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Preparation and Characterization Polypyrrole/Humic Acid Composite Electrode for Metal ion Extraction

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Redox and acid base properties of soil humic substances were studied. Phenolic groups predominated over the carboxylic groups. The oxidation capacity of humic acids (HA) show values from 1.7 and 2.2 mol$_c$ kg^{-1} at pH 7.0 and pH 9.0, respectively. A relationship between redox activity and both pH and humic acid content of carboxylic groups was observed. The formal potential ($^{F}E^{\circ}_{H}$) presented values of 1.50 V, demonstrating the oxidizing nature of the studied HAs. Based on these results, HA from Diguillin (D) soil was considered for the design of an electrode in the presence of polypyrrole (PPy). Consequently, a paraffin-impregnated graphite electrode (PIGE) modified with HA-D/Ppy was tested in copper solutions (Cu (II), $CuCl_4^{2-}$). The results showed that the device worked properly as analyte extractant, being 50% more efficient than the same electrode in the absence of HA-D (PIGE/PPy).

Keywords: Humic acid, formal potential, ion extractions, PIGE, polypyrrole.

1. INTRODUCTION

Extraction and removal of toxic metal ions from water originating from mining industrial activities is one of the most main aspects of current research interest. With this aim, are being developed a series of strategies, using different kinds of molecules such as calixarenes, that can to act as specific ligands for anions and cations [1, 2] polymers as resins, widely used in the preconcentration, separation, recovery, and hydrometallurgy of metal ions, in which various chelating groups have been incorporated and are attached to the polymer matrix [3] while that process based on a proper molecular imprinted polymer (MIP) resin are being developed for continuous separation of

Cu^{2+} from Mn^{2+} and Co^{2+}[4]. On the other hand conducting polymers are multifunctional materials, as Heeger mentions [5], these “offer a unique combination of properties not available from other known materials, which opens the possibility of use in a wide variety of applications”. These properties make them useful for SPME application [6], where polypyrrole and polyaniline (PANI) [7-10] were the most popular conductive polymers used for the SPME fibers. However, these conducting polymers has the possibility of doping-undoping of the p or n type, a feature of most of these polymers, that has been used scarcely for extraction of ions [11], where the results indicates that in fact the polymer could be used as extractant for arsenic. From these results, a novel and simple electrode of rapid preparation has been recently developed using humic acid (HA) and polypyrrole films [12]. The results showed that the presence of HA did not affect the electrical properties of the system, but indeed provoked morphological changes in the polymer turning it more granular. The modified electrode was evaluated utilizing As(V) solutions because this type of polymer can undergo p-doping – undoping processes [12], which accounts for its good extractant abilities toward the analyte.

In this context, humic a cids are part of soil organic matter (OM) has been studied from different points of view [13, 14] and in general, humic acids are partly responsible for the cation exchange, water retention, buffering capacity and an essential influence on plant growth. Furthermore, soils of southern Chile, constitute between 60 to 75% of the found organic matter [15], its structure presents functional groups with chelating abilities These groups immobilize nutrients that will be gradually released to plants, in addition to being a source of carbonated substrates to support microbial activity [16]. These features clearly indicate that HA plays an important role in determining the characteristics and properties of soil [17-19]. Without neglecting the fact that HA still have unknown structure and that great effort has been done to elucidate it, it is possible to state that most of these substances contain functional groups, such as carboxylic, phenolic, hydroxyl, carbonyl, amines, amides and aliphatic fragments, among others. Due to their polyfunctionality, HAs are, among the existing natural organic substances, one of the most powerful chelating agents: they are able to complex heavy metals [20, 21], inorganic anions and halogens [22, 23], organic acids [24], aromatic compounds [25, 26], pesticides and herbicides [27-33]. These studies demonstrated the importance of HAs interaction with various pollutants, forming complexes with different solubility and chemical and biological stability. This means that HA may alter the availability, transport, fixation, and toxicity of environmental contaminants.

On the other hand, humic compounds exhibit redox properties which had been clearly established through of their participation in a variety of reactions of this type with elements such as Fe (III) [34-36] , Mn (IV) [37], V (V) [38] and Hg (II) [39, 40]. These redox properties were related to the type and amount of humic substances and were quantified by Struyk and Sposito [41]. The main drawback in the electrochemical characterization lies in the fact that HA active redox components are an inseparable mixture of redox reactions [42]. Currently, no redox potential measurements of HAs extracted from natural samples of soils derived from volcanic materials have been reported. Therefore measurement of oxidation capacity and formal potential (${}^{F}E_{H}^{\circ}$) of these samples is fundamental and novel, since provides a clue concerning the quality of the OM present, predicts interaction with metals and contaminants, and the evolution of the OM properties in a prospective soil amendment or composting.

Finally, based on the described background, it was decided to characterize and apply the determined redox properties through the fabrication of a modified electrode to which soil humic acids and a conductive polymer layer will be incorporated. The assembly will be evaluated in solutions containing complexed Cu(II) species.

2. MATERIAL AND METHODS

2.1 Samples

2.1.1 Soil

Soil samples were collected at depths of 0 – 0.15 m from uncultivated areas of Diguillin in central-southern Chile. All samples were air-dried and sifted through a 2 mm sieve.

2.1.2 Humic substances

Extraction of humic substances of soil derived from volcanic materials was conducted according to the procedure recommended by the International Humic Substance Society. For the sake of comparison HA (Sigma–Aldrich) was incorporated and purified by precipitation as previously described [12].

Table 1. Chemical characterization of humic acid

Characteristics	Diguillin
Total Acidity (mEq g^{-1})	9.68±0.59
Carboxylic groups (mEqg^{-1})	3.73±0.02
Phenolic groups (mEqg^{-1})	5.95±0.57
Emf cell (mV)	
pH 7.0	438.3±9.8
pH 9.0	314.6±13.2
Oxidation capacity (molckg^{-1})	
pH 7.0	2.18±0.08
pH 9.0	1.69±0.09
${}^{F}E^{0}_{H}$ (V)	1.501±0.008
Organic matter (wt%)	10.0±0.0

2.2 Chemical characterization

2.2.1 Soil

Organic matter (OM) content based on the Walkley-Black method modified to Chilean volcanic soils, which is in close agreement with the dry combustion method ($R^2 = 0.853$ with $n = 60$) was determined in Diguillin soil.

2.2.2 Humic substances

Functional groups determination was performed experimentally for total acidity and carboxylic acidity, whereas phenolic acidity was obtained by difference [43, 44].

2.3 Redox characterization

Redox properties of soil HAs, namely redox formal potential (${}^{F}E_{H}^{\circ}$) and oxidation capacity, were assessed by potentiometric titration [41]. Titrations were conducted into a five-compartment electrolytic cell, connected to a potentiostat (PGP VoltaLab 201), to which measured aliquots of I_2 were added at constant pH and the potential recorded at open circuit. From these curves, the values of formal potential and oxidation capacity were obtained as described elsewhere [41].

2.4 Electrochemical experiments

2.4.1 Apparatus

All electrochemical experiments were carried out on a VoltaLab PGZ100 potentiostat system in a glass three-compartment/three-electrode cell under argon atmosphere. Paraffin-impregnated graphite was prepared and used as working electrode (PIGE). The exposed surface of the graphite electrode was mechanically regenerated prior to each experiment with emery paper (grain size 2000 and 2500) and thorough washing with double-distilled water. A Pt wire (20 cm^2) was the counter electrode. All potentials quoted in this article are referred to an Ag|AgCl reference electrode.

All electrodic surfaces were studied in solutions containing Cu(II) in 20 mM HCl + 100 mM KCl (solution A), that were prepared by dissolution of the appropriate amount of $CuCl_2$ in double-distilled water according to standard procedures. Pyrrole (Sigma–Aldrich) was purified by distillation, stored at 4ºC, and protected from light. All other reagents used were analytical grade (Merck), and all solutions were prepared and deaerated with pure Ar for at least 20 min.

2.4.2 Preparation of modified PIGE

As for PIGE, four electrodic surfaces were characterized by cyclic voltammetry: (1) PIGE, (2) PIGE modified with HA from Diguillin soil (PIGE/HA-D) or HA from Aldrich (PIGE/HA), (3) PIGE electrochemically modified with pyrrole (PIGE/PPy), and (4) PIGE modified with HA-D or HA and then electropolymerized with pyrrole (PIGE/HA-D/PPy; PIGE/HA/PPy). HA was transferred and immobilized onto the electrode surface using the abrasive transfer technique described elsewhere [33].

Electrochemical growth of PPy films was conducted on PIGE or PIGE/HA from 1.4 mM pyrrole + 50 mM Na_2SO_4 + 30 mM H_2SO_4 utilizing the potentiodynamic method applying five successive cycles between -0.2 and 1.0 V. The morphology and microscopic structure of the bare and modified electrodes were characterized by scanning electron microscopy (SEM; model LEO 1420 VP, Leo Microscopy, Ltd.).

2.4.3 Extractions

Two electrodic surfaces, PIGE/HA/PPy and PIGE/PPy, were studied in solutions containing 22.32 mM $CuCl_2$ + 20 mM HCl + 100 mM KCl (solution A, cell A) and 20 mM HCl + 100 mM KCl (solution B, cell B) to select the doping–undoping potentials to perform the extractions. The total volume of electrolyte in each cell was always 10.0 mL. Each extraction was conducted as follows: the modified PIGE/PPy or PIGE/HA/PPy was immersed into solution A and potentiostatically perturbed at 0.4 V for 5 min, after which it was dipped into solution B, wherein it was kept at – 0.6 V for 5 min. Initially and after several extractions, the copper concentration in solution A and B was determined by inductively coupled plasma/optical emission spectrometry (ICP–OES) on a Varian Liberty series II instrument.

3. RESULTS AND DISCUSSION

3.1 Redox characterization

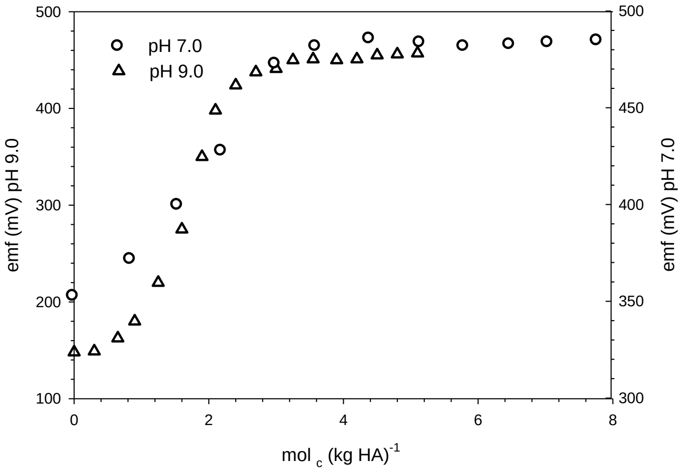

Figure 1. Potentiometric titrations curves for 6.25 mg HA-D suspended in 125 mL 0.05M KCl/0.05M phosphate buffer solution at pH 7.00±0.02 and pH 9.00±0.04. The inflection point of the curve corresponds to emf cells and oxidation capacity.

Redox properties of humic substances extracted from Diguillin soil was analyzed by means of titration curves at pH 7.0 and 9.0. From these curves, Fig. 1, oxidation capacity (mol$_c$ kg^{-1}), formal potential ($^{F}E^{0}_{H}$), and emf of HA was calculated and are listed in Table 1. From previously reported results in literature, the oxidation capacity or the amount of mass transferred per mass unit must be higher at pH 9.0 [41]. This behavior is related to a greater solubility of humic substances. Nevertheless, in the case of HA-D the opposite behavior was observed, decreasing the transferred charge at pH 9.0. This finding may be explained by the higher content of conjugated groups, *e.g.*, carboxylic acids, which become more active as pH decreases. Thus, the oxidation capacity at pH 7.0 probably increases due to the more acid pKa of their functional groups, as mentioned elsewhere [41]. From the observed behavior it can be established that the presence of carboxylate groups would influence this redox property, whether in its abundance with respect to phenolic groups and in its ability to participate in reduction processes. As for emf values, it is worth mentioning that this measurement quantifies the energy needed by the HA to carry out oxidation processes. According to the above, at pH 7.0 the studied HAs possess a more oxidizing character than at pH 9.0, promoting the oxidation of species in the nearby. The formal potential $^{F}E^{0}_{H}$ attained for humic substances from Diguillin soil have a considerable oxidizing potential. This condition would suggest that HAs under study possess the ability to oxidize a significant range of species, generating a wide spectrum of redox interactions with pollutants and heavy metals. In this context and considering that the interaction with metals depends on soil type and its components, pH, and redox potential, it has been put forward that the higher the content of condensed groups, the greater the interaction of HA with pollutants of environmental interest [45]. Therefore, having in mind redox characterization, acid-base, and OM content results, HA-D is a prospective candidate to be evaluated and studied concerning to its interaction with analytes of environmental interest.

3.1.1 Electrochemical experiments

All electrodes used and modified in this survey were characterized by cyclic voltammetry. The incorporation of HA was performed using the abrasive transfer technique, which is used for completely insoluble compounds in the medium where the experiment is performed [46]. All voltammetric profiles were stable (PIGE, PIGE modified with HA and HA-D) and the recorded current densities were *ca.* ± 10μA (data not shown). No redox process within the applied potential window was observed on any of the studied surfaces. However, HA introduction produced a lower capacitive response as a result of the decrease of available active sites. This fact would indicate inclusion of HA into the graphite in a reproducible manner and without loss during the experiment.

As previously done, once the PIGE/HA-D is obtained, a thin layer of polypyrrole was grown under the optimal electrosynthesis conditions [12]. Polypyrrole was obtained in its oxidized form, affording positive charges in its structure and, consequently, anionic species from the used electrolyte were incorporated into the film. This charge generated in the polymer can be employed for the extraction of negatively charged contaminants. Figure 2 depicts the last cycle of the experimental curve obtained for PIGE and PIGE/HA-D systems in the absence and presence of pyrrole, where the charge increases with the number of cycles, as a result of the conducting polymer formation *via* electrochemical [11, 12]. It is observed in the same figure that the charge associated to the polymer that grows on PIGE/HA-D was greater than that obtained for PIGE, which would indicate the presence of a more conductive surface.

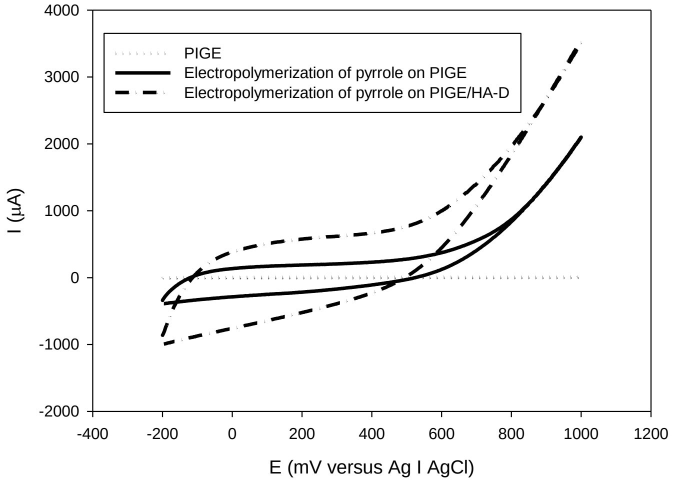

Figure 2. Typical cyclic voltammograms during electropolymerization recorded for the PIGE and PIGE/HA-D/Ppy system in 1mM Na_2SO_4 and 30 mM H_2SO_4 between -0.2 and 1.0 V at 0.1 V·s^{-1} (I is the current intensity, and E is the voltage).

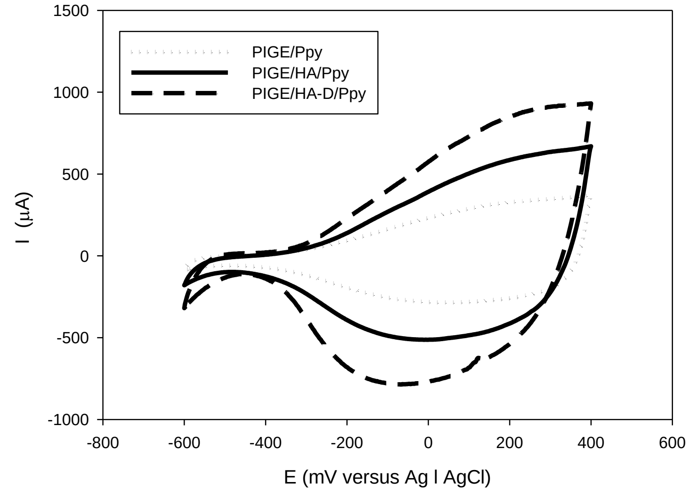

Figure 3. Potentiodynamic response of PIGE/Ppy, PIGE/HA/Ppy and PIGE/HA-D/Ppy in 20mM HCl and 100mM KCl between -0.6 and 0.4 V at 0.1V·s^{-1} (I is the current intensity, and E is the voltage).

PIGE/PPy, PIGE/HA/PPy and PIGE/HA-D/PPy electrodes showed a stable voltammetric profile within the studied potential window, Fig 3. Current difference for each modified surface was obtained with a PIGE < PIGE/HA < PIGE/HA-D sequence. However, despite these differences for all the deposits the charge density of the p-doping process (q> 0) is similar to the charge of p-undoping (q <0), suggesting a reversible anion extraction. This current increase may be related to PPy growth curves on both surfaces (Fig. 2), wherein a significant difference in the charge involved with HA-D was observed, and that might account for the difference in capacitive response in Fig 3.

These results could also be linked to the morphology presented in Fig 4, where PIGE/HA-D (Fig 4 (a), PIGE/HA-D/ppy (Fig. 4 (b)) SEM micrographs and a PIGE/HA-D cross section to determine its thickness, are depicted. PIGE and PIGE/HA morphology has been previously reported [12], both exhibiting irregular surfaces. Aldrich HA, included in the graphic, presented particle size in the range 1-3 µm. Compared with the abovementioned results, PIGE/HA-D and PIGE/HA-D/Ppy surfaces were found to be much more irregular, *i.e.*, there is a clear inclusion of HA-D into the graphite, and consequently a more rugged and porous polymer was obtained. Finally, PIGE/HA-D/Ppy cross section, Fig..4(c), shows a granular morphology much less uniform than Ppy in the absence of HA, with a thickness of 11.12 µm in the thinnest part and 13.40 µm in thickest one, which represents a PIGE/Ppy thicker thickness than previously reported [12].

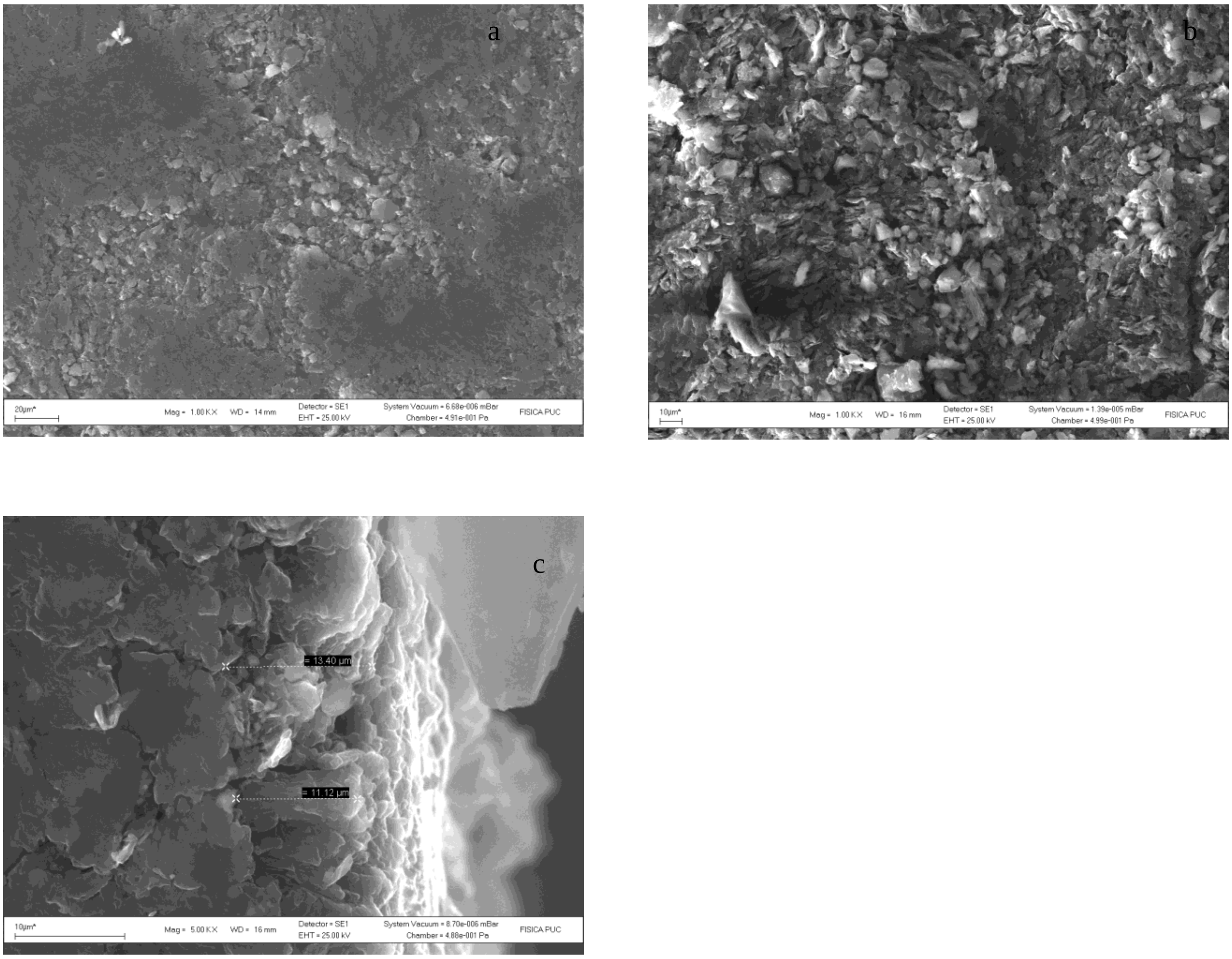

Figure 4. SEM micrographs showing surface morphology of (a) PIGE/HA-D, (b) PIGE/HA-D-Ppy, (c) a cross-sectional view of PIGE/HA-D-Ppy.

Table 2. Copper (II) extracted and doping and undoping charges in 10 extractions as a function of the modified PIGE referred to geometrical area electrode ($0.28 cm^2$).

Modified Electrode	Initial Cu (II) (g/L)	Extracted Cu(II) (×10^{-2} g/L)	Doping charge (×10^{-2} C)	Undoping charge (×10^{-2} C)
PIGE/PPy	1.401	0.152	0.406 ± 0.054	0.450 ± 0.081
PIGE/Ppy	1.416	0.200	0.398 ± 0.071	0.604 ± 0.046
PIGE/Ppy	1.397	0.179	0.400 ± 0.062	0.520 ± 0.060
PIGE/HA/Ppy	1.406	0.298	0.554 ± 0.088	0.662 ± 0.054
PIGE/HA/Ppy	1.477	0.310	0.538 ± 0.046	0.578 ± 0.071
PIGE/HA/Ppy	1.472	0.340	0.469 ± 0.048	0.512 ± 0.075
PIGE/HA-D/Ppy	1.382	0.490	1.106 ± 0.077	1.458 ± 0.093
PIGE/HA-D/Ppy	1.384	0.421	0.931 ± 0.077	1.041 ± 0.095
PIGE/HA-D/Ppy	1.386	0.552	1.050 ± 0.088	1.329 ± 0.221

3.1.2 Copper extraction

Table 2 contains the results obtained with modified electrodes for Cu(II) extraction. All electrodes were compared to each other, as a function of charge and concentration transferred. It was established that the amount of Cu (II) species extracted by a PIGE/HA-D/ppy modified electrode is higher than that obtained with PIGE/HA/Ppy and PIGE/Ppy electrodes. This behavior indicates that introduction of HA, whether natural (HA-D) or synthetic (Aldrich), brings about an increase in the insertion of Cu (II) anionic species, as determinated for As(V) species previously reported [12]. This extraction efficiency improvement has been associated to the kind of obtained polymer more specifically to the morphology and to HA incorporation [12]. This behavior has also been observed in humic substances of volcanic origin producing, as previously corroborated, a polymer of greater roughness. In the context of Cu (II) species–HA interaction, studies exist aimed at evaluating this behavior at acidic pH, where HAs coming from Vermicompost showed higher adsorption than fulvic acids (FA), following a pattern that describes the existence of a single adsorption/complexation site. Carboxylic groups were the dominant function over the phenolic and amino groups This is consistent with a configuration of chelate-forming functional groups, despite of having a smaller number of ionizable sites than FA [47, 48]. On the other hand, it is worth considering that HA have phenolic and carboxylic groups capable of forming chelates through interactions involving two carboxyl oxygen atoms and one oxygen from a phenolic hydroxyl group [47]. As for HA-D, this has a higher number of phenolic groups and less carboxylic groups, as compared with the HA-Aldrich, which could account for the extraction results of Cu (II)- containing anionic species.

Since humic acids are negatively charged, it would be expected that the presence of HA in the modified electrode, was independent of its origin, its acid-base features and in addition of a very weak character. However, the differences between the two modified electrodes having HA in their composition enable postulating that interactions would be not so weak and an effect of the existing functional groups do exists. In this regard, as proposed for AsO_4^{3-} functional groups such as phenolics [12, 49], could interact with Cu(II) positive formal charge in the $CuCl_4^{2-}$complex. This proposal is based on the fact that complexes with coordination number less than 6 may develop exchange mechanisms associated to positively charged metal centres [50], as well as to the existence of phenolates in the HA. This approach in conjunction with anion exchange of the conducting polymer, due to its doping-undoping properties, would cause, as previously reported by our group, synergistic effect of both electrode modifying materials [12]. Although for both materials a specific mechanism of interaction with $CuCl_4^{2-}$ species has been proposed is important to state that the morphology of the polymer is crucial, as its porous structure increases the surface area with the species in solution, as evidenced by SEM analysis for the materials under survey.

On the other hand, the average charge involved in the extractions carried out by each modified electrode is also included in Table 1. These results evidence the existence of a reversible p-doping/undoping process, demonstrating that all the studied electrodes were stable. The charge transferred in the PIGE/HA-D/Ppy electrode is greater than in all the other electrode surfaces, proving its superiority as extractant. On the other hand, if charge of the undoping process of 10 successive extractions is considered and n = 2, the application of Coulomb's law, affords an exchanged concentration 1.36×10^{-2} g L^{-1} for PIGE/HA-D/Ppy and 0.55×10^{-2} g L^{-1} for PIGE/Ppy. These values were all higher than those determined by ICP-OES listed in Table 2, indicating that the transferred charge is not only associated to $CuCl_4^{2-}$ species, but also to electrolyte species, *e.g.*, Cl^{-}, present in high concentration .

4. CONCLUSIONS

Humic acid in the studied soil showed acid-base properties that evidenced a large predominance of phenolic functional groups over carboxylic ones, which is also reflected in its chemical characterization and degree of humidification.

As for the redox properties of HA, they reflect the composition of functional groups, stressing the influence of carboxylic groups and their pH dependence on the oxidation capacity. All HAs showed to possess oxidative properties assessed by the measured emf and formal potential, suggesting that the studied HAs have conditions to interact and oxidize species present in the solution.

The incorporation of HA-D on PIGE and subsequent electropolymerization of a thin layer of polypyrrole, enabled the assembling of a device to be utilized as extractant of complexed Cu(II) species, *e.g.*, $CuCl_4^{2-}$. Morphological characterization showed that the presence of humic acid affected PPy deposit and provoked the formation of a rougher granular surface that might be assigned to HA-D surface adsorption in high-energy regions of the PIGE electrode and subsequent nucleation and electropolymerization of PPy on them.

The extraction efficiency of Cu(II), $CuCl_4^{2-}$, improved by 50% compared to the Aldrich HA and almost a three-fold increase compared to the same device in the absence of HA. PIGE results in the presence of HA-D evidenced differences in both potentiodynamic Ppy growth, with a higher charge, and CV, with a higher capacitive response, functioning thus as a more efficient extractant. This points out that the origin of HA and consequently its acid-base and redox properties are key points to be analyzed prior to the applications developed herein.

Finally, it was possible to establish that the observed synergistic effect between HA-D and conducting polymer can improve anions extraction, providing an excellent system for that purpose. This justifies go on investigating to determine and/or improve selectivity and reproducibility.

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