

Preliminary Evaluation of the Silica and Others Chemical Constituents of the Lyophilized Tea of *Equisetum Arvense* and Application of Its Biomass Wastes for Copper Adsorption

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Abstract

The herb *Equisetum arvense* is an herbaceous plant, commonly known as horsetail and as a medicinal plant. Its therapeutic resource is diffused intensely in the urban environment as an alternative or complementary form to allopathic medicines, therefore it is an important theme focused on medicine and popular health. In this context, the focus of the present work was to characterize the product of the tea from a manipulation form made by specialized pharmacy (M) and other natural product banking (B). The two horsetails were extracted in aqueous medium since this is the form in which the material is absorbed by the organisms. The M and B lyophilized products were preliminary characterized by infrared spectroscopy (FTIR), visible ultraviolet (Uv-vis), scanning electron microscopy (SEM) and X-ray dispersive energy (EDX). The resulting biomass adsorption (wastes) were applied in the cupric ions adsorption and the maximum adsorption capacity (N_t^{\max} of M and B horsetail were 4.4×10^{-4} mol g^{-1} and 2.6×10^{-4} mol g^{-1} respectively.

Keywords: equisetum arvense, horsetail, lyophylization, characterization, adsorption

1. Introduction

The herb *Equisetum arvense* is an herbaceous plant of Equisetopsida class, Equisetales order, Equisetaceae family and belonging to pteridófitas group, commonly known as horsetail. It is originated in Europe, which has in its composition: minerals, potassium, magnesium, aluminum, calcium, phosphorus, phosphorus and sodium besides it is also known as one of the plants with the highest accumulation of silica (biogenic silica) (Sola-Rabada et al., 2016). The horsetail usually has more than 10% of inorganic constituents (Mimica-Dukic et al., 2008) phenolic compounds, flavonoids, among others (Hodson et al., 2005).

The horsetail is a ground plant with the largest amount of silica, which allows it has several applications in medicine area (Des Marais et al., 2003). Researchers believe that the anti-bacterial and antiseptic medicinal properties associated with the plant are due to the high silica content. But the way how silica is found in tea can determine its property and use (Holzhuter et al., 2003; Ma et al., 2006).

The silica is deposited on plant stems in the form of a thin surface layer. Silicon in orthosilicic acid form $[Si(OH)_4]$ is absorbed by the plant and deposited on the amorphous form, remaining immobile and it is not redistributed (Ferraz et al., 2008; Vivancos et al., 2016)).

The horsetail is widely used in folk medicine to fight against tuberculosis (Di Giorgio et al., 2015) lung problems, internal bleeding, urine retention (night urinary incontinence of children and elderly), prostate problems, osteoporosis, gastric ulcers, loss of blood from nose, mouth and the rectum and for cellulite treatment (Franco & Fontana, 1997; Gürbüz & Yesilada, 2008) In addition to these applications, it can also be used as a diuretic, for controlling cholesterol and for treating senile skin. It is used in Europe as an abrasive and metal polisher due to the presence of silica (Dos Santos, et al 2005; Husby, 2013; Mitani & Ma, 2015).

Currently, the use of the horsetail as a medicinal plant is a therapeutic resource diffused intensely in the urban environment, as an alternative or complementary form to allopathic medicines, therefore it is an important theme

focused on medicine and popular health.

Phytochemical analyzes of *E. arvense* hydroalcoholic extracts revealed the presence of flavonoids (isoquercetin, camphorol), sterols (β -sitosterol, campesterol, isofucoterol), tannins, saponins and alkaloids (equispermine, palustine) (Ferraz et al., 2008; Cramer et al., 2005), these compounds are potential adsorbents and / or transition metal complexing agents. The adsorption is one of natural processes that results in immobilization and accumulation of a metallic ion, contained in a certain liquid, which fixes on a static solid surface the adsorbent (Datta et al., 2013). The adsorption process can be used to reduce the concentration of pollutant species when they are at levels above that are allowed to humans (Da Silveira et al., 2018).

The complete adsorption process can be described quantitatively by adsorption isotherms, which in constant temperature provides data related to adsorbed amount (Nf) and solute concentration (C) after the equilibrium be established (Da Silveira et al., 2018).

The focus of the present work was to characterize the product of the tea whose was extracted in aqueous medium (Since this is the form in which the material is absorbed by the organisms) by infrared spectroscopy (FTIR), visible ultraviolet (Uv-vis), scanning electron microscopy (SEM) and X-ray dispersive energy (EDX). In addition to carry out a study of its biomass adsorption (wastes) in aqueous medium with cupric ions (Cu^{2+}), thus determining its adsorptive capacity. Emphasis was placed on the presence of metals, mainly Si

2. Material and Methods

2.1 Reagents

All reagents were obtained from Merck. All solutions were prepared with deionized water from the Milli-Q system from Millipore at a resistivity no less than $18.2 \text{ M}\Omega \text{ cm}^{-1}$ at $25 \text{ }^\circ\text{C}$.

2.2 Material

The study was carried out with two types of horsetail teas purchased commercially in different establishments. The Horsetails were obtained in a natural product banking (B) and manipulated by specialized pharmacy (M). The sample M was manipulated using only leaves from the plant (as informed by the establishment) and it had extremely fine texture (powder) while the sample (B) has a coarser texture with visible parts of the plant and it was made with the leaves (bracts) and also the stalks of the horsetail.

2.3 Experimental Procedure

Initially B was transformed into powder using a knife mill (TECNAL-TE650 series 97003) with a 1.0mm porosity aluminum sieve. The tea (both B and M) was prepared by adding 25 g of the material in a beaker containing 350 ml of deionized water, kept under mechanical stirring for 7 hours, on a heating plate with a constant temperature of $50 \text{ }^\circ\text{C}$, with periodic monitoring of the process (Figure 1). The pH of all solutions was approximately 6.5 at the beginning of the process and remained at this value until the end.

After tea preparation, a 5-micron porosity sintered plate filter was used to separate the solid and liquid phases by vacuum filtration (Figure 2). The filtered liquid (extract) was transferred to smaller vials (filled with the liquid until its half) (Figure 3A). The vials were sealed with pieces of cotton and parafilm paper and then several small needle holes were made on the surface. The extract was frozen at $-10 \text{ }^\circ\text{C}$ for 36 h and was transferred to a campanula and lyophilized for 24 h which was employed a TERRONI LB1500TT lyophilizer. The lyophilized product was stored (Figure 3B) in a vacuum desiccator to prevent that the dried material would absorb water, as the horsetail is highly hygroscopic. The solid phase formed in all the processes was oven dried at $100 \text{ }^\circ\text{C}$ and stored in a dry flask to be used in the adsorption study.

2.4 Techniques

2.4.1 Infrared Region Spectroscopy (FTIR)

A Nicolet 5DXB FT-IR spectrophotometer (Nicolet Instrument, Madison, Wi) was used for the analysis of infrared spectroscopy of the lyophilized samples. A scanning for each sample at a resolution of $\pm 4 \text{ cm}^{-1}$, in the range of 4000 to 400 cm^{-1} , was employed.

2.4.2 Uv-Vis (Visible Ultraviolet Spectroscopy)

All samples were analyzed using Guided Wave spectrophotometry, model 260, equipped with tungsten-halogen lamp, silicon (200 to 1000 nm) and germanium (800 to 2500 nm) detectors.

2.4.3 EDX (Dispersive Energy Spectroscopy) and SEM (Scanning Electron Microscopy)

EDX and MEV were obtained by an electronic microscope of Jeol JTSM T-330 brand with EDX attached. Topological and qualitative analyzes of chemical constituents before (M1 and B1) and after the extraction (M and B lyophilized) as well as the wastes (residues) of the extracts filtration (denominated here B2 and M2) were carried out. The samples were mounted on metal support and placed into the electron microscope sample chamber. In this way, the elements content in the lyophilized extract and solid wastes were qualitatively determined by EDX.

2.5 Adsorption

The adsorption study was performed by batching technique with thermostatic flasks, using as adsorbent 50 mg of the solid phase obtained after the B and M horsetail tea extraction.

For time study, 50 mg of samples were placed with the $5.0 \times 10^{-3} \text{ mol L}^{-1}$ standard solution of $\text{CuCl}_2 \cdot 5\text{H}_2\text{O}$ in the thermostatic bottles. The system was submitted to magnetic stirring for predetermined time intervals (10, 20, 30, 40, 50, 60, 70, 80 e 90 minutes) at controlled temperature ($25 \pm 1^\circ$). After stirring time, the samples were resting for 10 minutes and then 10 mL aliquots were taken from each sample and carefully filtered on quantitative filter.

For concentration study, the same method was used, where 50 mg of each horsetails that were mixed with Cu^{2+} metal cations in a solution which was previously diluted, but this time in different concentrations of the standard aliquots solution (2.5, 5.0, 7.5, 10, 12.5, 15, 20, 25 and 30 mL). This system was also kept under stirring for a determined time in the previous study (70 minutes) and after that time the filtration and separation of the aliquots were repeated for atomic absorption spectrophotometry.

The cupric ions concentration at equilibrium was determined in triplicate ($n = 3$) by concentration difference using an atomic absorption spectrophotometer (FAAS) of Varian Model 55B Spectra brand.

Nf (amount of adsorbed metal) in each sample was determined by the equation: $N_f = (N_a - N_s) / m$, where m is the mass (g) of adsorbent and N_a and N_s are the initial and final concentrations of metal ions, respectively.



Figure 1. Horsetail tea preparation



Figure 2. Tea filtration by vacuum filtration process

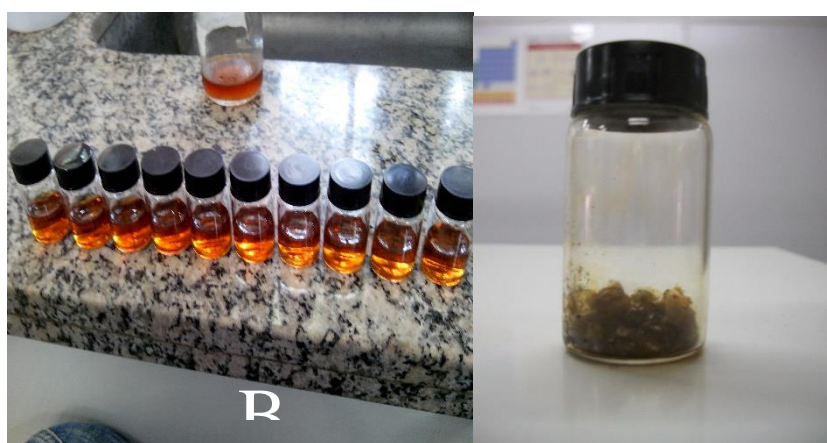


Figure 3. A. Extract filtered placed in vials for lyophilization process. B: Lyophilized extract

3. Results and Discussion

Through infrared spectroscopy, organic constituents' presence was observed in both materials (Figure 4). The horsetail presented typical absorption band of Silicon ($\nu\text{Si-O-S}$) in 1100 cm^{-1} , proving its existence. Absorption bands near 3500 cm^{-1} and between 1600 cm^{-1} and 1000 cm^{-1} indicate the presence of aromatic rings, possibly due to the presence of flavonoids; the band at 2500 cm^{-1} is typical of carboxylic acid (O-H); bands between 3500 cm^{-1} and 3070 cm^{-1} are characteristic of amides (N-H) (Lopes & Fascio, 2003). Therefore, some soluble compounds based on Silicon, $\text{Si}(\text{OH})_4$ or $\text{Si}(\text{OH})_3$, which are present in the stalks of the herb (Holzhuter, et al., 2003) are also present in the extract.

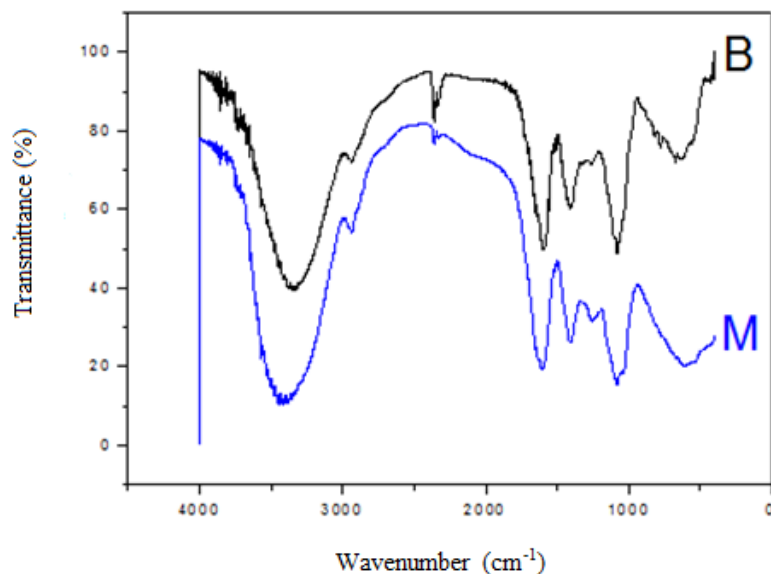


Figure 4. B and M Horsetail Spectra

Figures 5 and 6 illustrate the Uv-Vis spectra for both lyophilized horsetail samples where a band at 267 and 305 nm for B (Figure 6) can be observed after spectral deconvolution. For M (Figure 6) two bands located at 261 and 286 nm were also observed, all possibly related to apigenin presence (Francescato, 2013).

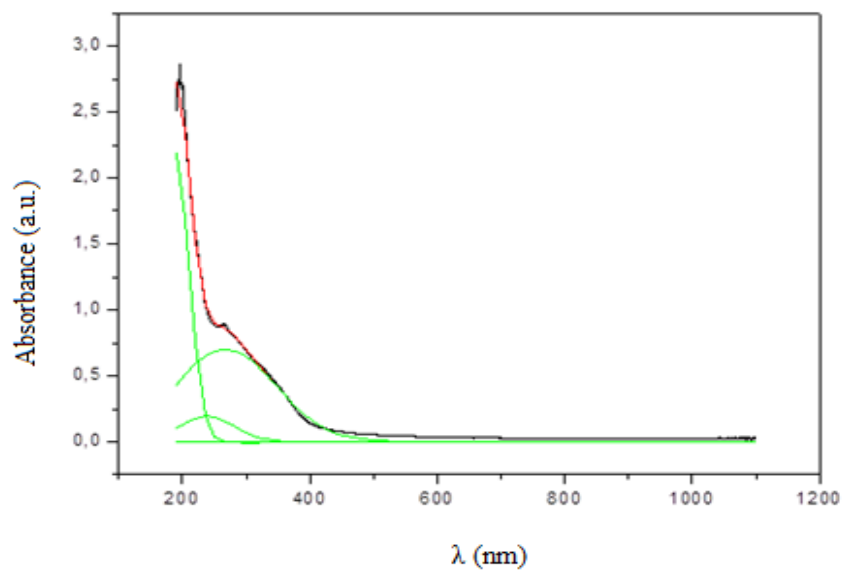


Figure 5. Electronic Spectrum with B sample deconvolution (Uv-Vis)

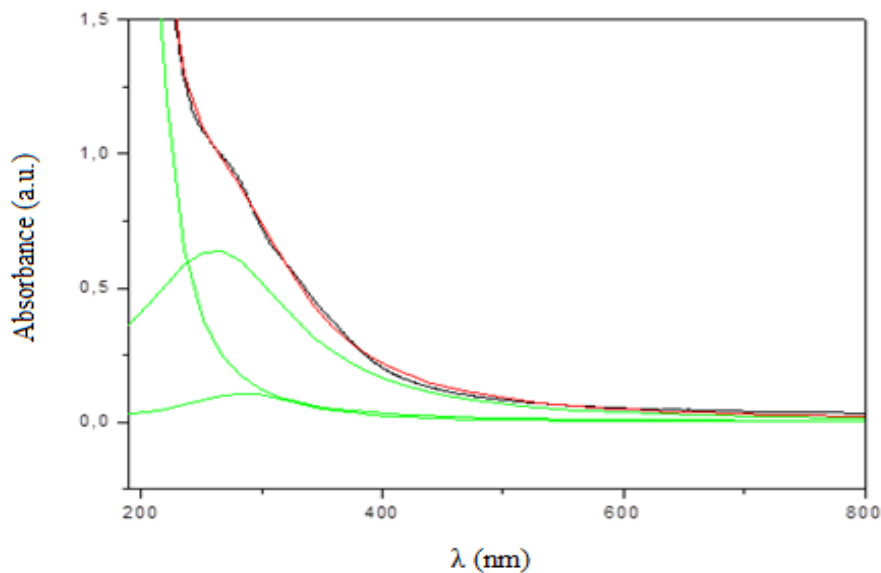


Figure 6. Electronic Spectrum with M sample deconvolution (Uv-Vis)

The great absorption capacity of the horsetail root gives it great diversity in the chemical constitution, which can be observed through the EDX. Both samples, B and M, presented the same chemical components and their approximate percentages. Aluminum was found in small percentage only in lyophilized sample M (Figure 7). The components found in the EDX analyzes are listed in Table 1.

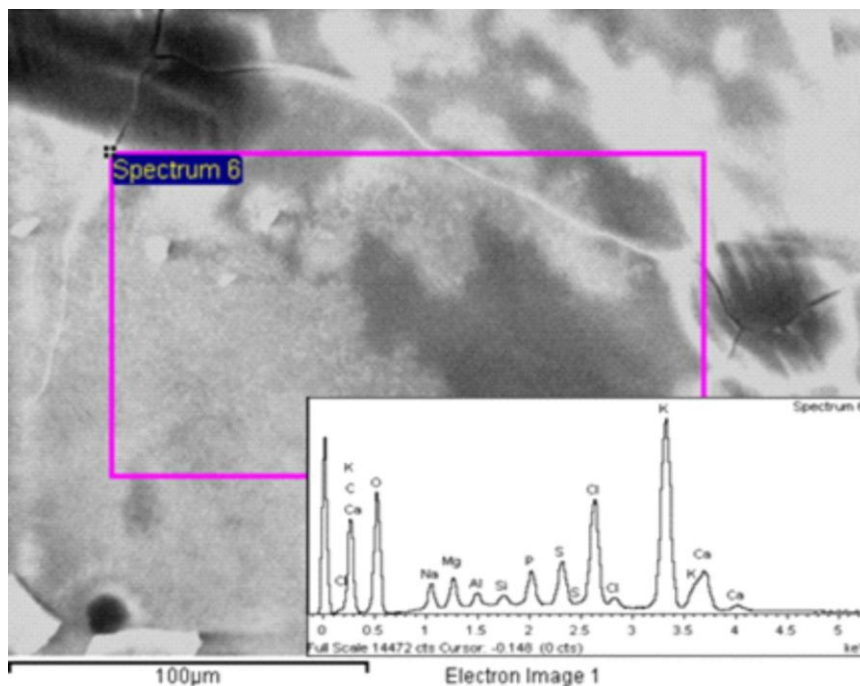


Figure 7. EDX analysis from lyophilized extract of M horsetail

Table 1. EDX analysis of teas (B1 and M1), lyophilized extracts (B and M) and wastes (residues) from tea extracts (B2 and M2)

Element	% B	%B1	%B2	% M	%M1	%M2
C K	34.22	42.89	39.27	30.88	43.08	45.30
O K	50.46	47.81	38.70	39.76	44.48	48.45
Na K	0.13	-	-	1.69	0.17	0.11
Mg K	1.56	0.33	0.16	1.41	0.15	0.20
Al K	-	-	-	0.51	-	0.16
Si K	0.43	2.94	18.57	0.40	8.81	2.66
P K	1.16	0.14	-	1.65	0.11	-
S K	0.66	0.14	0.09	2.13	0.19	0.28
Cl K	2.29	0.34	0.10	5.92	0.54	0.17
K K	7.07	4.40	1.07	12.72	1.18	0.86
Ca K	1.88	1.00	1.42	2.93	1.03	1.71
Mn K	0.13	-	-	-	-	-
Fe K	-	-	0.63	-	0.26	0.11

According to qualitative levels listed in Table 1, carbon and oxygen are the components present in a higher percentage in both samples, being present 70% of the samples. Therefore, organic compounds are predominant in the chemical composition of the herb *Equisetum arvense*, while inorganic compounds make up only about 30% of the same.

The main constituents found in larger amounts in *Equisetum arvense* are Mg, Si, and Ca. In addition to Si and Mg, presence of S was also observed, but aluminum and fluorine presence were not observed, as described in the literature (Hodson et al., 2005).

By scanning electron microscopy (SEM) shown by Figures from 8 to 13 for different samples. In some of them can clearly observe microparticles of approximately 0.22 microns, attributed to the superficial layer of silica, generally found in the leaf and stem, and this dimension is very close to that described in the literature (Holzhuter et al., 2003)

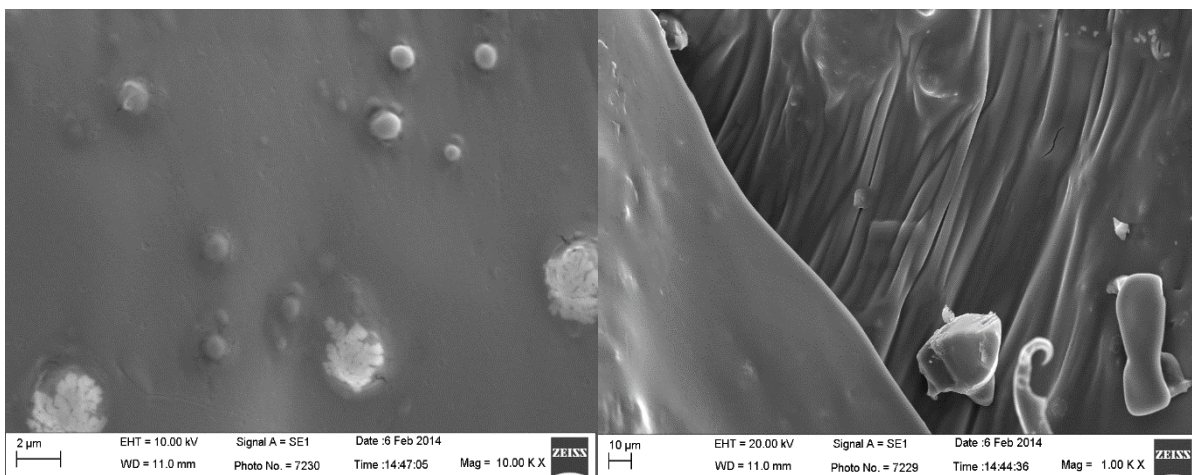


Figure 8. MEV of B horsetail sample

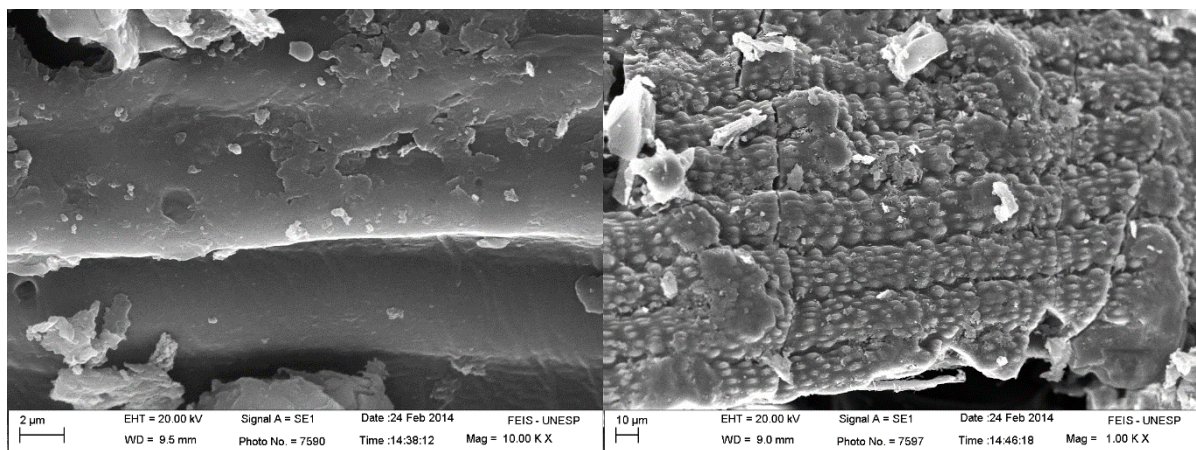


Figure 9. MEV of B1 horsetail sample

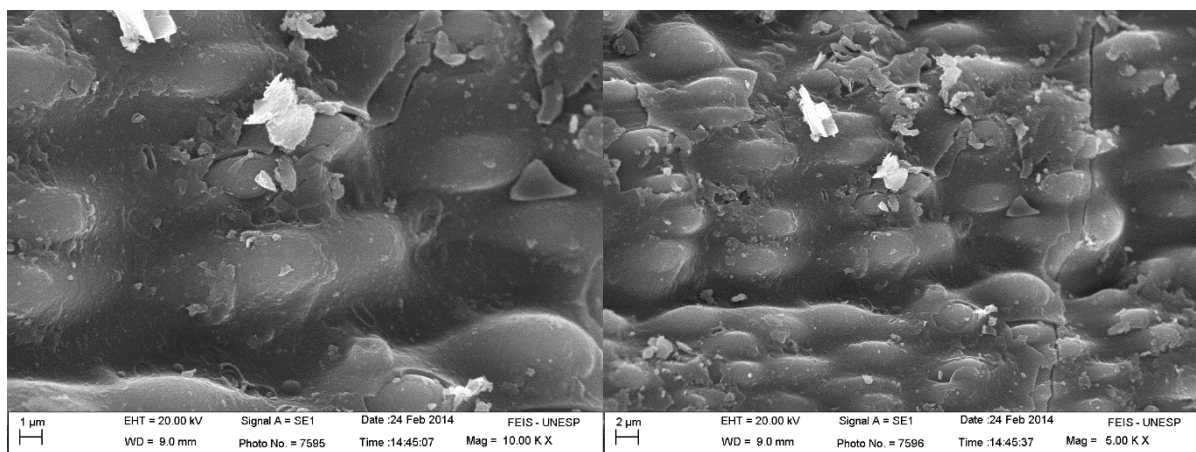


Figure 10. MEV of B2 horsetail sample

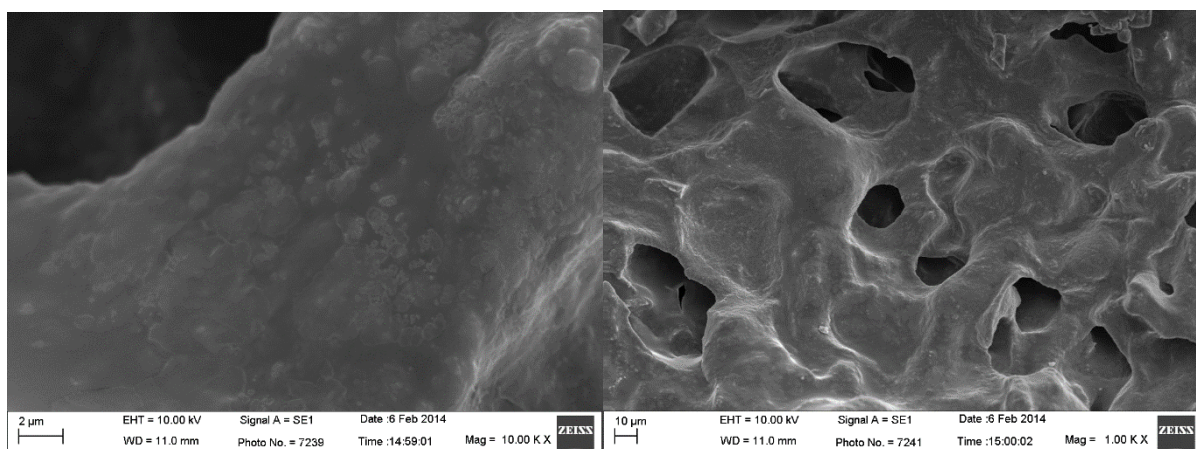


Figure 11. MEV of M horsetail sample

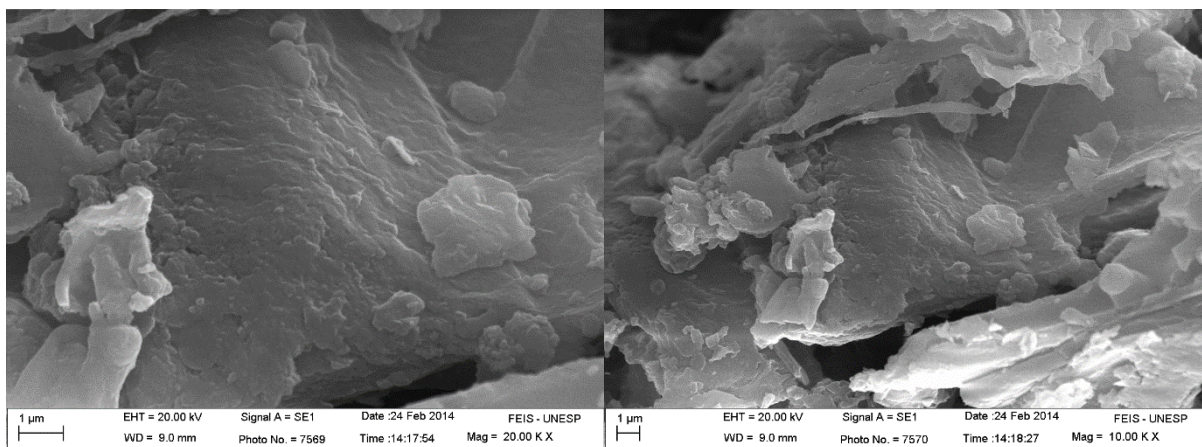


Figure 12. MEV of M1 horsetail sample

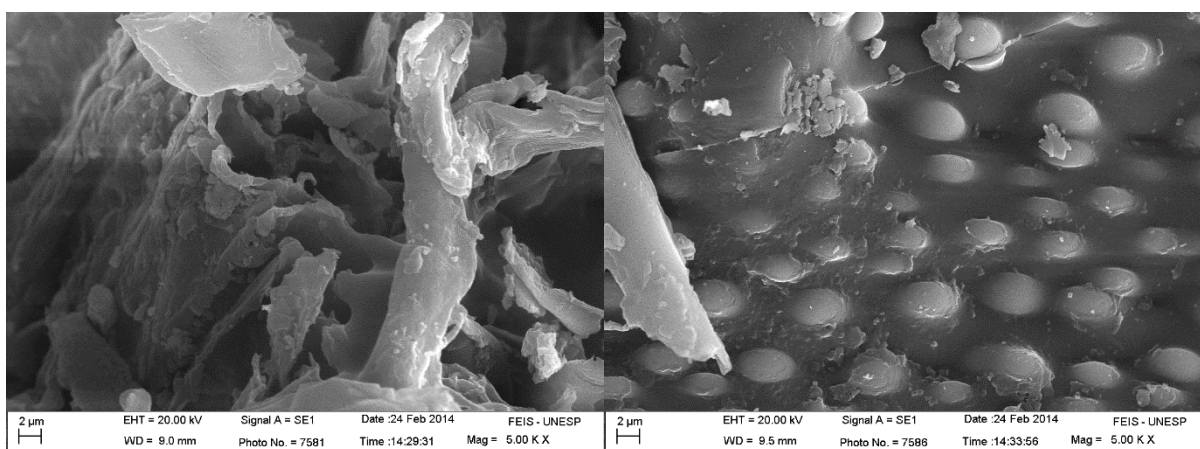


Figure 13. MEV of M2 horsetail sample

The solid phase (biomass) obtained after the extraction of the organic and inorganic components was applied in the metals adsorption process.

In the time study (adsorption equilibrium), adsorption curves were obtained by correlating N_f (number of moles of adsorbed metal ions) with time (minutes) and then the time required for the maximum adsorption of the metal ions was determined. In adsorption isotherms illustrated in Figure 14, it was found that the time at which the adsorption saturation of the Cu^{2+} metal ion was initiated for both horsetails was about 65 minutes, but a time of 70 minutes was used for the concentration study in order to have a safe margin of equilibrium time.

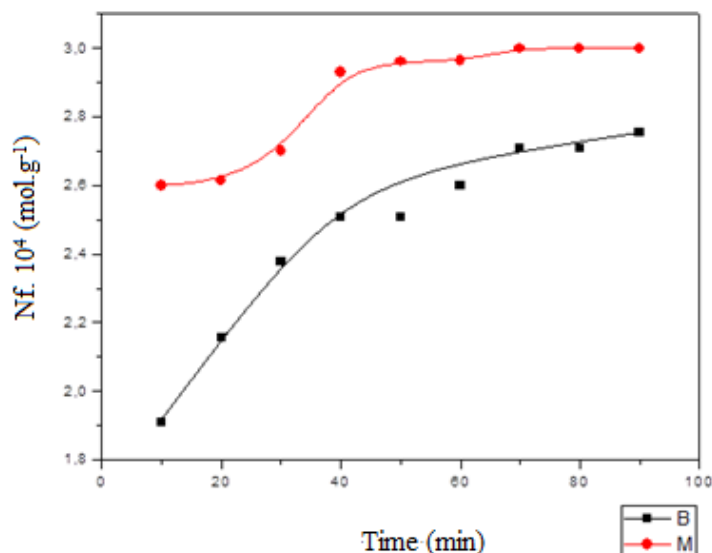


Figure 14. Kinetic curves of B and M horsetails

The adsorption capacity is expressed in adsorption isotherms, which relates N_f to the concentration of metal ion (C_s). As shown in Figure 15, the beginning of active sites saturation for the material occurred from the concentration of $12 \times 10^{-4} \text{ mol L}^{-1}$ of the metal for M horsetail and $13.7 \times 10^{-4} \text{ mol L}^{-1}$ for B horsetail. The maximum adsorption capacity N_f^{max} of M horsetail was $4.4 \times 10^{-4} \text{ mol g}^{-1}$ and for B horsetail was $2.6 \times 10^{-4} \text{ mol g}^{-1}$. It was observed that N_f increases with C_s and it was found that the horsetail with the highest adsorption capacity was the manipulated one in pharmacy (M). The N_f values for each horsetail are expressed in tables 2 and 3 for mackerel B and M respectively.

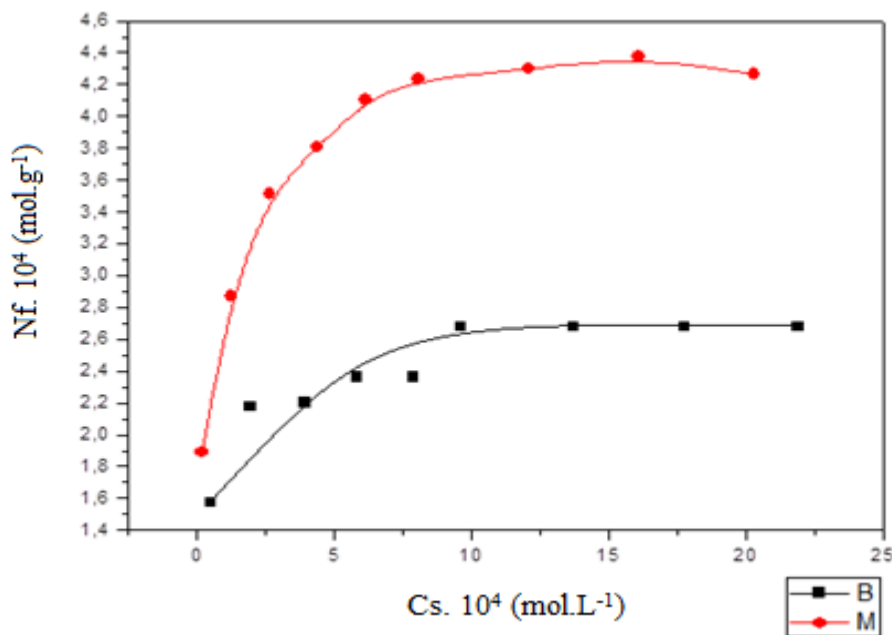


Figure 15. Adsorption isotherms of B and M horsetail

Table 2. Nf values for horsetail B

Cs.10 ⁴ (mol.L ⁻⁴)	Nf.10 ⁴ (mol.g ⁻⁴)
0,472	1,576
1,920	2,174
3,936	2,204
5,826	2,362
7,874	2,362
9,606	2,676
13,700	2,676
17,800	2,680
21,880	2,680

Table 3. Nf values for horsetail M

Cs.10 ⁴ (mol.L ⁻⁴)	Nf.10 ⁴ (mol.g ⁻⁴)
0,157	1,889
1,225	2,869
2,630	3,510
4,378	3,810
6,126	4,102
8,048	4,234
12,078	4,298
16,094	4,376
20,300	4,264

4. Conclusion

Through electronic and vibrational spectroscopy techniques, it was observed that the tea extract of the *Equisetum arvense* sample in aqueous medium, after lyophilization presented some organic constituents as compounds of flavonoids family, probably responsible for phytotherapeutic properties. By FTIR, MEV and EDX it is possible to prove the existence of soluble compounds based on Si, besides other elements (C, O, Ca, Mg, Na, P, S, Cl and K). It was verified that part of the organic compounds was found in the solid phase (extraction waste) and these present chelating properties with expressive adsorption capacity of copper ions in aqueous medium.

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