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Hierarchical Composite Polyaniline–(Electrospun Polystyrene) Fibers Applied to Heavy Metal Remediation

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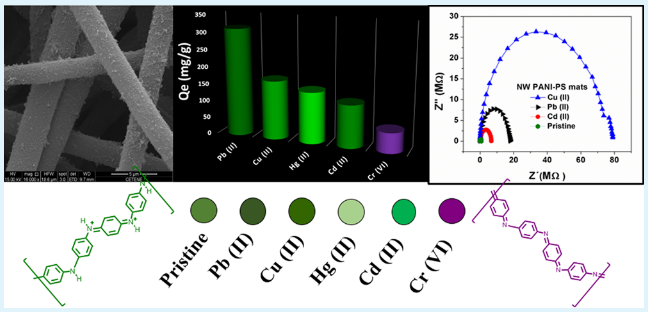
Supporting Information



ABSTRACT: We describe the in situ preparation of a multipurpose hierarchical polyaniline–polystyrene (PANI–PS) composite based in the chemical polymerization of PANI on nonwoven (NW) electrospun PS mats. We performed a detailed study of the properties of these materials to select the best strategies to incorporate PANI chains into pristine NW PS mats without compromising the original porosity and mechanical flexibility of the matrices. The resulting composites presented nanostructured PANI chains highly dispersed in the interior of the NW PS mat and showed good electrical properties and surface-wetting characteristics that could be easily controlled. In particular, we show that these NW PANI–PS mats exhibit interesting properties in their interaction with heavy metal ions. For instance, their high adsorption capacities toward dispersed Hg(II), Cd(II), Pb(II), Cr(VI), and Cu(II) ions make them promising materials for water remediation, by providing a simple manner of collecting and removing these metals from aqueous systems. In fact, the NW electrospun mats here presented do not suffer from the usual limitations found in materials commonly employed as adsorbents, such as a tendency to agglomerate or accumulate in the environment because of difficulties of properly recovering them after use. To better understand the nature of each pairwise metal–PANI interaction, we performed a thorough investigation of the optical and electrical changes induced by the metal adsorption in the NW PANI–PS mats. As a consequence of their interaction with the metal ions, the visual aspect of the mats change, a fact more evident in the case of Cr(VI) removal, when the matrices vary their color from green to purple. These changes are related to the variation of the oxidation state of the PANI chains: as the ion metals are progressively adsorbed into the mat, they promote the conversion in varying degrees of the PANI chains from salt emeraldine to the pernigraniline form, and the mats become more resistive. We implemented an electrical impedance investigation of the charge transport characteristics of NW PANI–PS mat, and the results indicate that they are sensitive to the type of metal ion adsorbed and that the amount of ions adsorbed in each case is mostly related to the standard electrode potential of the metal considered.

KEYWORDS: *electrospinning, conducting polymers, heavy metal ion removal, water remediation*

1. INTRODUCTION

Water and air pollution control are current environmental problems demanding the urgent development of new types of materials that could provide for efficient and practical ways to detect and remove toxic agents. In that regard, the contamination of aqueous reservoirs or water distribution systems by heavy metals ions, such as Hg(II), Cd(II), Pb(II), Cr(VI), and Cu(II), represents a potential risk to human and animal health.[1] Because of their low cost, high availability, and high adsorption efficiency, orange waste, husk rice, and pinewood are examples of bioorganic materials or agricultural waste-based adsorbents that have been employed in water remediation systems.[2] However, after being released in aqueous systems, soluble organic compounds usually demand high levels of chemical and biological oxygen that can jeopardize aquatic life and create new ecological problems.[3] A new kind of adsorbent that has been recently considered are nanostructured materials, which offer the possibility of exhibiting a higher number of metal absorption sites because of their high surface to volume ratio.[4] Nevertheless, the practical use of these materials is somewhat limited not only by their tendency to agglomerate (a phenomenon that would reduce their adsorption capability) but also due to the usual lack of control on their release extent during the remediation process (a factor that limits the degree of their subsequent recuperation, therefore generating an additional source of contamination). An alternative technique that also has been analyzed is the use of membranes bearing intrinsic or synthetically functional groups capable of interacting with heavy metal ions. Such a feature, combined with the characteristic high porosity, light

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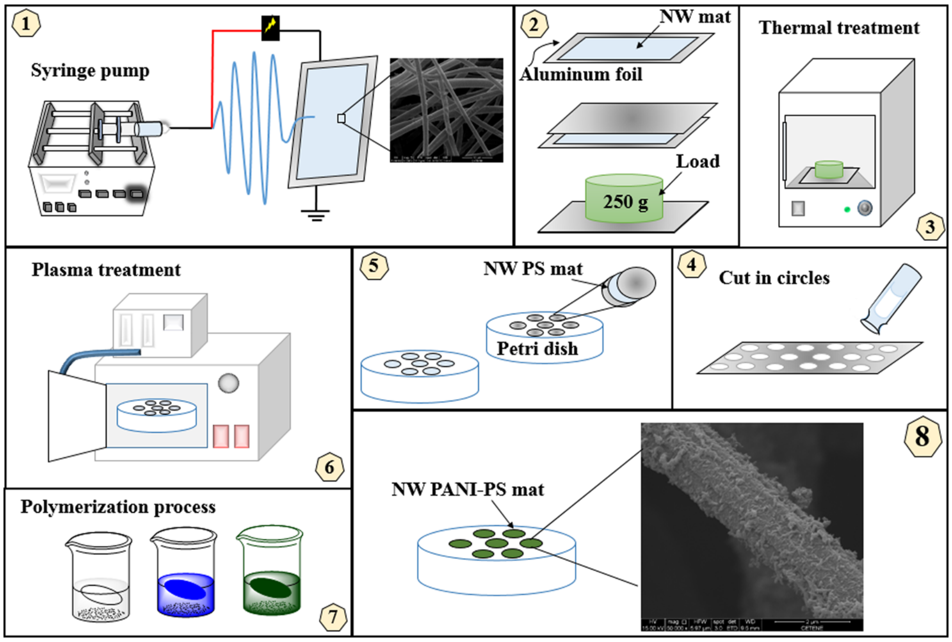
Scheme 1. Schematic Representation of NW PANI−PS Mat Production Process[a]



[a]ES process (1), sequence of steps for the treatment of the NW PS mats (2−6), polymerization process (7), and final NW PANI−PS mats (8).

weight, flexibility, and low cost of membranes, makes these functionalized systems to appear as promising active materials for trapping and filtering from aqueous solutions.[5]

In recent years, electrospinning (ES), an electrorheological process, has become a very popular technique as a simple and cost-effective enabling methodology to produce membranes composed of micro- or nanofibers.[6] The electrospun fibers can present new morphologies that confer special properties to their bulk, such as superhydrophobicity[7] or enhanced mechanical performance.[8] One of the most fascinating characteristics of the ES technique is the possibility of its use to tailor a new class of membranes that can be used for a wide range of possible applications, among them the selective adsorption of pollutants.[9]

The first strategies to use ES in the development of membranes capable of removing heavy metal ions employed ionic polymers such as poly(acrylic acid) or chitosan. Those materials possess intrinsic functional groups that allow the formation of metal complexes; however, this same advantageous characteristic has the down side of producing jet instabilities during the ES process. As a consequence, the corresponding membranes usually presented poor physical properties.[10−12] An alternative approach involves the blending of ionic polymers with others easier to process; however, this leads to a decrease in the amount of active sites and, hence, to a loss of performance.[13,14] A different procedure would be to adopt physical or chemical methods to create functional groups on membranes produced by ES. For instance, previous reports have discussed the modification of nonwoven (NW) mats of poly(methyl-methacrylate) (PMMA), poly vinylidene fluoride (PVDF), polyvinyl-alcohol (PVA), polyacrylonitrile (PAN), and polystyrene (PS) by incorporating amino, mercapto, or sulfonic groups on their surface.[15−17] Generally, after this modification, the mats exhibit a smooth surface with almost no apparent defects.

A more recent tendency in membrane modification consists in recurring techniques that allow the incorporation of nanostructures on previously formed membranes, such as layer-by-layer deposition, in situ chemical treatment, or sol−gel processes.[18−21] Because of the resulting increase in the final active surface area, those improvements bring new functionalities to the membranes. In particular, the use of intrinsically conducting polymers (ICPs) has received a greater attention because of the synergistic effects that result from the combination of the high flexibility of polymeric membranes with the inherent electrical properties of the ICPs. Materials with these enhanced properties have found application in flexible and highly sensitive sensors[22] or supercapacitors.[23]

Among the ICPs, polyaniline (PANI) stands out not only because of its easy and low-cost synthesis but also for conciliating excellent environmental stability to a set of special electrical and optical properties that can be controlled by its doping through simple chemical methods.[24] To the best of our knowledge, although several reports in the literature have focused on the deposition of PANI on PAN,[25] PMMA,[26] or copolymer membranes,[27] use of ICPs for the modification of PS membranes has not been widely explored. The interest in the use of PS as a matrix resides on its wide availability, low cost, and good thermal properties. In this work, we describe the details of a careful investigation on the production, modification, and characterization of a hierarchical PANI−PS composite and its application in the detection and removal of heavy metal ions from aqueous media.

2. EXPERIMENTAL SECTION

2.1. Materials. PS (MW of 280 kDa), ammonium persulfate (APS), and cadmium bromide tetrahydrate ($CdBr_2 \cdot 4H_2O$) were purchased from Sigma-Aldrich (U.S.A.). Aniline, dimethylformamide (DMF), hydrochloric acid (HCl), copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), potassium dichromate ($K_2Cr_2O_7$), lead(II) nitrate ($Pb(NO_3)_2$), and mercury(II) chloride ($HgCl_2$) were provided by Vetec-Sigma, Dinâmica, Fmaia, Nuclear, Quimex, Vetec, and ISOFAR (all of them Brazilian companies), respectively. All reagents were of analytical purity and used as received, except for aniline, which was distilled under reduced pressure before use. The water used in all experiments was of ultrahigh purity (Millipore).

2.2. Preparation of Nonwoven Polystyrene Mats. Initially, we prepared a PS solution of 20% w/v in DMF, and then 2 mL of this solution was loaded in a 3 mL syringe with a stainless steel spinneret 18G (Beckton Dickinson, U.S.A.). The ES process was performed in the horizontal configuration setup. As working conditions, we adopted a distance of 15 cm from the spinneret to the collector, a flux of 0.5 mL/h provided by a NE-4000 syringe pump (New Era Syringe Pumps, U.S.A.) and a high voltage (17 kV) produced by a homemade power supply. The fibers were collected on a grounded static collector covered with an aluminum foil, until the complete use of the initial 2 mL volume of the solution. The resulting mat was dried at room temperature for 8 h and then thermally treated to allow a better handling and an easier peeling off from the aluminum foil. For this, portions of the PS mat were sandwiched between two aluminum foils, and a weight of 250 g was placed atop of them; this setup was positioned inside a laboratory oven at 80 °C for 24 h, when finally the mats were retired and cut in 25 mm diameter circles.

2.3. In Situ Polymerization of Polyaniline on Nonwoven Polystyrene Mats. For the in situ PANI polymerization, the pristine NW PS mats were first subjected to an air plasma treatment using a PDC-002 plasma cleaner (Harrick, U.S.A.) during 3 min, and then placed in a 50 mL beaker containing 15 mL of HCl 1 M and 0.16 mmol of aniline. After 15 min, we added 0.1 mmol of APS dissolved in 5 mL of a 1 M HCl solution. The polymerization process was performed at room temperature under constant stirring for 24 h. Finally, the NW PANI−PS mats were washed several times with deionized water and methanol and subsequently dried in vacuum for 12 h. In Scheme 1, one can find a step-by-step representation of the processes of production and modification adopted in the preparation of the NW PANI−PS mats.

2.4. Characterization. We used a 15 kV Quanta 200 FEG scanning electron microscopy (SEM, FEI, U.S.A.) to investigate the surface features and the morphological structure of the fibers. The average diameter of the fibers was calculated after measuring 80 individual fibers shown in several micrographs and employing the ImageJ software.[28] The surface wettability was studied by examining the static behavior of 4 μL of water drops on the surface of NW mats deposited on glass slides using a CAM 100 contact angle meter instrument (KSV, Finland). The thickness of the NW mats was measured with a precision of 1 μm by using a digital micrometer (Mitutoyo, Japan). Fourier transform infrared spectra (FTIR) were obtained on a 400 FT-IR/FT-NIR (PerkinElmer, U.S.A.) in the 4000 to 500 cm^{-1} range. UV−vis absorption spectra were acquired in a Cary 5000 UV−vis−near-IR spectrophotometer (Agilent, U.S.A.), using a pristine NW PS mat as reference, whereas the electrical properties were determined by use of direct current (DC) and alternating current electrical measurements. The sample was prepared by cutting a 1.0 cm × 0.5 cm piece of the NW PANI−PS mat, which was fixed on a glass substrate, with the electrical contact made by applying silver paint at the edges. The current voltage curves were obtained by applying a −1 to 1 V tension in the linear sweep mode on a 2400 SourceMeter multimeter (Keithley, U.S.A.). The impedance response was obtained on a 1260 SI impedance gain-phase analyzer (Solartron, U.K.) equipped with a 1280 dielectric interface and use of an 1 V bias in the 1000 MHz to 1 Hz frequency range. All electrical measurements were performed in a nitrogen atmosphere at room temperature.

2.5. Adsorption Experiments. Stock solutions of Cd(II), Cu(II), Cr(VI), Pb(II), and Hg(II) with the same concentration (100 mg/L) were prepared by dissolving $\text{CdBr}_2\cdot4\text{H}_2\text{O}$, $\text{CuSO}_4\cdot5\text{H}_2\text{O}$, $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Pb(NO}_3)_2$, and HgCl_2 in deionized water. The experiments were performed by placing the NW PANI−PS mats in 20 mL of a heavy metal stock solution contained into glass flasks. The pH of the solution was adjusted to a value of 4.0 by adding small amounts of a 0.1 M HCl solution, and then the flasks were placed on an orbital shaker for 12 h at 120 rpm. After this time, the supernatant was collected, and the metal ion concentration was determined by use of an inductively coupled plasma atomic emission spectrometer (ICP-AES) (PerkinElmer, U.S.A.).

The adsorption capacity of the membrane was calculated as

$$q_e = \frac{V(C_o - C_f)}{m}$$

where q_e is the relative amount (mg/g) of metal adsorbed by the membrane, V is the volume of the solution, C_o and C_f are the initial and equilibrium concentration of the metal ions in the solution (mg/L), and m is the mass (in g) of the membrane used. For effects of comparison (see later), we also performed removal experiments using NW PANI−PS mats that were not previously subjected to a plasma treatment.

3. RESULTS AND DISCUSSION

3.1. Preparation and Characterization of Nonwoven Polyaniline−Polystyrene Mats. A homogeneous deposition of the NW PS mat on the aluminum foil was obtained by employing a DMF solution containing PS (20% w/v), as discussed in Section 2.2. The mat presented an average thickness of (85 ± 10) μm. In the SEM images of the NW PS mats shown in Figure 1, one can observe that the fibers have a roughened surface without the noticeable presence of beads or flat sections. The average fiber diameter was of (1.6 ± 0.4) μm, estimated after measuring 80 fibers. It was also possible to observe the absence of links among the fibers; unfortunately, this last feature makes the mat so mechanically poor that it tends to lose its original conformation when subject to rough handling. Hence, to overcome this liability is a crucial need for improving the range of possible applications of the fibers. With this in perspective, we treated the NW PS mats by applying heat and pressure, because a preliminary exploration has indicated that the mat became more compact and resistant to handling clear after thermal and mechanical response treatment. The SEM images of the thermally processed mat (Figure 2) now reveal the presence of more dense, flatter, and interlinked fibers that exhibit smooth surfaces (see inset of Figure 2a).

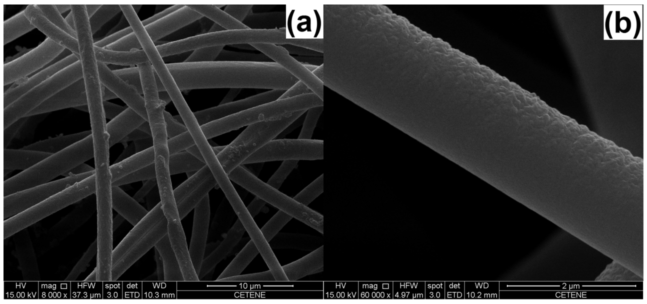


Figure 1. SEM image of NW PS mat (a) as-prepared and (b) magnification of one of its fibers.

As the objective of this work was the integration of PANI on the PS fiber surface, we needed to improve our understanding of the membrane surface properties. For this reason, we performed measurements of the static water contact angle on the fibers before and after the thermal treatment, because this technique can provide quantitative information about the wettability of materials. Although the value for the pristine NW PS mat was (130 ± 3)° (Figure 3a), an almost 10 degree (121 ± 3)° (Figure 3b) reduction of the contact angle was observed after the thermal treatment. Even so, both values indicate that the mat has a hydrophobic character, which should be a result of both the polymer chemical composition and fibril morphology.[29] It is noteworthy to observe the effect of the

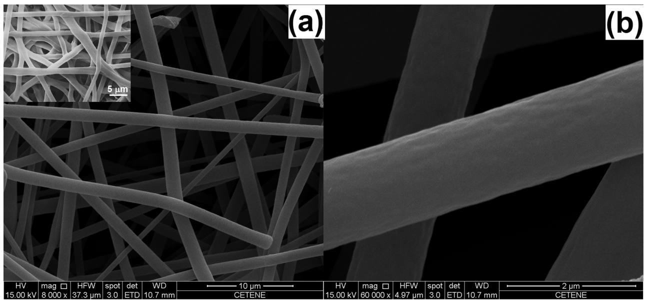


Figure 2. SEM images of a thermally processed mat. Note the presence of more compact, flatter, and interlinked fibers (see inset) that (b) exhibit smoother surfaces than before the heat treatment.

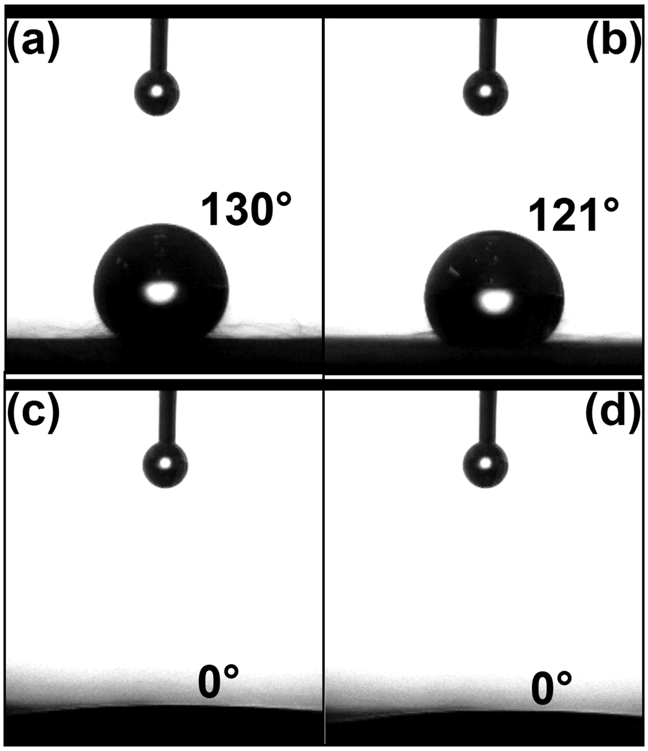


Figure 3. Contact angle for: (a) NW PS mat as-prepared, (b) NW PS mat thermally treated, (c) plasma-treated NW PS mat, and (d) NW PANI−PS mat.

thermal treatment, which leads to a lesser rough surface and, consequently, to a decrease in the water contact angle.

Once the hydrophobic character of the NW PS mats had been established, we faced the challenge of finding the best procedure to incorporate the PANI on the mat. Most papers found in the literature dealt with the blending of PANI chains to polymers that can be easily electrospun. However, because of the PANI low solubility, the resulting mats usually exhibited mainly the characteristics of the host matrix, with a noticeable reduction relative to pure PANI films of both the electrical conductivity and the electrochromic properties; this behavior is accompanied by a marked decrease in the number of active sites for interaction with the target compound.[13,14] To overcome these problems, some authors have adopted the inclusion of ionic species (such as surfactants or acids) that help the dispersion of the PANI chains into the host; however, even these procedures have not completely solved the limitations identified, such as the persistent poor electrical conductivity[30] of the resulting materials.

Our alternative approach to the problem was to induce the adsorption of aniline monomers followed by their in situ adsorption chemical polymerization on the host matrix (NW PS mats). In principle, this technique would allow a more external growth of the PANI chains, with no compromise of the matrix flexibility, while generating a larger number of accessible active sites.[31] However, when trying to form the PANI chains on the NW PS mats, we observed that the conducting polymer grows only poorly on the external surface of the fibers and not at all toward the interior of the NW PS mat (see the Supporting Information, Figure S1). We believe that this hindered growth may be associated with the hydrophobic characteristics of the PS fibers, which preclude the occurrence of polymerization in the internal volume of the mat by impairing the flow of the aniline solution toward that region.

It was exactly to overcome this problem that we decided to improve the wettability of the pristine NW PS mats by submitting them to an air plasma treatment. The carboxylic groups that are then produced confer a hydrophilic character to the fibers,[32] allowing the polymerization to occur into the whole mat (see ahead). In Figure 4, where we show an image of a NW PS mat treated by air plasma, one can verify that the effect of the plasma treatment is to produce a nanostructured roughness on the fiber surface, without sacrificing the bulk integrity. A similar nanostructured topology has been previously reported by Bonaccurso et al.,[33] who observed this phenomenon on PS films that were deposited by spin coating and later treated by air and argon plasma: in fact, those changes were a direct product of the etching process produced during the plasma.[34] By measuring the static contact angle of water drops on the surface of plasma-treated NW PS mats, it was possible to observe that the surface characteristics change from hydrophobic to hydrophilic, because afterward a water drop was rapidly adsorbed into the mat (Figure 3c). When compared to alternative chemical treatments, the plasma procedure that we adopted represents a significant advance because it is cleaner, easier, and faster, while at the same time dispensing the introduction of chemical species that could negatively affect the polymer properties.[35] Finally, the porosity of the host matrix was not affected by the plasma treatment, so that PANI chains were successfully polymerized in a homogeneous manner on the NW PS mats, as one can observe in Figure 5a. In Figure 5b, where we present a larger magnification of an individual fiber, one can notice the nanostructured rodlike PANI morphology. It is possible to explain the polymerization of aniline on the fiber surface by taking into account the low concentration

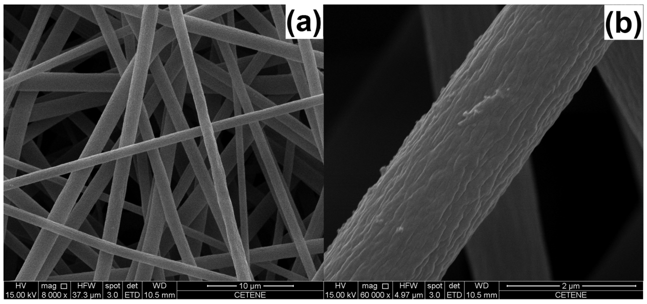


Figure 4. SEM image of (a) plasma-treated NW PS mat and (b) magnification of one of its fibers.

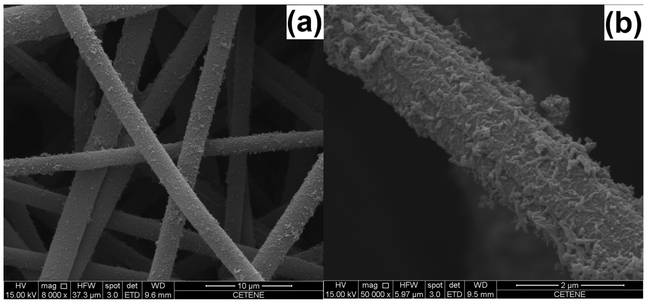


Figure 5. SEM image of (a) NW PANI−PS mat and (b) magnification of one of its fibers.

employed and considering a mechanism already proposed in the literature for the in situ polymerization of aniline on solid substrates.[36,37] According to this mechanism, oligomer species formed at the first polymerization stages tend to be mainly adsorbed on the available surfaces; because these species are more reactive and polymerize faster than the others present in the reaction solution, different nucleation sites are created on the PS fiber surface. Hence, when a given PANI chain grows on the surface, it fosters the growth of new PANI chains that, because of steric hindrances, tend to grow perpendicular to the axis of the original fiber.

We performed an FTIR investigation to examine the composition of the NW mats of PS and PANI−PS (Figure 6). In the PS spectrum (curve (a)), one can observe the presence of peaks at 3083, 3060, and 3026 cm^{-1}, which can be assigned to the C−H stretching vibration, and a peak at 1601 cm^{-1} that corresponds to the aromatic C=C stretching vibration; finally, the peaks at 1493 and 1453 cm^{-1} are due to the C−H bending vibration, and the band at 697 cm^{-1} is correlated to the out-of-phase monosubstituted aromatic rings.[38] In the corresponding spectrum for the composite (curve (b)), the characteristic peaks of the PANI are present, as well as those of the PS already mentioned. In the case of PANI, there are peaks at 1597 and 1497 cm^{-1}, which correspond to the C=C stretching deformation in the quinoid and benzenoid rings, respectively; the peak at 1304 cm^{-1} can be assigned to the C−N stretching vibration in a benzenoid ring, whereas the peak at 1144 cm^{-1} can be assigned to the aromatic C−H in plane bending. Finally, the peak at 820 cm^{-1} corresponds to the 1,4-substituted benzene ring.[31,39]

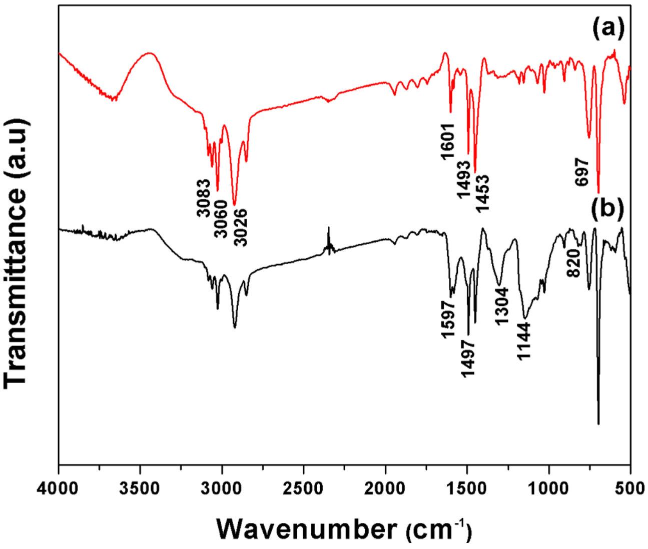


Figure 6. FTIR spectra of (a) NW PS and (b) NW PANI−PS mats.

Previous reports have mentioned a dependence between the doping state of the PANI and its wettability. Hence, we additionally implemented a study about the wettability properties of the NW PANI−PS mat. It is known that PANI is hydrophilic while in its emeraldine salt state (ESS) and that it is hydrophobic when in its base emeraldine state (BES),[40,41] so that the nature of the doping state could directly influence PANI's effectiveness to remove metal ions in an aqueous solution. We tested this assumption by placing a NW ESS PANI−PS mat in deionized water, a step that should lead to the PANI deprotonation. After we dried the mat, two modifications were easily identified: (i) its noticeable color change from a greenish ESS to a bluish BES and (ii) an increase in the measured value of the water contact angle, which rose to (106 ± 2)°. Hence, the NW BES PANI−PS mat became more hydrophobic, possibly because of a combined effect of the intrinsic chemical structure of BES and the physical barrier represented by the topology adopted by the PS fibers employed as support. It is important to examine the reversibility of this wetting behavior, and so we exposed the mat to HCl vapors: after a short period of time, we observed the gradual adsorption of the water drop, indicating the redoping of the NW PANI−PS mat (see video in the Supporting Information provided). This simple experiment makes evident how important the PANI protonation state is for the establishment of an effective contact between the adsorbent membrane and the target ions to be adsorbed. For this reason, all removal experiments here described were performed in an acidic medium.

We studied the electrical properties of the NW PANI−PS mats by two-probe DC measurements. The corresponding results indicate that the value of the electrical resistance is strongly affected by the degree of the environmental relative humidity: the conductivity of the NW PANI−PS mat at ambient conditions decreased by a factor of 20 when measured under a nitrogen atmosphere (from 0.016 S/cm to 8 × 10^{-4} S/cm). The presence of even small amounts of water may have a direct impact on the mobility of dopant ions. We note that the conductivity value of the NW PANI PS is comparable to that of electrospun fibers modified by in situ chemical polymerization of aniline[42,43] but smaller than those of pure PANI films. This can be rationalized by considering that the charge transport in the NW mats must be hindered by their porosity and the discontinuities on the PANI coating of the nonconducting matrix.[44]

3.2. Experiments of Heavy Metal Ion Removal. We examined the adsorption characteristics of the plasma-treated NW PANI−PS mats, and of similar mats not subjected to the plasma treatment, toward dissolved heavy metals ions in aqueous solutions. For the plasma-treated NW PANI−PS mats, the corresponding results of this mutual interaction are shown in Figure 7, where it can be observed that the mats possess the ability of removing different metals; hence, they can be used as active elements for the remediation of contaminated aqueous reservoirs or water-distribution systems. In descending order for the metals tested—Pb(II), Cu(II), Hg(II), Cd(II), and Cr(VI)—the measured adsorption capacity q_e (in mg/g) was 312, 171, 148, 124, and 58, respectively. As it could be expected, we have observed no activity toward heavy metal removal by the PANI−PS NW mats that were not subjected to a plasma treatment.

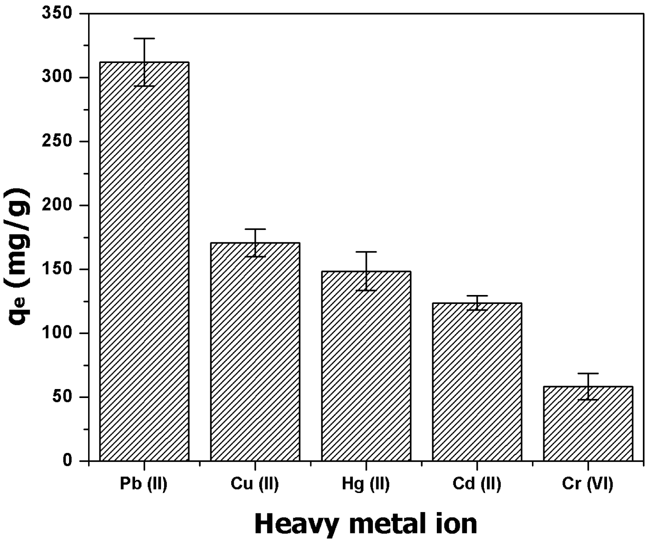


Figure 7. NW PANI–PS mat adsorption capacity for the different heavy metal ions employed.

The case of the chromium ions deserves special attention in the sense that in aqueous solutions they are dissolved as anions. The mechanism of their interaction with the NW PANI–PS mats can be explained as follows: at its first stage, the process involves an ionic exchange between the Cl^- counterion of the doped PANI and the dichromate anion ($Cr_2O_7^{2-}$). Subsequently, a redox reaction occurs, where the PANI is oxidized and the Cr(VI) is reduced to Cr(III) ions that later will be chelated.[45] In all other cases (Pb(II), Cu(II), Hg(II), and Cd(II)), the heavy metal ions are dissolved in the form of cations, and their interaction with the NW PANI–PS mats involves predominantly their chelation with the amine groups of the PANI.[46]

It is important to note that the values obtained for the adsorption capacity of the NW PANI–PS mats are higher than those of some adsorbents based on electrospun fibers reported in the literature. For example, Xiao et al.[10] produced a water-stable electrospun poly(acrylic acid) membrane for the removal of Cu(II), whose estimated q_e value was 9 mg/g. Wang et al.[47] tested the removal of Cu(II), Cd(II), and Pb(II) employing a membrane based on PVA/poly(ethylenimine) and estimated the corresponding capacity values as 67, 117, and 90 mg/g, respectively. Later, Wang et al.[25] reported the production of a polyacrylonitrile/polyaniline core/shell nanofiber mat system for the removal of Cr(VI), whose adsorption capacity was of 25 mg/g. Finally, Mahapatra et al.[48] employed an Fe_2O_3–Al_2O_3 ceramic-based nanocomposite fiber as adsorbent for Cu(II), Pb(II), and Hg(II), obtaining q_e values of 5, 24, and 64 mg/g, respectively.

As mentioned above, the NW PANI–PS mats reported in the present work exhibited higher adsorption capacities than similar adsorbents discussed in the literature. Even so, it should be pointed out that there is still a need for a more extensive study where the microscopic interaction of the dissolved metal ions and the membrane is better analyzed so as to eventually optimize the corresponding adsorption capabilities with respect to important parameters, such as a larger range of pH variation, interaction time, and temperature, among others.

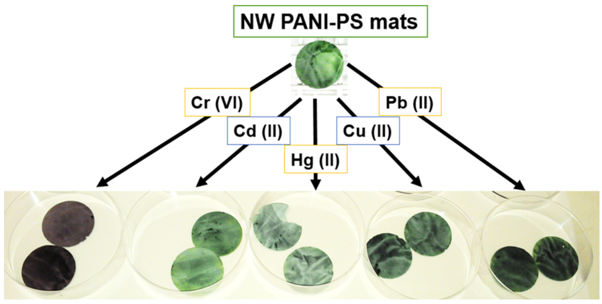


Figure 8. Photographs of NW PANI–PS mats before and after the interaction with the heavy metal ions.

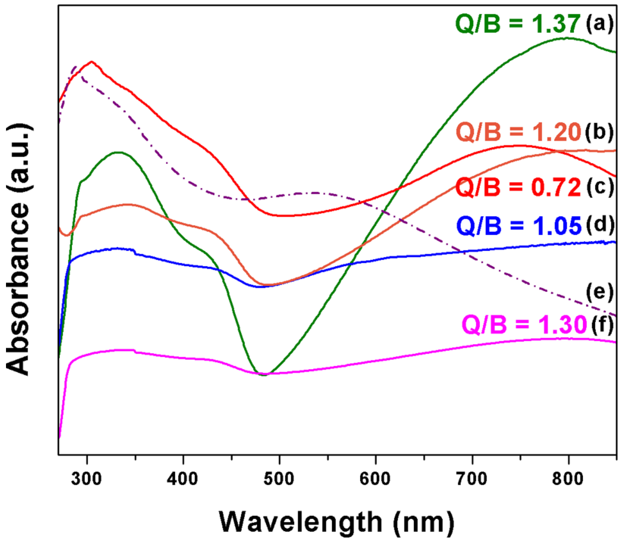


Figure 9. NW PANI–PS UV–vis absorption spectra for mats before and after the interaction with the heavy metal ions: (a) pristine, (b) Cd(II), (c) Cu(II), (d) Hg(II), (e) Cr(VI), and (f) Pb(II).

3.3. Nonwoven Polyaniline–Polystyrene Mat Changes Induced by the Interaction with the Heavy Metal Ions.

Another important characteristic of the NW PANI–PS mats that deserves our attention is the fact that, after each removal experiment, they experience a noticeable color variation (Figure 8). The most drastic example of such changes was observed for the chromium case (when the originally green mat turns purple), whereas for the other metal ions, the accompanying color variation is more subdued, involving only subtle changes in the characteristic green color of the emeraldine salt. To understand more about such color changes, we examined the UV–vis absorption spectra of the NW PANI–PS mats employed in the experiments, both before and after their interaction with the metal ions. In the curve of Figure 9a, which corresponds to the spectrum of a pristine NW PANI–PS mat, it is clearly assigned according to the presence of three peaks at 350, 430, and 800 nm. Those features can be attributed to a π–π^* transition and to the polaronic and bipolaronic bands, respectively, in concordance to the idea that PANI is in the ESS form.[49,50] In fact, for each one of the NW PANI–PS mats used to remove cationic ions (curves b, c, d, and f), it was possible to observe changes on its polaronic and bipolaronic bands, even though the PANI chains remain in their salt emeraldine form. The polaronic band experiences both a redshift and a decrease in its intensity; meanwhile, a blueshift and a corresponding decrease in the intensity were identified in its bipolaronic band. This suggests that, after their interaction with the metal ions,

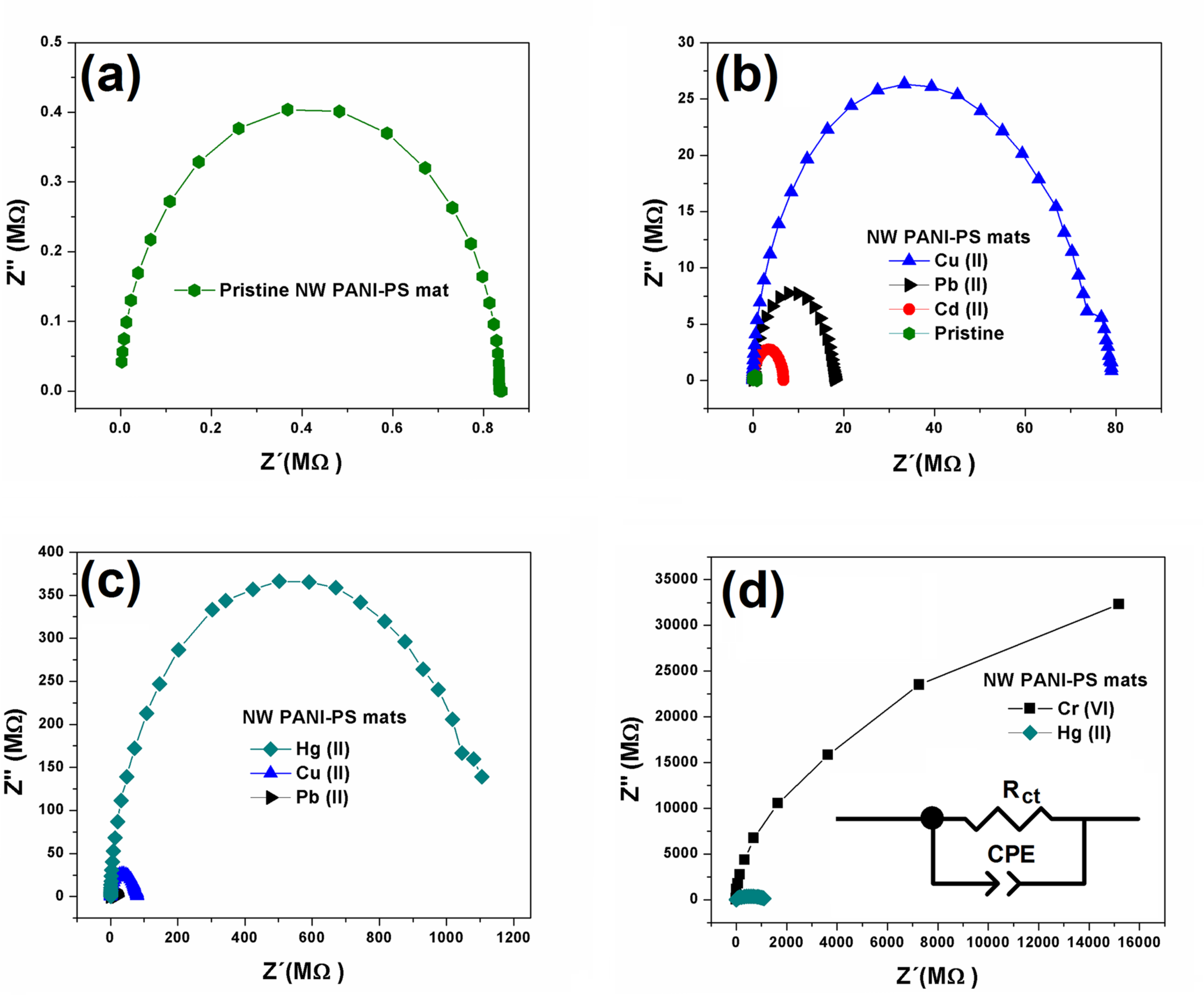


Figure 10. NW PANI−PS Nyquist plots for mats before and after the interaction with the heavy metal ions. (a) Pristine NW PANI−PS; (b) pristine, Cd(II), Pb(II), and Cu(II) NW PANI−PS; (c) Pb(II), Cu(II), and Hg(II) NW PANI−PS; and (d) Hg(II) and Cr(VI) NW PANI−PS. Equivalent circuit used for modeling the impedance curves (inset).

the NW PANI−PS mats exhibit a lower degree of electron delocalization along the polymer chains, an observation consistent with the idea of an effective lower doping level[51] of the PANI chains. On the other hand, for the case of removal of the $Cr_2O_7^{2-}$ anion, the corresponding spectrum (curve e) exhibits peaks at 282, 321, and 540 nm, which are characteristic of the PANI pernigraniline state.[52] We have assessed the doping level of each NW PANI−PS mat-metal complex by estimating the relative quinoid/benzenoid (Q/B) concentration when the PANI chains are in the ESS form, through the ratio of their absorptions at 800 and 350 nm, respectively.[53,54] The Q/B ratio for the pristine PANI was 1.35,which is an indication that the polymer is in its conductive state. Meanwhile, the Q/B ratio for the NW PANI−PS mat−metal complexes was equal to 1.3, 1.2, 1.05 and 0.67, for Pb(II), Cd(II), Hg(II), and Cu(II), respectively. These changes in the absorption spectra indicate that the interaction of the heavy metal ions with the PANI results in a dedoping process involving the oxidation of the polymeric chains. Initially, these chains were protonated because of the presence of HCl in the medium, and thus the most probable sites for interaction with the metal ions are the amine nitrogen atoms in the benzenoid rings. This interaction consists of a two-step redox mechanism, in which first the metal ions oxidize the amine nitrogen atoms producing imines, with the coordination of the lone pair on the imine nitrogen by the reduced metal; then, the metal cations are oxidized by the imine groups, generating radical cation segments and the oxidized cations. This mechanism has been well-studied by Dimitrev[55] and Izumi.[56]

It is well-known that color changes in the PANI chains are directly associated with their oxidation states, with direct repercussions on the overall electrical conductivity.[57] To pursue this structure−conductivity connection further, we used electrical impedance spectroscopy to investigate the response of the NW PANI−PS mats before and after the removal experiments. In Figure 10, we show the corresponding Nyquist plots and the model circuit we used to simulate the observed response. This circuit consists of a resistance R_{ct}, which represents the charge-transport resistance of the composite, in parallel with a constant phase element (CPE). The impedance of the latter can be written as $Z_{CPE} = [q^{-1}(\omega i)]^{-n}$, where q is a constant that accounts for a combination of properties related to both the mat and the charged species and n is the CPE exponent, which would be equal to 1 only in case of a pure capacitive response. In these plots, it is possible to identify a variation in the values of R_{ct} (which, in each case, is expressed by the diameter of the corresponding semicircle). In Table 1, we list the corresponding values for R_{ct}, q, and n, where it can be seen that R_{ct} exhibits a large range of variation, according to the type of metal ion incorporated in the mats. In addition, the value of n remains in an interval between 1 and 0.8, which corresponds to a small distortion of a pure capacitance behavior in the pattern of distribution/accumulation of charge carriers.[58] (For more details of the electrical impedance spectroscopy characterization of NW PANI−PS mats, please see the Supporting Information.)

Table 1. Comparison of the Impedance Parameters of Mats Containing Heavy Metal Ion X to Those of Pristine Mat

nature of the mat	R_{ct} (Ω)	q	n	R_{ct}^{X}/R_{ct}^{HCl}
HCl	7.97×10^{5}	4.51×10^{-12}	0.98	1.0
Cd (II)	6.72×10^{6}	1.93×10^{-11}	0.88	8.4
Pb (II)	1.78×10^{7}	1.02×10^{-11}	0.92	10.0
Cu (II)	7.10×10^{7}	2.54×10^{-11}	0.84	89.0
Hg (II)	9.99×10^{8}	2.28×10^{-11}	0.82	1250
Cr (VI)	8.36×10^{10}	3.84×10^{-12}	0.99	105 000

One should observe that although the R_{ct} for the NW PANI−PS mat−metal complex decreases in the order Cr(VI), Hg(II), Cu(II), Pb(II), and Cd(II), in fact the amount of metal adsorbed by the NW PANI−PS mat does not seem to be the variable to most influence its electrical properties. Indeed, it is the standard electrode potential (SPE) of each metal that seems to a priori determine the final electrical properties of the NW PANI−PS mat. For instance, in the case of Cr(VI), which presents a high SPE value (1.33 V), a complete transformation of the ESS to its insulating state was observed. This can be explained in the following manner: in the initial stage of our procedure, the PANI chains are doped with Cl^- as the counterion, but, after contact with the chromium solution, the Cl^- ions are exchanged from the nitrogen of both quinoid and benzenoid groups by the $Cr_2O_7^{2-}$ anions,[59,60] forming redox pairs. Thus, the PANI chains are transformed to their pernigraniline form, and the Cr(VI) is reduced to Cr(III). On the other hand, the cations Cd(II), Pb(II), Cu(II), and Hg(II), which possess a relatively high SPE (−0.40, −0.13, 0.34, and 0.80 V, respectively), lead to a partial oxidation of ESS PANI. Those metals tend to form complexes with the nitrogen of the electron-rich benzenoid groups of the PANI. The above results are consistent with previous studies of the effects of doping PANI with transition metal salts.[55] These changes were correlated to both a decrease in the concentration of charge carriers along the PANI chains and a reduction in their mobility due to the pinning by the counterions.

4. CONCLUSIONS

A polymeric composite mat presenting a hierarchical structure has been successfully produced by the in situ chemical polymerization of aniline on electrospun PS fibers. We submitted the pristine PS mats to a plasma surface treatment to improve their wettability and change their mechanical properties so that a more complete deposition of the PANI on the PS fibers was achieved. In the resulting composite, the PANI chains are organized in rodlike nanostructures that offer an increased surface area for the interaction with heavy metal ions dispersed in an aqueous solution. Even though the experimental conditions adopted were not fully optimized, in our remediation experiments the adsorption capacities of the PANI−PS mats were very large, suggesting that these materials present competitive removal characteristics when compared to other heavy metals adsorbents discussed in the literature. Also, we have used UV−vis absorbance and electrical impedance spectroscopy to investigate the differences observed when different metal ions are incorporated into the NW PANI−PS mats.

In conclusion, on the basis of the collected experimental evidence, we suggest that NW PANI−PS mats are promising materials for use in removal and detection of heavy metals, as well in other species capable of forming complexes with the doped PANI chains, such as biomolecules[39] or organic dyes.[51]

■ ASSOCIATED CONTENT

Supporting Information

Image of the NW PANI−PS mats with and without plasma treatment, Bode plots of the real (Z') and imaginary (Z'') parts of the impedance as a function of frequency, and video showing the wetting properties of the NW PANI−PS mats as a function of the PANI doping state. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare the following competing financial interest(s): We have applied for a patent at the Brazilian Patent Office (INPI) for the material described in this work.

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