Sensor arrays to detect humic substances and Cu(II) in waters

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ABSTRACT

The interaction between poly(*o*-ethoxyaniline) (POEA) adsorbed onto solid substrates and humic substances (HS) and Cu^{2+} ions has been investigated using UV–vis spectroscopy and atomic force microscopy (AFM). Both HS and Cu^{2+} are able to dope POEA and change film morphology. This interaction was exploited in a sensor array made with nanostructured films of POEA, sulfonated lignin and HS, which could detect small concentrations of HS and Cu^{2+} in water.

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1. Introduction

One of the main challenges facing materials scientists is to develop devices that may help solve problems associated with degradation of the environment, as is the case of sensors to monitor the quality of water resources. In water treatment plants for human consumption, for instance, detecting humic substances is important as they facilitate the transport of organic and inorganic pollutants across the water treatment facilities. Indeed, humic substances affect the activity of cations and organic substances, thereby controlling their biological availability, toxicity and physicochemical properties [1,2]. Furthermore, upon reacting with chloride during water disinfection, humic substances can produce the carcinogenic trihalomethanes [3].

Humic substances are ubiquitous in the natural environment, including in soils, sediments, and various surface and ground waters [4]. Their detection in natural waters is important due to the interaction and complexation with metals such as Cu^{2+}. Metals are not chemically or biologically degraded, and therefore represent a potential risk to the environment [5,6]. They can be found in solution or in the solid phase depending on their oxidation state and complexation with inorganic or organic substances. The mobility in soils also depends on the concentration of the metal and on the acidity and buffer capacity of the soil. If large quantities of metal/HS complexes are disintegrated, equally large amounts of free metals will be released, making the water potentially toxic [7].

Although films of conducting polymers are already used as active elements in sensor devices, *e.g.*, "electronic noses" [8] and "electronic tongues" [9], there is interest in the development of new materials to be used as environmental sensors. The high electrical conductivity and good environmental stability of doped polyaniline (PANI) and its derivatives, *e.g.*, the poly(*o*-ethoxyaniline) (POEA), have made it possible to produce chemical sensors [10,11].

In this paper, we describe the interaction of solutions containing HS and Cu^{2+} with nanostructured films of POEA. Then, we exploit the strong dependence of the electrical properties of nanostructured films on small changes in solutions to produce a sensor array capable of detecting HS and Cu^{2+}. More specifically, we employ the concept of electronic tongues [9] with a sensor array made with POEA and sulfonated lignin films adsorbed onto interdigitated gold electrodes. A comparison is then made with an array consisting of bare chrome electrodes.

2. Experimental

Sulfonated lignin (SL) was obtained by modifying lignin, extracted from cellulose pulp, by breaking the bonds in the α carbon of phenol units and incorporating HSO_3^- groups in acidic media, which increases solubility in water. Films were obtained with the Layer-by-Layer (LbL) assembly method [12], which consists

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in the alternate deposition of POEA and SL layers during an immersion time of 3 min (POEA/SL films). They were characterized using UV–vis spectroscopy (Hitachi U2001 model). The LbL films were adsorbed on quartz substrates that were cleaned according to the procedure described by Kern [13]. SL was provided by Melbar (Brazil) in the form of sodium lignosulfonate (Vivilex SD) and used as received. According to the producer, SL has 6.5% of reductor sugars and an Mw of 3000 g mol^{-1} [14]. Obtaining soluble complexes of POEA–SL was only possible after a systematic investigation of the effects from preparation conditions. Aliquots of stock aqueous solutions (in Milli-Q water) at pH 3.0 of POEA at 0.4 g L^{-1} or 1×10^{-3} M (based on the tetramer unit mass, 692 g mol^{-1}) and of SL at 0.3 g L^{-1} or 1×10^{-3} M (based on the C9 unit mass, 298 g mol^{-1}) were mixed under magnetic stirring for 5 min.

LbL films of POEA, POEA/SL films and of the complex between POEA and SL (POEA-ES films) were used as conducting materials. POEA was chemically synthesized in the emeraldine salt form following the procedures described by Mattoso et al. [14]. For film fabrication, POEA solutions were prepared as described by Leite et al. [15], with pH adjusted to 5.0.

The aquatic humic substances were extracted from water samples collected from João Pereira River (23°47'10"S; 46°04'10"W), in the city of Bertioga, Brazil. They were prepared initially in a concentration of 20 mg L^{-1}. Details concerning the HA extraction, purification, and characterization can be found in Ref. [16]. Briefly, HA was extracted from peat using NaOH solution and purified according to the International Humic Substances Society (IHSS) [17]. The chemical interaction between POEA (film and aqueous solution), HS and Cu^{2+} ions were evaluated using UV–vis spectroscopy. Atomic force microscopy measurements were carried out in the non-contact mode using a Topometrix TMX 2010 atomic force microscope to investigate the surface topography of POEA films after interacting with HS and Cu^{2+}.

The sensing units for the sensor array were produced by depositing the LbL films onto interdigitated gold electrodes [9]. The array contained 6 sensing units made from different materials including POEA, sulfonated lignin and humic substances. Also used was another sensor array, containing 5 sensing units made with chrome electrodes with no films, in a strategy developed by Borato et al. [18]. The CuSO$_4$ 5H$_2$O initial solution was prepared at a concentration of 50 mg L^{-1}. The detection of HS in water and the complexation with Cu^{2+} ions were carried by additions of: (i) HS in distilled water; (ii) CuSO$_4$ 5H$_2$O in distilled water and (iii) CuSO$_4$ 5H$_2$O in aqueous HS solution (20 mg L^{-1}). Impedance spectroscopy was employed to characterize the water and HS samples. All measurements were taken at frequencies varying from 200 Hz to 1 kHz, and the film capacitance calculated using an equivalent electric circuit for the film/electrolyte system. The data were treated with Principal Component Analysis (PCA) [9].

3. Results and discussion

Fig. 1 shows the UV–vis spectra of POEA in solution (a) and in a one-layer film (b), featuring a band at 300 nm due to $\pi-\pi^*$ transitions of the aromatic rings and another at larger wavelengths, which may denote the doping state. POEA is already partially doped, particularly in solution. Both in solution and in the film, interaction with HS or Cu^{2+} causes further doping, which is indicated by the shift to higher wavelengths in the polaronic band at ~720–770 nm. For HS the additional doping is explained by the acidic groups (phenolic and carboxylic) in the structure. This interpretation is consistent with Venancio et al. [19], who have shown that HS induce doping of POEA by protonation and may extend the doping state of PANI derivatives up to higher pHs. For Cu^{2+} solution, doping may be attributed to a screening effect of the counterions of the positive
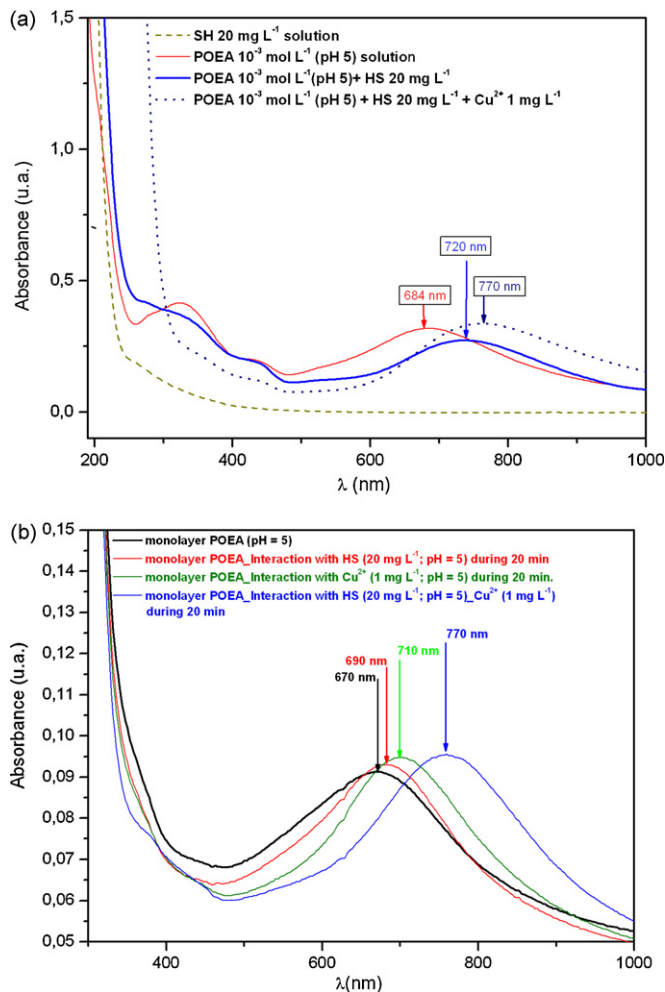

Fig. 1. (a) UV–vis absorption spectra for POEA in (a) solution and (b) in film adsorbed onto a glass substrate, depicting interaction with HS and Cu^{2+} ions.

charges in the conducting polymer, which facilitates protonation of POEA [12].

Fig. 2 shows AFM micrographs of POEA films, as deposited, and after being immersed for 20 min into solutions containing HS, HS/Cu^{2+} and Cu^{2+} ions and then dried. For the as-deposited POEA film adsorbed during 3 min, the image in Fig. 2a displays a globular morphology with grains distributed all over the sample surface, similar to images from the literature [20,21]. The appearance of smaller domains in Fig. 2b may be due to the incorporation of counterions from HS in the polymeric matrix of POEA, causing changes in morphology. The same occurs for the film immersed in HS/Cu^{2+} complex in Fig. 2c. When only Cu^{2+} interacts with POEA, in the absence of HS, there are apparently Cu^{2+} nanostructures over the film surface. This analysis illustrates how film morphology may be affected by interaction between cations and the film. The interaction between POEA in the film and HS or Cu^{2+} increases film roughness, as indicated in Fig. 2, especially for Cu^{2+}. Such changes in morphology may be due to a rearrangement of POEA chains in solution caused by interaction with Cu^{2+} ions and water [15].

It is possible that the morphology changes should also affect the electrical response of sensing units produced from nanostructured POEA films, which can be easily built using the LbL method as well documented in the literature [22,23]. Indeed, LbL films have been used in sensors, biosensors and in chemically modified surfaces [20,24]. In order to verify the possible changes in the electrical properties, a sensor array was used which contained the following sensing units: bare gold electrode, POEA film, POEA/SL film, POEA-
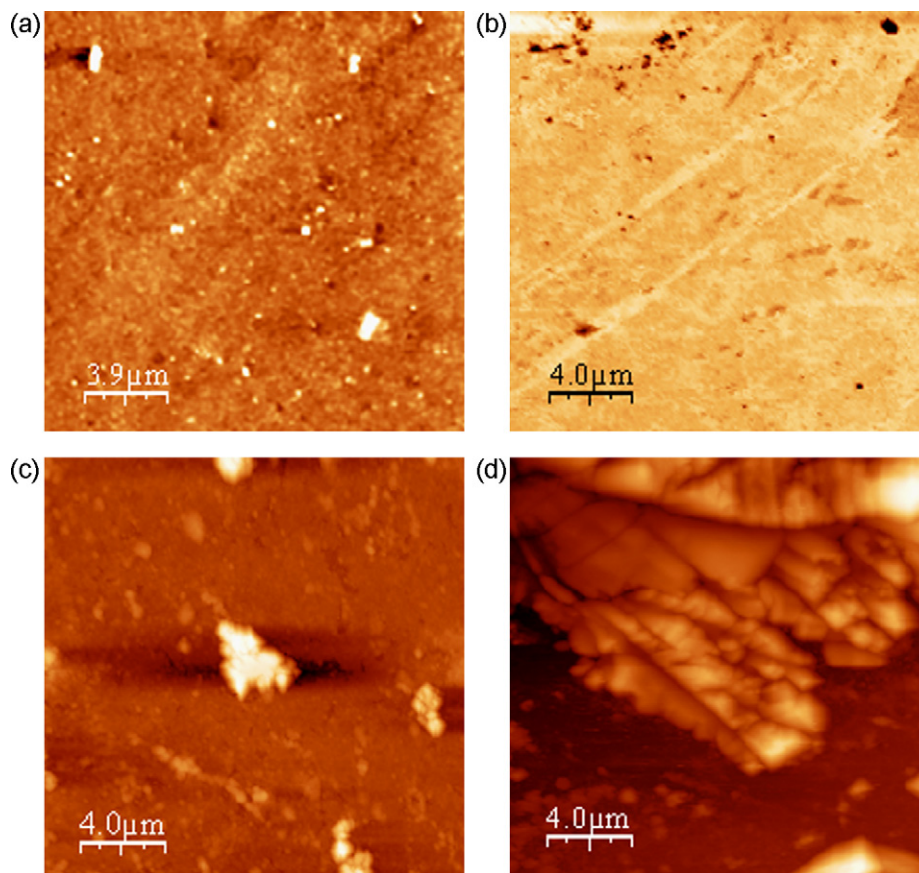
Fig. 2. AFM images for (a) as-deposited POEA film (RMS = 3.5 nm), (b) POEA films after being immersed into solutions containing HS (RMS = 20.7 nm), (c) HS/Cu^{2+} (RMS = 67.9 nm) and (d) Cu^{2+} (RMS = 983.1 nm).

LS (complexed) film, POEA/HS film and HS film. Note that HS is now used in nanostructured films obtained by physical adsorption. In a subsidiary experiment, a sensor array built with five bare chrome electrodes was employed. Measurements were carried out with the sensing units immersed into distilled water or aqueous solutions containing HS or Cu^{2+} ions. The PCA plot in Fig. 3a shows that a distinction can be made of the capacitance data for solutions with various concentrations of HS (0.5, 1, 5, 10, 20 and 50) mg L^{-1}, and

distilled water. Moreover, the first principal component increased monotonically with the HS concentration. The data for capacitance obtained with sensing units immersed in Cu^{2+} solutions with concentrations of 1, 2, 4, 6, 8 and 10 mg L^{-1} are shown in Fig. 3b. With the exception of 1 mg L^{-1}, whose signal almost coincided with distilled water, concentrations of 2 mg L^{-1} or higher could be detected.

The effects of adding Cu^{2+} into a HS aqueous solution can be monitored with electrical measurements, as indicated by the PCA
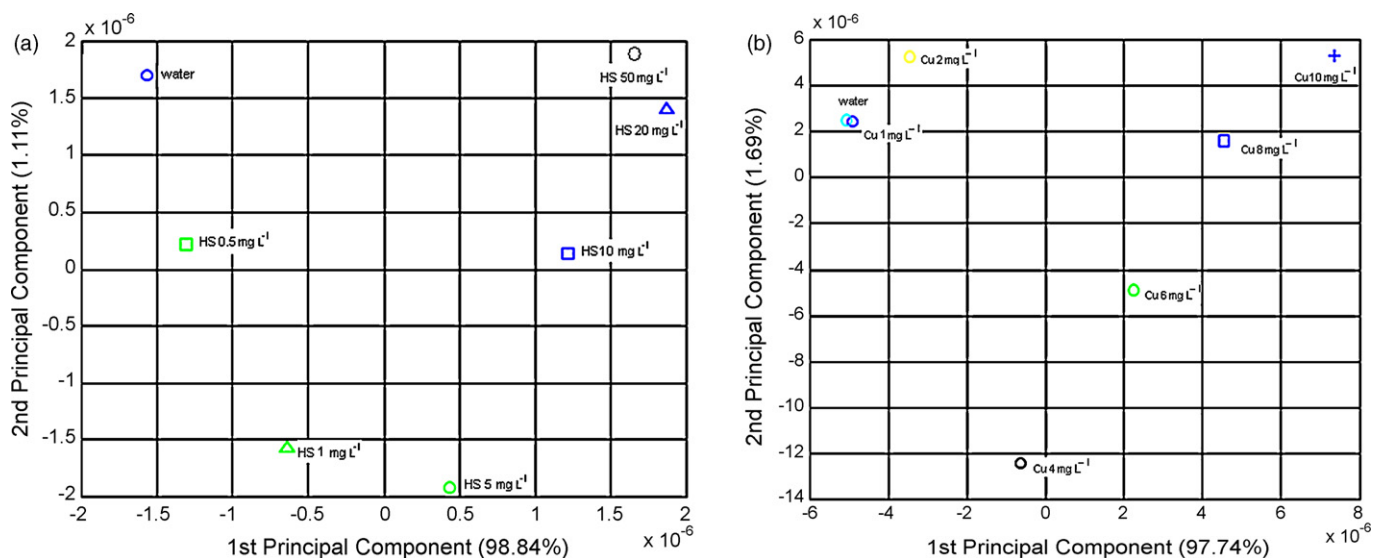

Fig. 3. (a) PCA for HS aqueous solutions and (b) PCA for Cu^{2+} aqueous solutions.
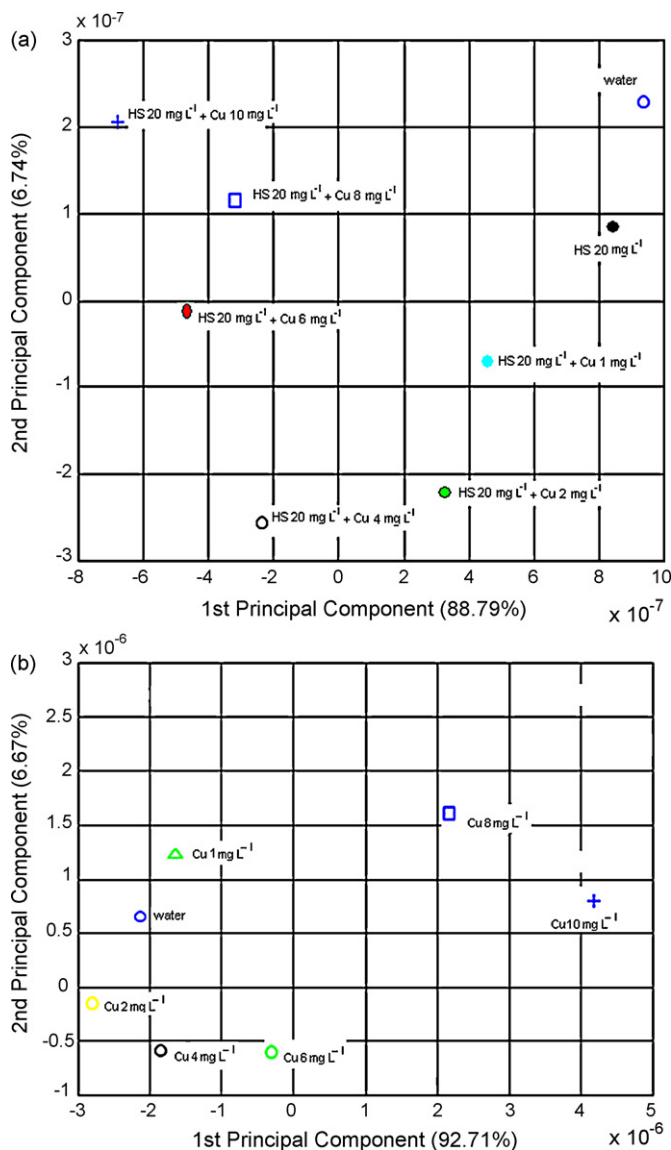
Fig. 4. PCA plot for (a) standard addition of Cu^{2+} in HS aqueous solution ($20\,mg\,L^{-1}$) and (b) for Cu^{2+} solutions, obtained with the sensor array made up of 5 chrome electrodes (no film deposited).

plot in Fig. 4a, in which one can distinguish between the various concentrations of Cu^{2+} added to a solution of $20\,mg\,L^{-1}$ of HS. In subsidiary experiments, we observed that if the HS concentration is increased – say to $50\,mg\,L^{-1}$ – the effects from adding Cu^{2+} become less important. This occurs because humic acids complex with metal ions and change the electrical properties of the latter. HS can also hamper the electrical contact between metal ions and the electrode surface [25], which tends to decrease the sensitivity of the sensor array, as observed experimentally.

In attempts to reduce cost and increase sensitivity of taste sensors we have found out that a novel, inexpensive set of chrome-deposited electrodes may be used in impedance spectroscopy measurements for sensing with good performance [18]. The electrical response of these electrodes differed from each other owing to their distinct morphologies. Fig. 4b illustrates this finding for detection of Cu^{2+} ions with several concentrations (1, 2, 4, 6, 8 and $10\,mg\,L^{-1}$). That a sensor array with no films could be equally efficient in detecting trace amounts of ions indicates the predominance of interfacial phenomena governing the electrical response. It is clear therefore that as far as

the sensing ability is concerned, one may merely employ bare metal electrodes. However, the distinct interactions with POEA films demonstrated here point to a further avenue to explore, in which non-specific interactions may be combined with specific interactions. Indeed, this appears to be the case of highly efficient sensors made of nanostructured films of humic acid, which are capable of detecting pentachlorophenol down to 10^{-10} M [26].

The sensing units could be reused after the experiments with the liquid samples and then being cleaned with copious amounts of pure water. This was tested by repeating all the experiments five times, with the sensing units being immersed in solutions with concentrations varying from 0 to $10\,mg\,L^{-1}$ and back. All the sensors showed good reproducibility and reversibility in the response, which may be ascribed to a good stability of the LbL films. The data were extracted from impedance spectroscopy measurements, and refer to the capacitance of the system at 200 Hz. For all frequencies studied, viz. 200, 400, 600, 800, and 1000 Hz, it was possible to distinguish between the different samples; however, only at low frequencies was it possible to distinguish between low concentration solutions and pure water. The reason for the higher sensitivity at 200 Hz is associated with the physical phenomena governing the electrical response, especially double-layer effects [18].

4. Conclusions

The interaction between a POEA film in the sensing units and HS/Cu^{2+} complexes in liquid samples was investigated using atomic force microscopy and UV–vis spectroscopy. With the latter, we observed that the absorption spectra of POEA films are altered owing to contact with HS and Cu^{2+} ions, thus indicating important interactions between these substances. With the electronic tongue concept with a sensor array either containing nanostructured films of POEA, SL and HS, or a set of bare chrome electrodes, we could distinguish between water samples containing humic substances and different concentrations of Cu^{2+}. Using such sensor arrays may therefore be a fast, low-cost strategy to monitor the quality of water in treatment plants.

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