

Cassava root husks powder as green adsorbent for the removal of Cu(II) from natural river water

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ABSTRACT: cassava root husks were turned into a fine powder of controlled particle size (63 – 75 μm). Based on the analysis of FTIR, NMR and elemental analysis it was observed the existence of some groups alcohol, carboxylic acids and amines and the presence of sulfur, nitrogen and oxygen also methionine and thiamine, respectively. The material was applied in solid-phase extraction of Cu(II). The adsorption maximum amount of metal species extracted from the solution, N_s , was determined to be $\sim 0.14 \text{ mmol g}^{-1}$. The material was utilized in preconcentration experiments, which culminated in an enrichment factor of 41.3-fold. With the aid of the enrichment factor, experiments were carried out to determine the Cu(II) content in tap water and natural water. Preconcentration method was also applied to a certified reference material (1643e) and the concentration found was $23.03 \pm 0.79 \text{ g L}^{-1}$, whereas the specified Cu(II) concentration was $22.7 \pm 0.31 \text{ g L}^{-1}$.

KEYWORDS: cassava husks; copper ions; metal–surface interaction; high regeneration capacity.

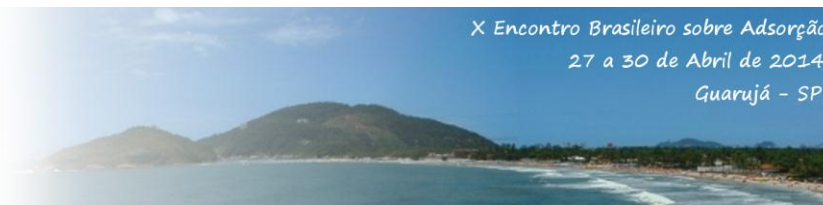
1. INTRODUCTION

Toxic metals are still one of the greatest concerns regarding environmental pollution (Manahan, 1997; Reeve, 2002; Baird and Cann, 2011). Their use is exploited in many human activities and they are present in pesticides, dyes, fertilizers, fossil fuels, batteries, etc. (Baird and Cann, 2011). Then, due to such an extensive use, they may be later dispersed in the environment as contaminants, which occur through a large variety of ways. One of the most common dispersion way is through the water, solubilized in some liquid media and then dumped into water bodies that carry them for long distances from its sources, or yet infiltrating the soil and attaining the ground water. Another dispersion way is through the atmosphere, adsorbed onto solid particles arising from the burning of materials/substances that

contain such elements (Baird and Cann, 2011). In this case they also may reach remote Earth's regions, and finally depositing themselves onto soils, lakes, rivers, etc., or then precipitating along with the rains, causing the contamination of vast areas (Reeve, 2002) and (Baird and Cann, 2011).

Once they are found as pollutants in some biota, they may be subjected to interactions with organisms, originating phenomena like bioaccumulation and conversion to organometallic species, as examples.

Some health diseases that are associated to the contamination by metals are Alzheimer's, kidney damage, abnormal thyroid artery, polycythemia, over-production of red blood cells, right coronary artery problems, fatal cardiac arrest, blood pressure, lung cancer, stomach cancer, gliomas and others diseases (Strachan, 2010;



Goyer and Golub, 2003; Dieter et al., 2005; Nordberg, 2002).

In view of the high risk that metals pose to living beings' lives, it is of great importance that their emission to the environment is greatly reduced or, if possible, eliminated, and also that a rigorous control over their emission is accomplished. To do so, many techniques have been proposed to remediate wastewaters (Knight, 1997; Shokrolahi, 2010; Mohan and Singh, 2006; Babel and Kurniawan, 2003). One of the main techniques is the use of adsorbent materials like zeolites, silicas, polymers, cellulose, industrial/agricultural wastes, activated carbon and clays among others (Mohan et al., 2002; Babel and Kurniawan, 2003; Liu et al., 2005). Nevertheless, some of these materials in their bare forms do not present extraordinary adsorptive capacity and, thus, require an organofunctionalization step, prior to their application as adsorbents (Jorgetto, 2013). In spite of the current great success acquired by organofunctionalized materials, they still present a serious drawback in detriment of their wide application, which is the use of costly high purity reagents and solvents involved in their manufacturing. Furthermore, the synthesis and functionalization of such materials are usually associated to the generation of toxic residues (Castro, 2011).

In order to circumvent such a drawback, biomaterials have presented themselves as a great alternative to produce a less costly sorbent for the remediation of wastewater. Biomaterials like castor tree leaves (Martins, 2013), sugar cane bagasse (Gurgel and Gil, 2009), orange peels (Gönen and Serin, 2012), banana peels (Castro, 2011), and peanut hulls among others (Johson, 2002), were already studied regarding their adsorption capacities, and showed that they can effectively remove toxic metals from aqueous media.

In Brazil, cassava is a very common plant whose root is highly appreciated for its characteristic flavor. On the other hand, cassava root husks do not have any known application, rather than maybe vegetal manure. Due to the cassava industrial/agricultural exploitation, it is expected that its husks are abundantly generated, and so its reuse as a metal biosorbent acquires an interesting application for such a waste.

In view of this, in the present work, minced cassava root husks were characterized by FTIR and elemental analysis to identify functional

groups responsible for its capacity to coordinate metal ions. The material, was tested in the extraction of Cu(II) from water and was applied in column experiments to test its ability to preconcentrate metal from natural river water. The accuracy of the preconcentration method was evaluated by comparison against a certified reference material (SRM 1643e).

2. MATERIALS AND METHODS

2.1. Preparation of the Cassava Husks Biosorbent

Cassava roots were acquired in a conventional market, in Botucatu city (São Paulo, Brazil), and they were washed. Then, their husks were separated from the inner flesh with the aid of a knife. The husks were taken to a ventilated heated chamber at 100 °C in which they were kept for 24 h. Then, the dried husks were grinded to form a gross powder. The fraction of whose diameter was comprehended between 63 and 75 µm was selected to perform the adsorption experiments. Though, prior to such experiments a washing step was necessary to remove soluble organic substances that could be present in the material.

2.2. Batch Experiments

In order to elucidate the adsorptive properties of cassava husks, important parameters were investigated, such as kinetic equilibrium, effect of the pH and maximum adsorptive capacity.

All the experiments were performed by weighing approximately 20 mg of cassava husks powder and by stirring the material's mass with 1.8 mL of the metal solutions under controlled conditions. After mixture filtration, the supernatant was collected for further analysis through Flame Atomic Absorption Spectrometry (FAAS) (or Grafite Furnace Atomic Absorption Spectrometry (GFAAS), when needed). The adsorptive capacity for each condition was obtained by comparing the metal content in solution before and after each experiment.

Kinetic experiments were performed to uncover the minimum time required for the material to reach kinetic equilibrium. These experiments were carried out by stirring the

material with the analyte solution at 1–240 min intervals at room temperature. To perform the kinetic experiments the concentration of Cu(II) solution was set as 45 mg L^{-1} .

Also, the effect of the solution's pH over the Cu(II) uptake was evaluated. From adsorption experiments under different pH values, it was possible to determine the optimum pH whereby the material attains the highest adsorptive capacity. Such experiments were carried out by stirring the material with 70 mg L^{-1} solutions whose pH values were adjusted in an interval of 1 – 6.

Finally, in order to determine the material's maximum adsorption capacity, it was stirred with solutions of different Cu(II) concentrations, which varied from 10 to 430 mg L^{-1} . For all these experiments, the contact time and the pH were settled at 10 min and 5 min, respectively.

2.3. Preconcentration experiments

Continuous flow experiments were performed with 5 mg of cassava husks powder, which was packed into a 4 mm across a glass cylindrical tube. Such a tube was found coupled to peristaltic pumps and to a flux commutator by Tygon tubes, and the system was set to provide a continuous flow of 1.5 mL min^{-1} .

Firstly, one of the pumps injected 50 mL of a $10 \text{ } \mu\text{g L}^{-1}$ Cu(II) solution (pH 5–6) through the tube containing the material. Later, the flux commutator was shifted to switch the metal solution to 2 mol L^{-1} HNO₃ solution, and then the Cu(II) ions were eluted from the column. 1 mL of the eluent was collected prior to its analysis through Atomic Absorption Spectrometry.

The experiment enabled to uncover the material's enrichment factor for Cu(II), which was later employed to determine the amount of Cu(II) in tap water and in natural river water. The same procedure was also applied to a certified reference water standard (1643e) to validate the developed methodology. Tap water was collected in the laboratory of the Chemistry Department of the São Paulo State University, in Botucatu city (Brazil), and the natural water sample was collected from Paraná river, in Ilha Solteira city (Brazil).

In addition, a reutilization experiment was accomplished to evaluate the material's endurance after several sorption/desorption processes, until decrease in the extraction capacity was observed.

2.4. Preparation of the natural water sample

The natural water sample was subjected to a mineralization process so that metal ions could be released in the medium prior to the preconcentration step. To do so, aliquots of 50 mL of water samples were first filtered in $45 \text{ } \mu\text{m}$ pore size membrane and then transferred to a beaker. The samples were heated near to boiling point until they have their volumes reduced to $\sim 10 \text{ mL}$. Then 2 mL of concentrated nitric acid was added to the beakers, and then the samples were left at rest overnight. The next day, the natural water samples were heated again to boiling point, and 200 μL of H₂O₂ were added to the samples to complete the mineralization for 1 h. The samples had their pH adjusted to 5 with the aid of a 1 mol L^{-1} NaOH solution and the samples were adjusted to 50 mL in volumetric flasks. Tap water samples were preconcentrated without any treatment, since it presented adequate pH.

3. RESULTS AND DISCUSSION

3.1. Characterization of the cassava husks powder

The infrared spectrum of cassava husks powder was recorded to identify functional groups responsible for metal ion coordination. Figure 1 shows the FTIR spectrum, which indicated the presence of large OH stretch band in the wavenumber of 3400 cm^{-1} alongside with intense CH stretch band found in 2929 cm^{-1} . These bands are expected for vegetal materials, since these groups are the main constituents of cellulose. Those absorption bands found between 1000 and 1200 cm^{-1} may be assigned to C—O stretching vibration from alcoholic groups. The appearance of an absorption band in the region of 1738 cm^{-1} is an evidence of the existence of acid groups (such as carboxylic), which is directly related with the adsorption process. Previous published papers also reported the occurrence of substances containing acid groups in cassava, such as methionine, tryptophan and phenylalanine (King and Bradbury, 1995; Nambisan, 2011). The strong band at 1640 cm^{-1} may be attributed to primary and secondary O—H vibration from glucoside units.



The infrared absorption bands observed from 1368 to 1244 cm^{-1} may be assigned to C—N stretch from aromatic molecules such as thiamine and other aminoacids that may be present at low amount. The absorption bands corroborates with the elemental analyses that confirmed the presence of carbon (41.42 wt%), hydrogen (6.64 wt%) nitrogen (1.02 wt%) and sulphur (0.6 wt%).

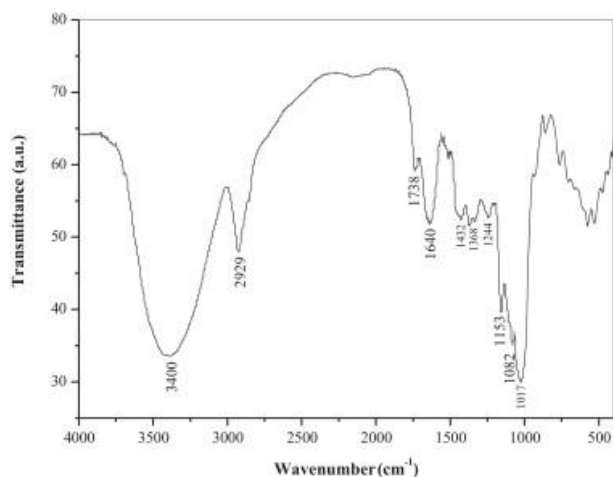


Figure 1. Infrared spectrum of cassava root husk with some organic groups absorption bands. Measuring conditions: 200 scans; resolution 4 cm^{-1} ; room temperature ($28\text{ }^{\circ}\text{C}$).

Although the absence of sulphur absorption bands its presence may be expected as the results of ^{13}C nuclear magnetic resonance obtained through cross-polarized technique suggest the presence of sulphur containing molecules. The main resonances observed are in the region of CO (from 62.4 to 75 ppm and from 102 to 103 ppm) and may assigned to glucoside carbons. The resonance at 81.5 ppm suggests the presence of apiosyl, as described in the literature (King and Bradbury, 1995). There is no evidence of C \equiv N bond, as its characteristic signal is usually observed at 120 ppm and hence the material does not present significative amount of linamarin and lotaustralin. The signals observed at 55 and 54 ppm may be assigned to CNH $_2$ and CN $^+$ from methionine and thiamine, respectively. As the signal between 37 and 40 ppm corresponding to C $_{\beta}$ -S-S was not observed and as the signal of C $_{\alpha}$ (expected at 50 ppm) is far from the observed signal at 55.5 ppm the presence of cysteine is not confirmed.

The specific surface area was analyzed through BET method (Braunauer et al., 1938) and

provided a superficial area smaller than $1\text{ m}^2\text{ g}^{-1}$ and a low pore volume, which implies that the material is practically non-porous. According to these data, a rapid adsorption kinetic may be expected, since Cu(II) adsorption will preferentially occur at materials surface.

The pH $_{pzc}$ was evaluated to be 5.2, above this value the material surface is negatively charged and the adsorption may be favored.

3.2. Batch experiments

From the kinetic experiment, it was possible to uncover the minimum dynamic contact time required for the material to reach equilibrium. As it can be seen from Figure 2, the material presents a rapid kinetic, as the adsorption equilibrium is attained in less than 1 min. This indicates that cassava husk's structure provides high accessibility for Cu(II) ions to be coordinated to its adsorption sites.

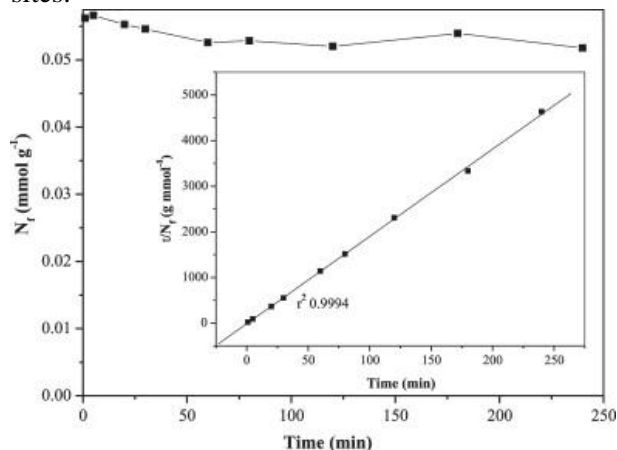


Figure 2. Kinetic study of Cu(II) adsorption in aqueous medium using 20.0 mg of cassava roots powder and pseudo-second-order kinetic study for Cu(II) in aqueous medium (inset).

The data provided by kinetic experiment, which consists of the linearized form of the pseudo-second-order kinetic model (Ho and Mckay, 1999), provided a high linear correlation coefficient of 0.9994, demonstrating the great accordance between the experimental data and pseudo-second order kinetic model. Such an agreement implies that the adsorption process occurs through the coordination of Cu(II) ions to the non-bonding electron pairs of the material's structure. Also the experimental data enabled to obtain the theoretical adsorption capacity at



equilibrium (N_f), $0.052 \text{ mmol g}^{-1}$. This value corroborates to the experimental data observed from Figure 2, which provided an adsorption capacity of $0.054 \text{ mmol g}^{-1}$. The obtained results corroborate with the data presented related to pore characteristics.

The influence of pH related to Cu(II) adsorption process was investigated under solution pH values between 1 and 6, because the concentration of H^+ species will affect the reaction equilibrium due to the adsorption sites protonation. Figure 3 presents a plot of Cu(II) adsorption capacity over a range of solutions pH values. As can be seen from Figure 3, the present natural adsorbent can be easily applied in the adsorption of Cu(II) under acidic medium, pH 3. Above this value the adsorption capacity remains constant, which is an indicative that H^+ species does not exert high influence over adsorption equilibrium. Below pH 3, adsorption sites (amine and carboxyl groups) are protonated due to the high concentration of H^+ species, this way the adsorption capacity is reduced. pH values above 6 were not investigated due to the metal hydrolysis, which may occur compromising the adsorption investigation.

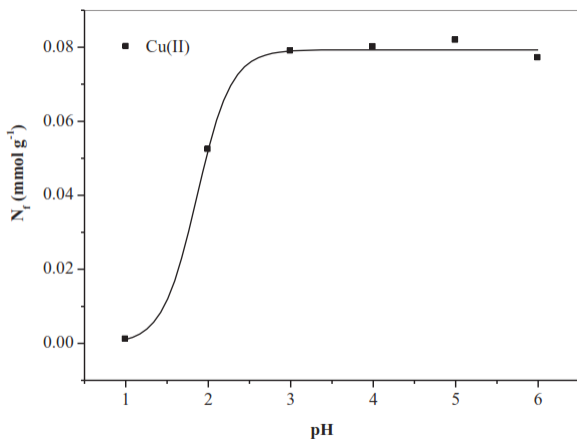


Figure 3. Effect of pH solution on the adsorption of Cu(II) onto the surface of minced cassava husk.

Under optimum contact time and pH conditions, an experiment to determine the maximum adsorption capacity was performed by the saturation condition of Figure 4. The experiment was carried out as a function of Cu(II) concentration, which provided a N_f value for each condition. From the concentrations (in mmol L^{-1}) and its respective N_f , an adsorption isotherm was plotted (Figure 4).

As can be seen from Figure 4 the plotted data approaches a maximum value at approximately 0.14 mmol g^{-1} , at the highest Cu(II) concentrations. In order to elucidate the adsorption process that occurs in the material, the experimental data were also fit to linearized Langmuir equation (Eq. (1)) (Langmuir, 1932):

$$\frac{C_s}{N_f} = \frac{C_s}{N_s} + \frac{1}{N_s b} \quad (1)$$

In this expression, C_s is the concentration of solution in equilibrium (mmol L^{-1}), N_f the concentration of metal ions adsorbed on the surface (mmol g^{-1}), N_s the maximum amount of metal ions adsorbed per gram of adsorbent (mmol g^{-1}), which depends on the number of adsorption sites, and b is a constant.

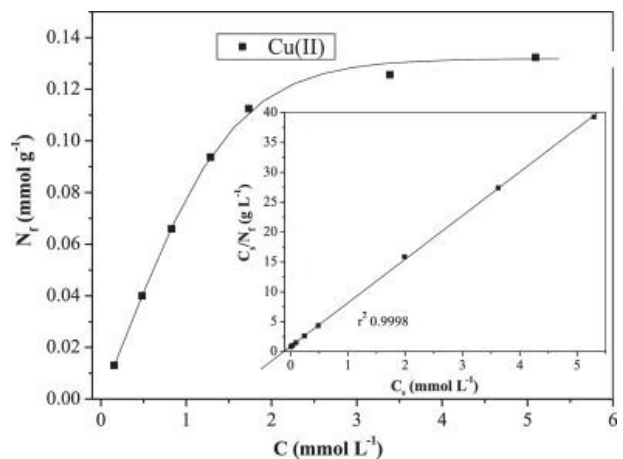


Figure 4. Adsorption isotherm of Cu(II) from aqueous solution at room temperature ($27 \text{ }^\circ\text{C}$) and linear shape of adsorption isotherm of Cu(II) (inset). Stirring time 10 min; adsorbent mass: 20.0 mg.

As can be seen from Figure 4 (inset), the linearized Langmuir model presented great agreement with the experimental data, demonstrated by the high linear correlation coefficient of 0.9998. So, the best-fit straight line of Figure 4 (inset) allowed to estimate the maximum adsorption capacity for Cu(II), based on the determination of the angular coefficient ($1/N_s$), obtaining $N_s = 0.137 \text{ mmol g}^{-1}$. The closeness of N_s and N_f values suggests that all available adsorption sites are occupied by metal species and due to this small difference the interaction may be related to a covalent bond formation, thus the adsorption



process can be classified as a chemisorption. In case where natural adsorbents are applied in solid-phase extraction experiments, it is not possible to establish a connection between nitrogen and sulphur content and the adsorption capacity, as a great amount of sulphur and nitrogen atoms are distributed at material's structure and not available. A schematic interaction between material surface and metal ions is represented in Figure 5.

According to other available materials in the literature cassava husks showed an adsorption capacity similar to other synthetic and natural materials as can be seen from Table 1.

3.3. Preconcentration experiments

The preconcentration system used was described in the previously published work (Jorgetto et al., 2013). The column was packed with 5 mg of cassava husks powder, 50 mL of standard solution of Cu(II) ($\mu\text{g L}^{-1}$) was preconcentrated, the eluent volume (HNO_3 2.0 mol L^{-1}) used was 1 mL and the eluent and sample percolation flow were kept constant at 1 mL min^{-1} . After several experiments the best recoveries and

the highest enrichment factor were attained with the mentioned conditions. Through the comparison between the proposed material (cassava husks powder) with other solid supports materials applied in the Cu(II) adsorption and preconcentration, presented in Table 1, is possible to infer its advantages. Cassava husks showed higher enrichment factor compared with several materials.

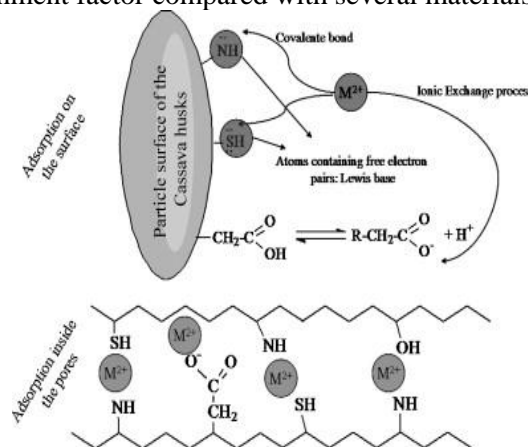


Figure 5. Schematic representation of possible interactions between material's surface functional groups and divalent metal cations.

Table 1. Comparison of Cu(II) ions adsorption capacity and preconcentration in solid support materials.

Type material	N_s (mmol g^{-1})	Mass used (g)	Enrichment factor	Reference
Cel-DTX	0.058	0.003	50.0	(Jorgetto, 2013)
Peanut hull pellets	0.18	–	–	(Johson, 2002)
AMP modified silica	0.45	0.005	20.0	(Pereira, 2010)
GMZ bentonite	0.10	–	–	(Li, 2009)
p-Aminobenzoic modified cellulose	1.96	1.00	10.1	(Castro, 2004)
Amidoamidoxime silica	0.016	0.04	20.0	(Ngeontae, 2009)
Cassava husks powder	0.14	0.005	41.3	a

a Data presented by the developed natural adsorbent.

The enrichment factor is an important analytical parameter which enables to determine the concentration of samples based on the amount

of preconcentrated analyte from such samples. In view of this, the same preconcentration procedure was applied to tap water, natural water and to a



certified reference water standard (1643e), so that their Cu(II) content could be measured. The main advantage of this technique is that it allows the safe analyte quantification in diluted solutions through Flame Atomic Absorption Spectrometry, without resorting to more sensitive and costly techniques (GFAAS, ICP-OES and ICP-MS). The data obtained from the preconcentration experiments are summarized in Table 2.

Table 2. Determination of Cu(II) in natural water, tap water and in the reference material (1643e).

Sample	Preconcentrated sample ($\mu\text{g L}^{-1}$)	Calculated Cu(II) concentration ($\mu\text{g L}^{-1}$)
Natural water	74.65 ± 1.6	1.808 ± 0.039
Tap water	150.56 ± 0.01	36.87 ± 0.13
Reference material	951 ± 32.92	23.03 ± 0.79 (22.7 ± 0.31) ^a

a. Reference material's specified Cu(II) concentration

As it may be noted from the obtained data and the specified Cu(II) concentration of the reference material, the technique provided a good agreement for the determination of Cu(II) in real

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samples prior to its mineralization procedure, which is required to oxidize organic matter that may complex metal species in solution.

Regarding the reutilization experiment, the material kept its adsorptive capacity above 95%, demonstrating no significant loss until 40 cycles (adsorption/desorption). The decrease in metal ion recovery above 40 cycles may be attributed to the oxidation of coordination sites existing on the surface of the material.

4. CONCLUSIONS

Among several qualities such as low cost and availability, cassava husks still present good adsorptive properties. The existence of carboxyl, amine and other functional groups at material's surface is the main responsible for its adsorption capacity. After adsorption data linearization, according to Langmuir equation, the maximum adsorption capacity was similar to other related materials (0.14 mmol g^{-1}). The low cost adsorbent, when applied in continuous flow mode, presented an enrichment factor of 41.3 and an exceptional regeneration capacity, which easily enable its safe use through 40 adsorption/desorption cycles. Due to these mentioned advantages cassava husks may be useful in the determination of Cu(II) ions at trace levels when expensive equipments are not available.

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