"Gheorghe Asachi" Technical University of Iasi, Romania

CASTOR LEAF POWDER AS A BIOSORBENT FOR Cu(II) REMOVAL AND PRECONCENTRATION OF NATURAL WATER SAMPLES

Milene S. Pereira[1], Amanda E. Martins[1], Alexandre O. Jorgetto[1], Felipe A. Santos[1], Rafael I.V. Silva[1], Margarida J. Saeki[1], Marco A.U. Martines[2], Sônia M.A. Jorge[1], Gustavo R. Castro[1]*

[1]*IB-UNESP, Dept. Química e Bioquímica, C.P. 510, 18618-000 Botucatu, SP, Brazil*
[2]*UFMS – Dept. Química, 79074-460 Campo Grande, MS, Brazil*

Abstract

This paper describes the preparation and use of a low cost biosorbent made of castor leaves for the extraction of Cu(II) from an aqueous medium. The biosorbent was characterized by Fourier transform infrared spectroscopy (FTIR), surface area and pore diameter measurements. The results showed absorption bands of carboxylic and amide groups at 1738 and 1540 cm^{-1}, respectively, and the measured surface area was 1.3728 ± 0.0160 m^2 g^{-1}, with predominance of microporous < 10.51 Å. Quantitative extraction was achieved at pH above 4 and kinetic equilibrium was reached within 10 minutes. Isotherm adsorption data were adjusted to a modified Langmuir equation, yielding a N_s value of 0.321 mmol g^{-1}. The continuous flow system showed, after the optimization parameters, a 47-fold enrichment factor (preconcentration factor) when applied to standard and real water samples (Paraná River and Tap water). The developed preconcentration method was validated against the certified reference material (CRM 1643e).

Keywords: castor plant leaves, copper extraction, natural river water, preconcentration

1. Introduction

Over the last decade, pollution of soil, water and air by toxic substances has raised increasing concerns. Environmental contamination can be considered as a consequence of human population growth with the increasing demand for natural and industrialized products to meet the humanity's daily needs (Manahan, 2000).

However, a positive consequence of this growth is the significant advances in pollution control technologies and remediating of contaminated areas (Ahmed and Ahmaruzzaman, 2016; Inyang et al., 2016; Muya et al., 2016). A good example of these technologies is the development of materials to extract metal ions from natural water samples. Some important features of environmental metal contamination that have attracted increasing attention of the scientific community stems from their toxicity to aquatic organisms such as fish, plankton and benthic species (Arain et al., 2008; Castro et al., 2009; Deheyn and Latz, 2006; Huang rt al., 2016; Liu et al., 2002; Minello et al., 2009).

These materials generally consist of a porous or modified substrate such as silica (Alcântara et al., 2004; Mahmoud and Al-Bishri, 2011; Mahmoud et al., 2012; Pereira et al., 2010a, 2010b; Souza et al., 2011), cellulose (Melo et al., 2009), activated carbon (Ghaedi et al., 2008; Xuejiang et al., 2011; Wang et al., 2011) resin (Ghaedi et al., 2009), or natural products such as coconut coir (Gonzalez et al., 2008), *Zea mays* seed chaff (Babalola et al., 2016) and banana peel (Castro et al., 2011). Among these materials, the most commonly employed for metal

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* Author to whom all correspondence should be addressed: e-mail: castrogr@ibb.unesp.br; Phone: 55 14 38116255; Fax: 55 14 38116255

ion extraction are based on silica matrices, which can yield materials with desirable characteristics such as large surface areas, thermal stability, possibility of reuse and surface modification by molecules containing Lewis bases (Al-Bishri et al., 2012; Castro et al., 2008; Ferreira et al., 2011; Iler, 1979; Moraes et al., 2003). However, despite these interesting characteristics, the preparation of these materials through modification reactions using highly pure chemicals is very expensive, rendering their large scale production and use unfeasible. To overcome this disadvantage, several researches have studied the properties of extracting metal species provided by natural materials (Agunbiade et al., 2009; Anwar et al., 2010; Ghaedi et al., 2009; Gonzalez et al., 2008). The metal extraction ability of these materials stems from the presence of organic groups containing nitrogen, sulfur (Lewis bases) and carboxylic acids, which can act as electron pair donors and ion exchangers, respectively.

In Brazil and other countries, biodiesel is produced from various types of plants, including the castor oil plant (*Ricinus communis* L), as an alternative to fossil fuel. This plant is native to Ethiopia and has become cultivated in countries with tropical and temperate climates around the world. The castor oil plant has also been used as a dietary supplement for animals and is the primary food for the *Eri* silkworm (*Philosamia ricini*) because of the high protein content of its leaves, feature that motivated this work.

In this study, castor leaves were pulverized and analyzed by Fourier transform infrared spectroscopy (FTIR) to identify the functional groups responsible for the coordination of metal ions. The powder was applied to the extraction of Cu(II) in an aqueous medium and a continuous flow system was developed to preconcentrate trace metals in natural river water and tap water. The method was validated against the certified reference material (CRM 1643e).

2. Experimental

2.1. Chemical and solution

Metal solutions were prepared by dissolving nitrate salts (Sigma Aldrich-Germany) in ultrapure water obtained by the ELGA Purelab Ultra water purification system. Nitric and chloric acids (Synth-Brazil) were previously distilled in a sub-boiling distillation system (Marconi). Standard metal solutions for atomic absorption spectrometry were prepared by stepwise dilution from 1000 mg L^{-1} stock solution (Specsol-Brazil). The sodium hydroxide solution that was used to adjust the pH of the metal solution was prepared by dissolving a proper amount of NaOH in ultrapure water.

2.2. Preparation of the material

Castor leaves were collected in the vicinity of the researchers' workplace in the city of Botucatu,

state of São Paulo, Brazil. The leaves were placed in paper bags and dried for five days in an air circulating oven at 60°C. The dry leaves were then pulverized in a planetary ball mill (FRITSCH, Pulverisette 6) for 50 min at 500 rpm. The resulting powder was size fractionated with plastic sieves and particles with diameters of 75 to 45 μm were selected for the extraction/adsorption experiments. Prior to its use as extractor, the powder was washed with an ethanol/water mixture 1:1 (v/v) in order to remove certain products that usually give color to the washing residue. The washing procedure was performed in a soxhlet system for 24 hours. The obtained powder presented a brownish beige color and even in the water it did not lose its characteristics of particles.

2.3. Instrumentation

The concentration of Cu(II) in the supernatant in the adsorption experiments and in water samples was determined using a Shimadzu AA-6800 atomic absorption spectrometer. The spectrometer's monochromator was adjusted to 324.7 nm, that corresponds to a highly sensitive resonance line for Cu(II). The mixture (pulverized castor leaves and metal solution) was stirred mechanically in an end-over-end stirrer and the supernatant was separated using a centrifuge (FANEM Excelsa II) operating at 3500 rpm for 10 min.

The extractions were performed in 50 mL plastic tubes (Sarstedt). In continuous flow experiments, the flow was induced through a vacuum pump fitted with Tygon tubing. FTIR spectra were recorded on a Nicolet Nexus 670 spectrometer equipped with a Smart Collector, using 200 scans and 4 cm^{-1} resolution. The particles surface area and pore size distribution of the powdered leaves were measured with a Micromeritics ASAP 2010 and porosimetry analyzer, using 1.2 g of material.

2.4. Batch method

All the adsorption experiments were performed with 0.02 g of adsorbent. The kinetics of metal ion extraction was analyzed using aliquots of 10 mL of Cu(II) standard solution (0.315 mmol L^{-1}) in an interval of 1-50 min, stirred at room temperature (298.15 K). The influence of pH on the extraction capacity was investigated in a range of 1.0-5.0 to determine the lowest pH at which quantitative extraction could be achieved. The maximum extraction capacity of metal ions was determined using solutions with different concentrations to saturate the extraction sites on the material's surface. The extraction capacity, N_f, in all experiments was calculated as represented (Eq. 1):

$$N_f = \frac{n_i - n_s}{m} \tag{1}$$

where n_i is the initial metal mole number in solution, n_s in the final metal mole number in solution after stirring, and m is the mass of employed adsorbent.

2.5. Preconcentration of metal ions

The preconcentration system consisted of a vacuum pump and a micro column, closed on both ends with fiberglass insulation, built directly on a Tygon tubing (2.86 mm of internal diameter), into which 3.0 mg of powdered castor leaves was placed. The operation of the system was optimized using the univariate procedure where all parameters were kept constant except the one under investigation. Thus, the percolation flow of sample and eluant and the volume and eluant (HNO_3 solution) concentration were analyzed. The sample volume was kept at 50 mL in all optimization procedure. A schematic representation of preconcentration system is depicted in Fig. 1.

Before using the system to preconcentrate natural water samples, these were analyzed to determine the presence of interfering ions that can be found in these samples. Five ion species (NO_3^-, Cl^-, PO_4^{3-}, Ca^{2+} and Mg^{2+}) were investigated at three concentrations, 10, 50 and 100 mg L^{-1}.

The preconcentration of Cu(II) in the natural water sample was performed after mineralizing the sample (Pereira et al., 2010b), since naturally occurring organic substances may interfere with the extraction process (Romão et al., 2003). For the preconcentration of mineralized natural water, aliquots of 50 mL (after pH adjustment with NaOH and HNO_3 diluted solution) were placed in the system and the optimized conditions were adopted. Aliquots of tap water (50 mL) were subjected to the preconcentration procedure with no previous preparation.

3. Results and discussion

3.1. Characterization

Castor leaves have high protein content; hence, several absorption bands attributed to amine in the protein structure were observed, as can be seen in Fig. 2. A band at 1738 cm^{-1} was assigned to the stretching vibrations of the C=O bond of carboxylic acids, an important group that may be involved in metal ion coordination through ion exchange process. The intense absorption band at 1063 cm^{-1} is characteristic of polysaccharides or similar substances, while the absorption band at 1540 cm^{-1} corresponds to protein, indicating that the material may contain protein-bound polysaccharides (Zhang et al., 2008).

The absorption bands at 1404 and 1234 cm^{-1} can be attributed to the C-N stretching vibrations of primary amides resulting from C-C-C stretching. The broad absorption band observed at 3400 cm^{-1} was assigned to the stretching of the O-H bond of hydroxyl functional groups. The comparison between the spectra of pure castor leaf powder (castor leaf) and castor lead powder with adsorbed Cu(II) (castor leaf-Cu(II)) showed no difference. Usually a displacement of the absorption band, which participates in the metal coordination, is expected. Nevertheless, the results should not be analyzed separately since the shift of the bands may be associated to the amount of adsorbed metal and other variables related to the materials theirselves.

Analysis of the material's surface indicated that the castor leaf powder area was 1.373 ± 0.016 m^2 g^{-1} that is consistent with that of a similar material (Castro et al., 2011). The pore size distribution and the behavior of adsorption and desorption isotherms were also analyzed. The results are illustrated in Fig.3 and indicate that the material has type II adsorption-desorption isotherms, that are common for non-porous or macroporous adsorbents. The hysteresis loop was type IV, which is normal for capillary condensation taking place in mesoporous materials (see inset in Fig. 3) and commonly found in this kind of material (Sing et al., 1985). As this inset shows, the castor leaf powder was both mesoporous (68Å) and macroporous (110 and 170Å), with predominance of micropores smaller than 10.51 Å, what explains the material's small surface area.
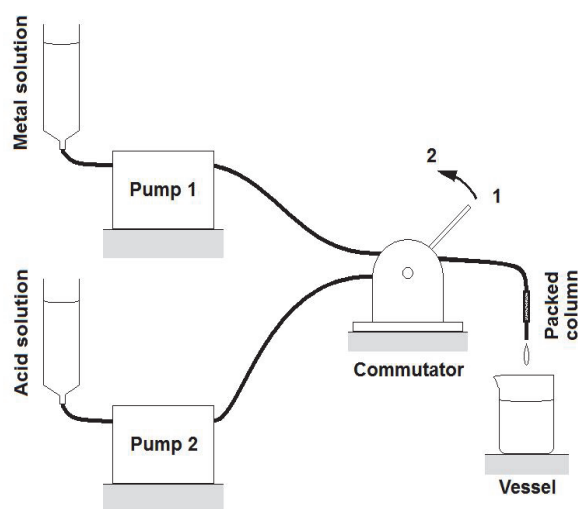

Fig. 1. Preconcentration system. Schematic representation of preconcentration system used. An injector/commutator is coupled to two peristaltic pumps, which controls the sample flow (pump 1) and eluant flow (pump 2)
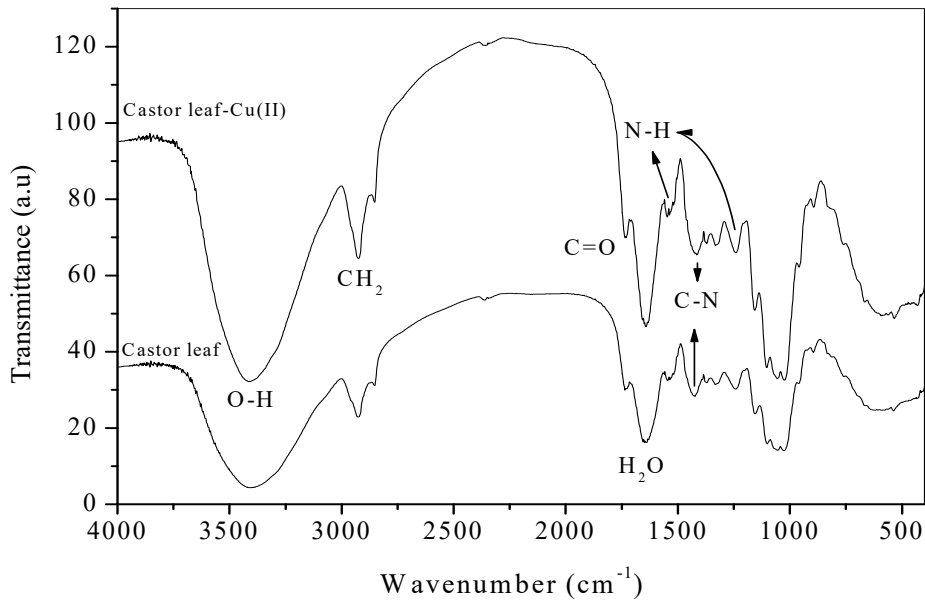
Fig. 2. Castor leaf powder FTIR spectra. Infrared spectra of pure castor leaf powder (castor leaf) and castor leaf powder with adsorbed Cu(II) (castor leaf-Cu(II))

3.2. Batch experiments

Parameters, such as extraction kinetics, pH and maximum extraction capacity, were investigated in batch experiments. In the extraction kinetics experiment, the concentration of the solution was fixed at 0.315 mmol L^{-1}, the pH at 5.0, the solution volume at 10 mL, the biosorbent mass at 0.02 g and the time factor was studied in a range of 1-50 minutes.

The adsorption increased rapidly from 1 to 10 minutes when the dynamic equilibrium was reached. At this point, almost all the accessible sites of the leaf powder were occupied by the metal ions in solution, reaching equilibrium with the remaining ions in solution (Fig. 4).

The rapid kinetics achieved with this material is in agreement with other related materials (Alcântara et al., 2004; Castro et al., 2007, 2011) and confirms that castor leaf powder can be effectively applied in preconcentration studies using a continuous flow system. The influence of pH on metal ion extraction was investigated using a stirring time of 10 minutes and keeping the other parameters mentioned in the kinetics experiments constant.

The results (Fig. 5) indicated that the quantitative extraction only occurred at pH 4 and 5. This behavior can be explained by the high concentration of H^+ ions and the consequent protonation of adsorption sites. However, this is not a problem since the pH of natural water is usually higher than 4.
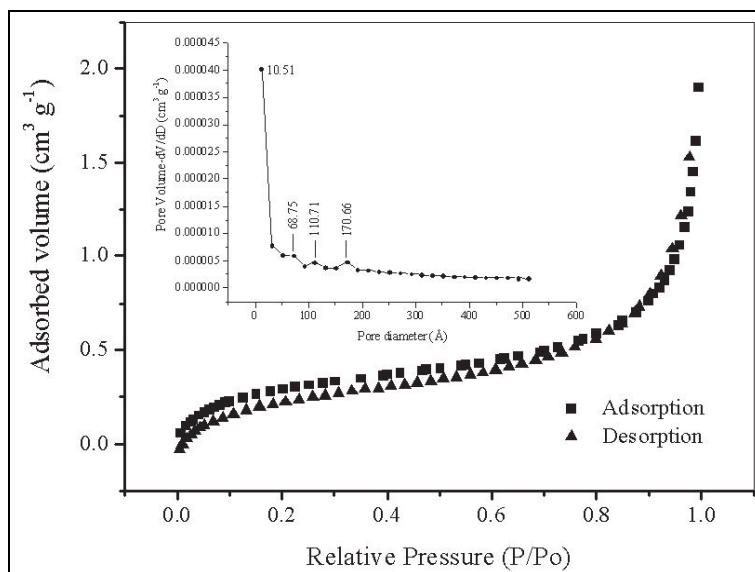

Fig. 3. Adsorption and desorption of nitrogen isotherms. Adsorption-desorption isotherms of nitrogen and distribution of pore diameter and pore volume (inserted Figure)
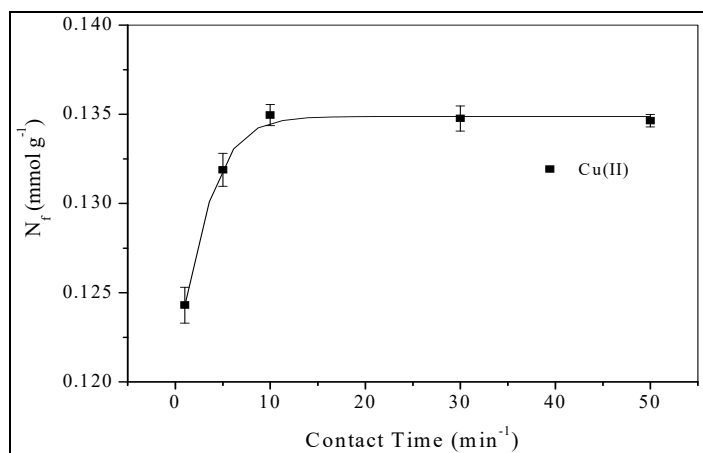
Fig. 4. Cu(II) adsorption as a function the contact time. Influence of stirring time on Cu(II) removal from aqueous solution using 0.02 g of castor leaf powder

The maximum extraction or adsorption capacity of castor leaf powder was determined based on the increasing concentrations of metal ions in solution. The stirring time was kept constant at 10 minutes, the pH of the metal ion solution was adjusted to 5, and the other parameters were the same as those used in the preceding experiments. The extraction capacity (N_{fmax}) of Cu(II) reached equilibrium at 0.310 mmol g^{-1}, as indicated in Fig. 6.
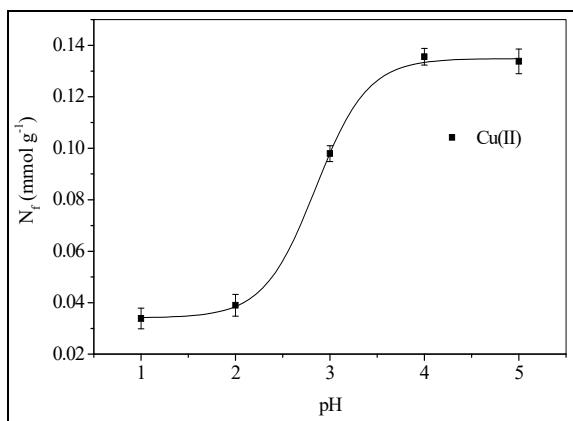

Fig. 5. Cu(II) adsorption as a function of the pH. Influence of pH on Cu(II) removal from aqueous solution using 0.02 g of castor leaf powder

The modified Langmuir equation (Eq. 2) was applied to the experimental data from the adsorption experiments and the process was found to follow the model (Machado et al., 2004; Santos and Airoldi, 1993):

$$\frac{C_s}{N_f} = \frac{C_s}{N_s} + \frac{1}{N_s b} \tag{2}$$

where C_s is the concentration of the solution (mmol L^{-1}), N_f is defined as the amount of metal ion extracted from the solution per gram of adsorbent (mmol g^{-1}), and N_s is the maximum amount of metal ion extracted from the solution (mmol g^{-1}). According to Eq. (2), the N_s value obtained for Cu(II)

was 0.321 mmol g^{-1}. The linear shape of the metal ion adsorption isotherm is depicted in the inset of Fig. 6.

The similarity of the N_f and N_s values for Cu(II) ions indicates that the adsorption sites were almost fully occupied by metal species, and the high adsorption capacity attained can be explained by G. R. Pearson's classification of acids and bases. Because nitrogen atoms are classified as an intermediate base, they are expected to develop some affinity for borderline acids such as Cu(II) (Pearson, 1963).

3.3. The enrichment factor (E_f) and interfering ions

The proposed method for the enrichment of metal ion concentrations was applied to the preconcentration of 50 mL Cu(II) standard solution of 1.574 x 10^{-4} mmol L^{-1} considering several parameters. The first parameter investigated was the sample flow rate in a range of 0.5-5.0 mL min^{-1}; the elution was performed with 1.0 mL of nitric acid solution percolated at 1.0 mL min^{-1}. The results for this parameter optimization are summarized in Fig. 7a. According to Fig. 7a, at 0.5 and 1.0 mL min^{-1} the recovery is about 100% and at higher flow rates the recovery decreases until approximately 60% at a flow rate of 5 mL min^{-1}. This behavior may be related to the low interaction time between metal species and adsorptive sites at a flow rates higher than 1.0 mL min^{-1}; thus the metal species are not removed from the solution. As a quantitative adsorption was only achieved at 0.5 and 1.0 mL min^{-1}, the last one was chosen to carry out the next experiments.

The eluant flow, Fig. 7b, showed similar results. At flow rates higher than 1.0 mL min^{-1} metal ions desorption was not quantitative (less than 100%). These results may be associated to the low contact time between the H$^+$ species existing in the acid (2 mol L^{-1} nitric acid solution) and adsorptive sites containing the metal species. So, the flow rate of 1.0 mL min^{-1} was chosen to perform the next experiments.
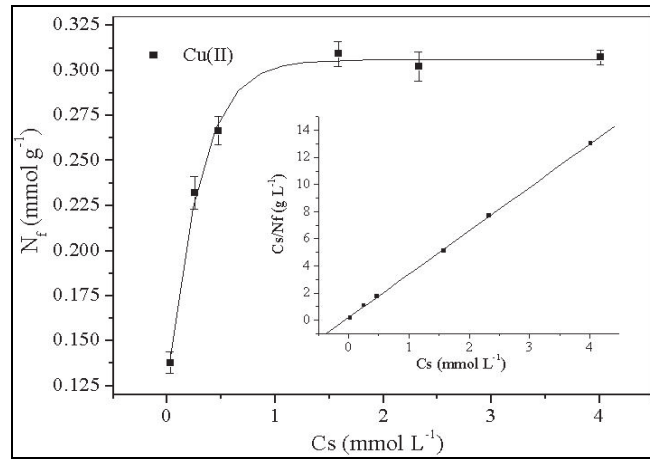
Fig. 6. Cu(II) adsorption as a function of the concentration. Adsorption isotherm of Cu(II) in aqueous solution and linearized adsorption isotherm according to Langmuir model (inserted figure). Linearized isotherm data: $r^2 = 0.9998$; angular coefficient = 3.20 and linear coefficient = 0.19

The eluant concentration (nitric acid solution) was also studied and the results (Fig. 7c), showed that at concentrations lower than 1.0 mol L^{-1} the recovery was not quantitative. This finding can be related to the quantity of H^+ available to be exchanged with occupied adsorptive sites. As suggested by Fig. 7c, a 0.5 mol L^{-1} solution does not present enough H^+ species to remove all adsorbed metal species in castor leaf powder. However, at concentrations higher than 1.0 mol L^{-1} the recovery was about 100%. In order to achieve a quantitative recovery and avoid the fast adsorbent deterioration, a concentration of 1.0 mol L^{-1} was chosen to do the next experiments.

The last optimized parameter was the eluant volume and as can be seen in Fig. 7d, at volumes lower than 1.0 mL the recovery was not quantitative. This result can be attributed to the low amount of H^+ species. Despite the high enrichment factor achieved in theses volumes, poor percent recoveries do not allow their use. At higher volumes, above 1.0 mL, the recovery is about 100%. Thus, a volume of 1.0 mL was chosen because it enables a quantitative recovery and a high enrichment factor.
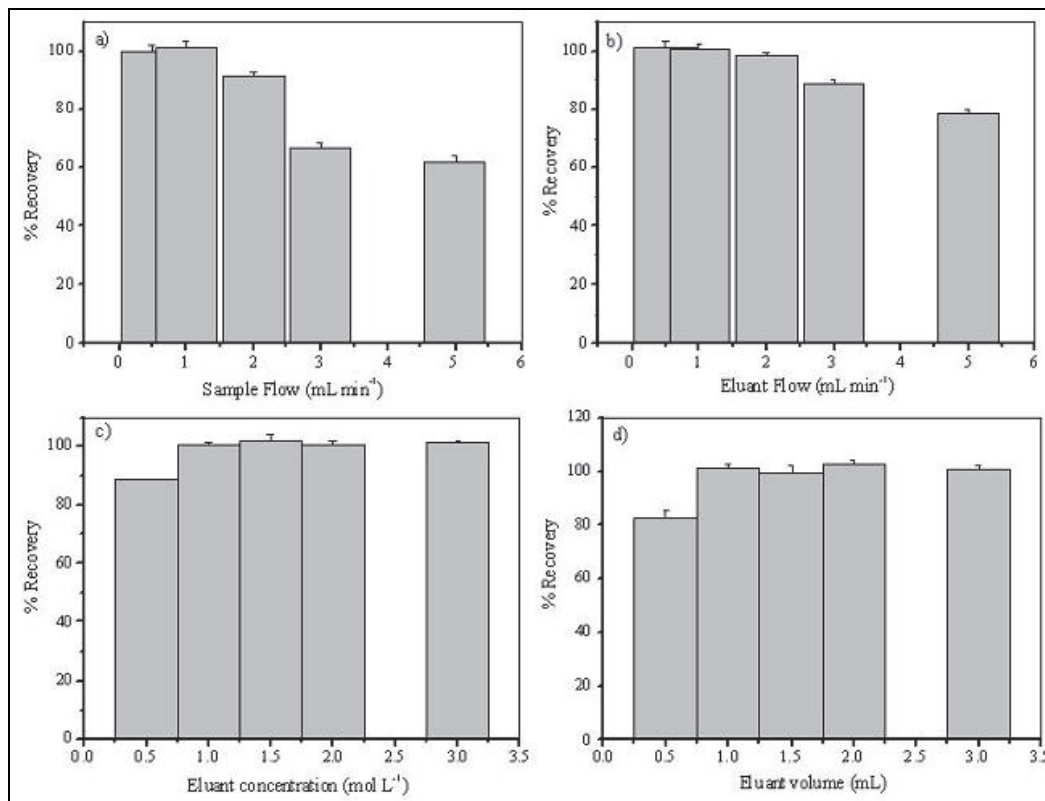

Fig. 7. Preconcentration parameters evaluated. Effect of preconcentration parameters (sample and eluant flow rate, eluant volume and concentration) on the Cu(II) recovery

Taking into account the optimized parameters, the enrichment factor (Cu(II) concentration in the eluate/Cu(II) concentration in the standard solution) was about 47-fold (Table 2).

To evaluate how certain ions that are normally present in natural water samples affect the Cu(II) adsorption process, solutions of all the species (NO_3^-, Cl^-, PO_4^{3-}, Ca^{2+} and Mg^{2+}) were prepared in a concentration range of 10-100 mg L^{-1}. The effects of these ion species are summarized in Table 1. As this table shows, the main influence came from chloride ions, which strongly coordinate metal species, preventing their access to adsorption sites when the anion concentration is higher than 10 mg L^{-1}.

The chloride concentration in natural water contaminated with domestic sewage is usually higher than 10 mg L^{-1}, but this concentration was lower in the water used in this study. Regarding to other ions examined here, a slight decline on the Cu(II) recovery rate was observed in the presence of high concentrations (100 mg L^{-1}) of PO_4^{3-} and Ca^{2+}. On the other hand, NO_3^- and Mg^{2+} did not interfere in the adsorption process even at high concentrations. The maximum Cu(II) ion extraction/adsorption capacity of castor leaf powder was compared to that of the other materials, as shown in Table 2. As indicated in Table 2, the Cu(II) adsorption capacity of castor leaf

powder is higher than that of the other natural and synthesized materials. This feature confirmed the validity of the preparation method, which is an environmentally friendly process that requires no type of reaction. Moreover, the low cost of this material makes it highly attractive for industrial and environmental applications.

3.4. Sample preconcentration

After the mineralization step, the pH of the natural water samples was adjusted to 5 with a diluted solution of sodium hydroxide, after that aliquots of 50 mL were injected into the preconcentration system under the previously described conditions. The tap water sample was injected into the system with no pretreatment.

To validate the proposed continuous flow system, spiked samples of natural and tap water and a standard reference material (1643e) were also tested and the results are summarized in Table 3. As can be seen in Table 3, all the water samples, including the spiked samples, showed a 47-fold enrichment factor. The copper concentration of tap water was 4.85 µg L^{-1}, which was also confirmed by the preconcentration of a spiked sample.

Table 1. Influence of certain natural ions on the extraction of Cu(II) from a 0.01 mg L^{-1} solution

Interfering ions	*Concentration (mg L^{-1})*		
	10	*50*	*100*
		% Recovery	
Cl^-	98.3 ± 1.5	73.5 ± 3.1	64.1 ± 0.3
NO_3^-	100.3 ± 1.5	101.2 ± 1.2	99.0 ± 2.0
PO_4^{3-}	100.5 ± 1.0	98.8 ±5.2	91.7 ± 4.7
Ca^{2+}	98.1 ± 2.1	94.4 ± 1.6	82.7 ± 2.2
Mg^{2+}	99.0 ± 1.2	101.1 ± 0.8	100.2 ± 1.3

Table 2. Comparison of the Cu(II) adsorption capacity and enrichment factor (E_f) of castor leaf powder with other materials

Material	N_s *(mmol g^{-1})*	E_f	*Mass (g)*[b]	*Reference*
Modified silica (Si-AMP)	0.447	20	0.005	Alcântara et al. (2004)
Minced banana Peels	0.330	20	0.02	Castro et al. (2011)
MT-SiDav-NH$_2$	0.450	----	0.5	Mureseanu et al. (2011)
Modified silica (Ami-SiO$_2$)	0.016	----	0.04	Ngeontae et al. (2009)
Activated Carbon	0.166	----	----	Xuejiang et al. (2011)
Amberlite XAD-2000	0.100	200	----	Duran et al. (2009)
castor leaf powder	0.321	47	0.003	[a]

[a] *The present study;* [b] *Mass used in the preconcentration studies*

Table 3. Levels of trace copper determined in fresh water sample from Paraná River, tap water and CRM 1643e

Sample	*Spike (mg of Cu(II))*	E_f	*Concentration (mg L^{-1}) after preconcentration*
Paraná river[a]	------		
Paraná river	------	47	2.213 ± 0.08
Paraná river	5.0x10^{-4}	47	2.722 ± 0.09
Tap water	------	47	0.228 ± 0.02
Tap water	1.25x10^{-4}	47	0.340 ± 0.009
	Reference value (µg L^{-1})	E_f	Concentration (µg L^{-1})
CRM 1643e	22.76 ± 0.31	47	1090 ± 20

[a] *Water without mineralization*

The concentration of the spiked tap water sample was about 4.73 µg L^{-1}, taking into account the 47-fold enrichment factor and an amount of 1.25x10^{-4} mg of copper added to a 50 mL aliquot. The concentration obtained in the preconcentration of the mineralized natural water sample was about 47.09 µg L^{-1}, and the 47-fold enrichment factor was also observed in the preconcentration of spiked river water.

The preconcentration results of the CRM were in agreement with the enrichment factor attained and with certified values, demonstrating that the system can be applied for the determination of trace copper in aqueous samples.

4. Conclusions

Castor leaf powder showed good adsorption capacity (0.321 mmol g^{-1}) compared to other adsorbents. This was attributed to its high protein content, confirmed by the FTIR spectra. The adsorption capacity, combined to the simplicity of the preparation step, makes this material a low cost candidate for the treatment of wastewater and industrial effluents containing toxic metals.

The preconcentration step demonstrates that the material can be easily applied for determination of low copper concentration in aqueous samples after the mineralization procedure. Preconcentration of a certified reference material attested the good performance of the system, since the 47-fold enrichment factor was reproduced.

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