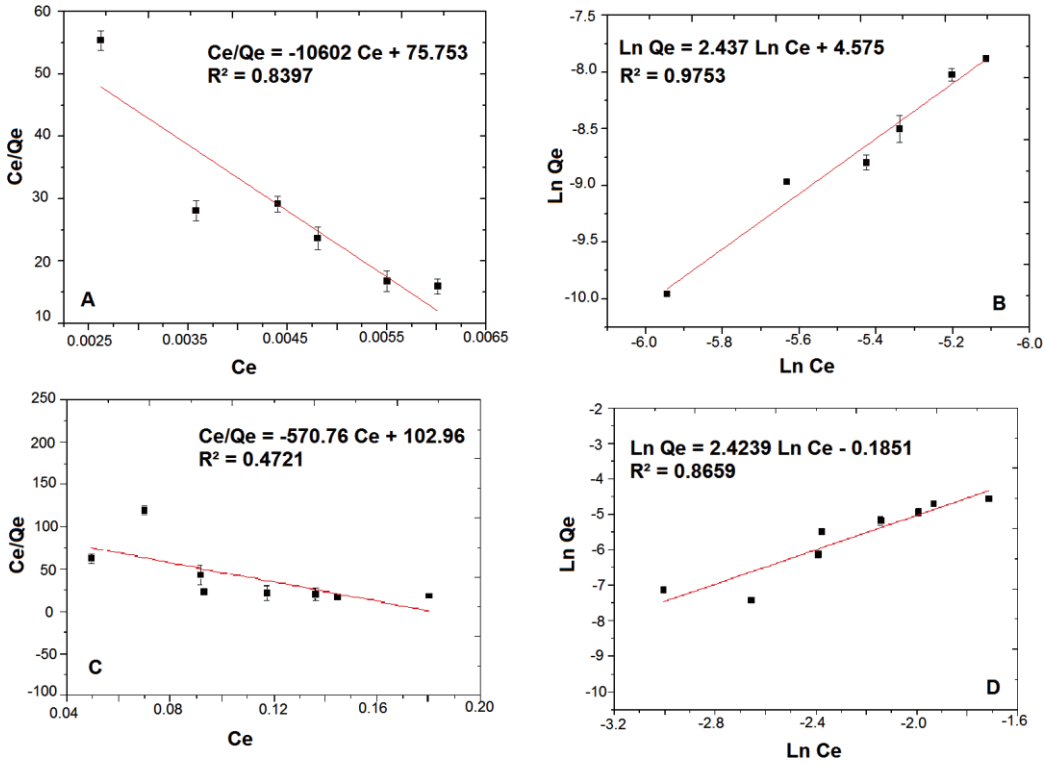

Fig. 4 A. Cadmium adsorption isotherms, in conventional coffee; Langmuir's isotherm, B. Freundlich's isotherm, C. Representation of the lead adsorption isotherms in conventional coffee; Langmuir's Isotherm, D. Freundlich's Isotherm.

As the cadmium adsorption process, in conventional coffee, the followed model in organic coffee was the Freundlich's, for it was that having the highest correlation coefficient (0.2346 *versus* 0.0425). The n value was 1.0934, almost 1, which indicates a favoring of the process.[17] The K_f value was 0.02.

In both types of coffee, the adsorption isotherm for cadmium was Freundlich's. Thus, it is inferred that the process occurred in multilayers, namely, the adsorbent surface was heterogeneous,

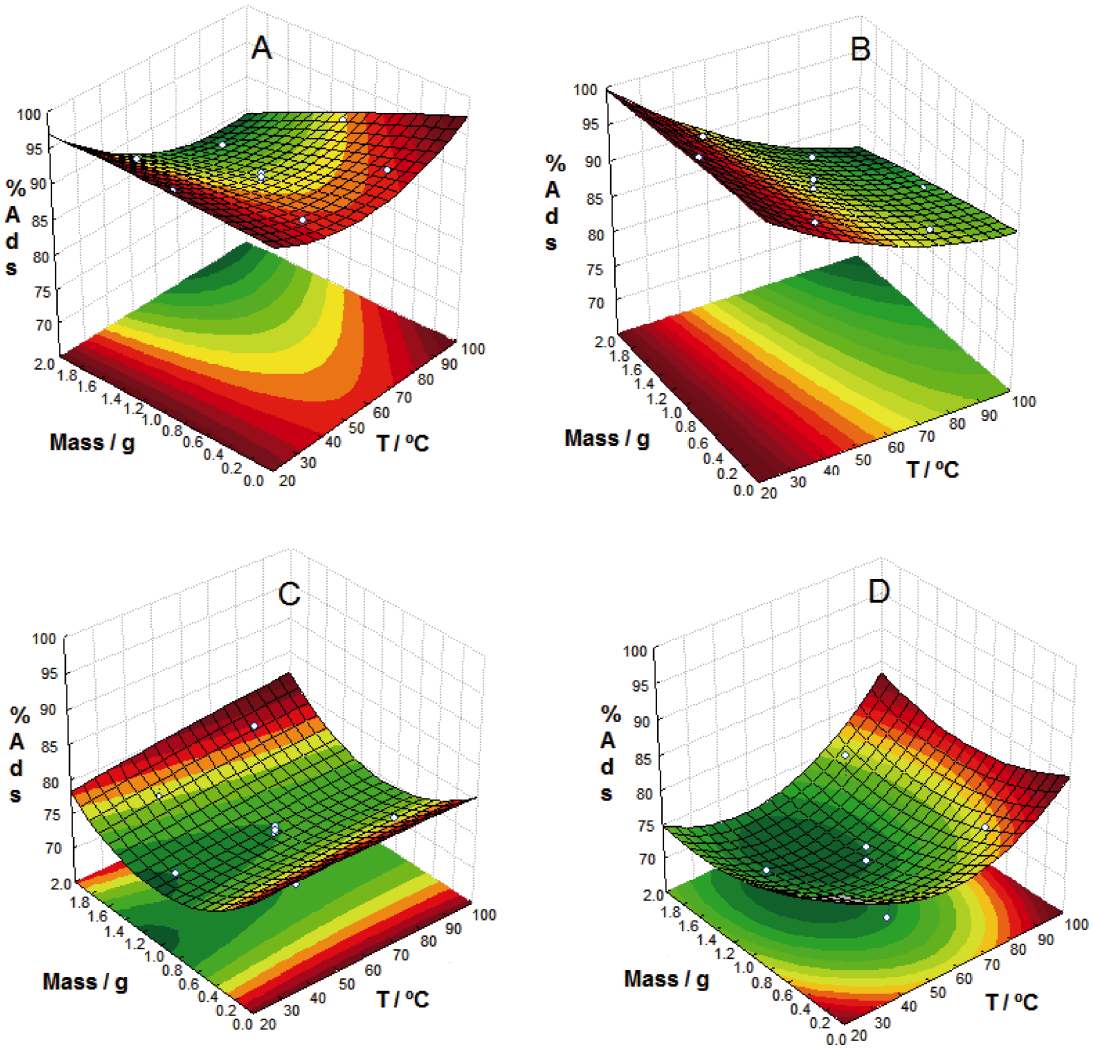

Fig. 5 Doehlert matrix, A. For cadmium adsorption process in conventional coffee, B. For the cadmium adsorption process in organic coffee, C. For lead adsorption process in conventional coffee, D. For lead adsorption process in organic coffee.

with a difference in adsorption energy among different sites. The K_F value allowed identifying the adsorbent ability to retain the metal.[12] Therefore, the cadmium adsorbing ability in conventional coffee was greater than that in organic coffee (97.03, in conventional coffee, against 0.02, in organic one). The n value indicated the heterogeneity of the adsorption sites,[18] thus the process in organic coffee, which had the largest value of n (1.0934), occurred with greater diversity, making it less favorable compared to conventional.

The lead adsorption isotherms in conventional coffee are shown in Figs. 4C and 4D.

The calculated constants for the lead adsorption isotherms in conventional coffee were: Langmuir's constants, $Q_m = -5.54$ L mg^{-1}, $K_L = -1.75 \times 10^{-3}$ and $R^2 = 0.4721$; Freundlich's constants, $K_F = 0.83$, $n = 0.4126$ and $R^2 = 0.8659$. These results show that the model that best described the process was the Freundlich's, because it was the one with the highest correlation coefficient. The n value was less than 1, indicating that the process was favorable.[17]

The Freundlich's model was also followed in the lead adsorption in organic coffee, as demonstrated by the constants, which highest correlation coefficient was presented for this model (0.9824 *versus* 0.7219). The n value less than 1 was also observed, confirming that this model may be followed (n = 0.4031).[17] The value of K_f was 8.3×10^{-4}.

The K_F value in conventional coffee was greater than in the organic (from 0.83 to 8.3×10^{-4}), indicating that conventional coffee retained more lead. The n values in the lead adsorption process in conventional and organic coffee were similar, 0.4126 and 0.4031 for the first and the second, so there is a heterogeneity of adsorption sites in both types of coffee.

The obtained data for both metals adsorption, in both organic and conventional coffee, are according to some other authors that analyzed environmental samples. Linhares *et al.*[18] proved that the Freundlich's isotherm was followed by the lead and cadmium adsorption in different soils. However, most of the adsorption processes occurred according to the Langmuir's model, as noted by several authors. Azouaou *et al.*[6] concluded that the Langmuir's isotherm model was in agreement with the experimental data obtained in the cadmium adsorption experiment on untreated coffee grounds. Porpino *et al.*[12] also concluded that the iron adsorption by crab shell followed the model proposed by Langmuir. This variation depends on the analyzed material, because the adsorption process is linked to

the adsorbent's free sites, where links with the metal occur, influencing both whether the process occurs in mono or multilayers.

Metal adsorption evaluation in usual conditions of beverage preparation

The mass and temperature interferences and the usual beverage preparation variations in the cadmium and lead adsorption percentage for the two types of coffee are shown in Fig. 5.

Figure 5A shows that, regardless of temperature or mass analyzed, the cadmium adsorption percentage in conventional coffee was high, 85 to 94%. However, there was a slight temperature and mass influence, that is, with decreasing temperature and mass there was a slight increase in adsorption. Clearly, there was the absence of maximum or minimum point on the graph, which means that it was not possible to determine the best temperature and mass for the process.

Figure 5B shows the temperature and mass influence for the cadmium adsorption process in organic coffee. It was possible to observe the high adsorption percentage for all analyzed points, ranging from 84 to 98%. Note that the temperature influenced the process, *i.e.*, as there was a decrease of it, the adsorption process was favored. On the other hand, the mass influenced slightly the process. The determination of maximum or minimum point was absent.

Both types of coffee had the same response surface profile, that is, at any mass and temperature ratios, there were an adsorption over 70%. This is advantageous because if the coffee or water used for the preparation were contaminated with metal, this would be retained and would not be transferred to the drink. In both types of coffee, there were temperature interferences. With the decrease of it, the adsorption process was favored. Thus, if the coffee preparation technique from the Brazilian Association of Coffee Industry[19] is followed, which recommends the use of water at temperatures less than 100°C, the consumers would be better protected because of the increase in metal retention.

Lead adsorption, in conventional coffee process, presented high percentage of adsorption, regardless of temperature and mass (varying from 73 to 80%), as shown in Fig. 5C. It was noticed that the temperature had little influence on the adsorption process, *i.e.*, in all temperature range (from 26 to 96°C) there was high adsorption, however the process was favored at the mass extremes (0.25 and 1.75). The response surface graph showed a minimum point, which had mass 0.9250 g and temperature 111°C, that is to say, at this point occurred the lowest adsorption percentage. However, this point could not be reached, since the water for coffee preparation boils at approximately 90°C.

Figure 5D shows temperature and mass influences on lead adsorption process in organic coffee, allowing verify the high metal adsorption regardless of the variables, going from 68 to 79%. At higher temperatures we noted the adsorption process improving, and at lower temperatures there was a tendency to favor the process. Mass would slightly interfere on the process, since at higher temperatures, all mass range (0.25 to 1.75 g) presented high adsorption percentage, however it was noted an increasing adsorption tendency in mass extremes. There was the minimum point on the response surface graph, which had 1.3946 g mass and 51°C temperature. So at this point, there was the minimum adsorption percentage.

For both types of coffee there was high lead adsorption, being greater than 68%, which is advantageous for coffee, since the metal would be retained in the ground coffee and would not be available aplenty for human consumption. Either in organic coffee or in conventional one, there was a tendency of better adsorption in mass extremes. Whereas the ratio studied ranged from 8.75 to 12.5% of coffee mass/water volume, and usually coffee preparation is carried out at a ratio of 8 to 10% coffee mass/water volume,[18] it is inferred that adsorption process will be high in preparations normally carried out, thus increasing the protection for the consumer.

The present study allowed analyzing the high lead and cadmium adsorption percentage in organic and conventional ground coffee, indicating that the majority of these toxic agents will be retained in the powder and will not be consumed by man, avoiding possible deleterious effects. It is still concluded that, regardless of the beverage preparation form, there is a high adsorption percentage, and the best preparation conditions were low temperatures and a mass/water volume proportion from 8 to 10%. It was also possible to characterize physico-chemically the adsorption mechanisms, either with kinetic or isotherms studies. Cadmium and lead adsorption occurred in multilayers, following Freundlich's model, and the kinetic model obeyed was the pseudo-second order.

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