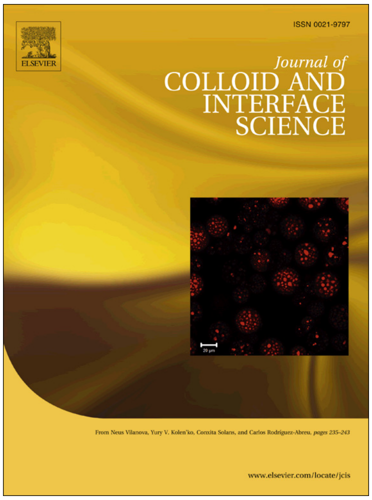

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PII: S0021-9797(17)30103-0
DOI: http://dx.doi.org/10.1016/j.jcis.2017.01.081
Reference: YJCIS 21987

To appear in: *Journal of Colloid and Interface Science*

Received Date: 7 November 2016
Revised Date: 22 December 2016
Accepted Date: 22 January 2017

Please cite this article as: M. Jesús García-Fernández, S. Sancho-Querol, M. Mercedes Pastor-Blas, A. Sepúlveda-Escribano, Surfactant-assisted synthesis of conducting polymers. Application to the removal of nitrates from water, *Journal of Colloid and Interface Science* (2017), doi: http://dx.doi.org/10.1016/j.jcis.2017.01.081

Surfactant-assisted synthesis of conducting polymers. Application to the removal of nitrates from water

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KEYWORDS: Polypyrrole; polyaniline; polytiophene, nitrate removal.

ABSTRACT: Three different conducting polymers, polythiophene (PT), polypirrol (PPY) and polyaniline (PANI) have been synthesized via oxidative chemical polymerization in aqueous media, in such a way that the synthesis protocol did not involve any toxic solvents. They have been tested in the abatement of nitrates from an aqueous solution without the need of any metal catalyst. The N-containing polymers (PANI and PPy) were able to remove nitrates to a level that accomplishes the European legislation requirements; however, the nature of each polymer greatly influenced the process mechanism. Whereas ion exchange between Cl^- and SO_4^{2-} counter-ions in the polymer and NO_3^- from water is the main responsible for the effective nitrate removal in PANI, as assessed by FTIR and XPS analyses, the nitrate removal mechanism on PPy is based in an electron transfer from the polymer to nitrate through N sites located in the pyrrolic ring. On the other hand, PT was not able to exchange nitrate unless it was synthesized with $FeCl_3$ as oxidant/dopant and an anionic surfactant (sodium dodecyl sulfate -SDS-) is used. In that case, the electrostatic attraction between sulfate (OSO_3^-) groups from the surfactant and Fe^{3+} ions from $FeCl_3$ produced the anchoring of Cl^- to the oxidized PT growing chain, this favoring ion exchange with nitrate in the aqueous solution, followed by a redox process.

1. Introduction

Conducting polymers as polypyrrole (PPy), polyaniline (PANI) and polytiophene (PT) have a heteroaromatic and extended π-conjugated backbone structure that provides them with chemical stability and electrical conductivity, respectively. However, the π-conjugated structure is not enough to produce appreciable conductivity by its own. A doping process, which produces a partial charge extraction from the polymer chain is mandatory.[1]

Conducting polymers are prepared by chemical or electrochemical oxidation of the corresponding monomers. As a result, they have positive charges along the polymeric backbone, which become charge carriers. Counter-anions called dopants are introduced during the synthesis of the conducting polymers to neutralize the positive charges of the backbones. The intrinsic conducting polymers in a doped or oxidized state become insulating when they are reduced. Upon reduction, the cationic charge carriers are lost and the small-sized dopant molecules are extracted from the polymer.[2] Schemes S1 and S2 show the reduced and oxidized forms of PT and PPy, respectively, where A^- is the counter-anion of the oxidized polymer backbone.

PANI can exist in a large number of interconvertible oxidation states (Scheme S3). Leucoemeraldine is the fully reduced one; it shows only benzenoid rings with amine (-NH-) links and it is white/clear or colorless; pernigraniline is the fully oxidized state with imine (=N-) links instead of amine links, and it is blue/violet in color. Emeraldine base, the half oxidized form, has half benzenoid half quinoid rings, with an equal amount of amine and imine sites. Imine sites are subjected to protonation to form bipolarons, *i.e.* dications (emeraldine salt form). PANI in the form of emeraldine base (blue) can be doped (protonated) to the conductive form of emeraldine salt (green). Emeraldine base is regarded as the most useful form of polyaniline due to its high stability at room temperature and the fact that, upon doping with an acid, the resulting emeraldine salt form of is highly electrical conducting. Leucoemeraldine and pernigraniline are poor conductors, even when doped with an acid. Thus, PANI is electrically conductive in its emeraldine oxidation state when doped with an acid that protonates the imine nitrogens on the polymer backbone. Dopants can be added in any desired quantity until all imine nitrogens (half of total nitrogens) are doped, simply by controlling the pH of the dopant acid solution. PANI's conductivity increases with doping from the un-doped insulated base form ($\sigma \leq 10^{-8}$ $S \cdot m^{-1}$) to the fully doped, conducting acid form ($\sigma \geq 10^{2}$ $S \cdot m^{-1}$). Doping and un-doping processes can be carried out electrochemically or chemically. The synthesis of PANI by chemical oxidative polymerization involves the aniline monomer, an acid and an oxidant (e.g. hydrogen peroxide, ferric chloride, ammonium or potassium peroxydisulfate). Different oxidants provide different dopants, which act as counter-ions which compensate the positively charged (semioxidized) polymer chain in the conductive form (emeraldine salt). Doping can be produced with common acids such as hydrochloric acid and de-doping with bases such as ammonium hydroxide. The doping process can drastically change the electronic, optical, magnetic and/or structural properties of the polymer and increases its conductivity significantly.[1]

These intrinsic conducting polymers have been used in a great variety of applications such as lightweight battery electrodes, electromagnetic shielding devices, anticorrosion coatings, electrochromic displays, chemical/gas sensors, photo-electrochemical cells, actuators and artificial muscles, etc. The combination of electrical conductivity and polymeric properties such as flexibility, low density and ease of structural modification make them very interesting for many processes. In this work, the use of PPy, PANI and PT in the removal of nitrate anions from water has been considered.

In previous studies, PPy and PANI have been used as supports of copper, palladium[3-5] or platinum[6-7] metal catalysts in the hydrogenation of nitrates. Nitrate is a common contaminant detected in surface water and underground aquifers which presents serious human health risks, as methemoglobinemia (blue bay syndrome) and cancer.[8] The catalytic reduction of nitrates with hydrogen using a supported metal produces nitrite (non-desired intermediate), and desired nitrogen and non-desired ammonium as the two main products.[9-10] The results of this work show that conducting polymers can be used for the abatement of nitrate from water without the need of a metal catalyst. The intrinsic conducting nature of these polymers, with switchable oxidation states, determines that the polymeric chain may act either as a source or a drain of electrons depending on the redox process in which it is involved. Therefore, it is expected that the polymeric chain takes part in the reduction of nitrate without the need of a metal catalyst.

2. Experimental

2.1. Materials preparation

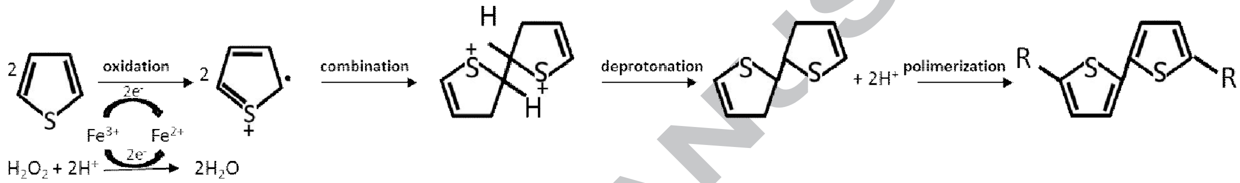
The synthesis conditions as pH, temperature and doping level affect the morphology and also the conducting properties of the polymer. Therefore, optimized polymerization procedures have been carried out in this work.

PPy and PANI were synthesized by chemical oxidative polymerization. $K_2S_2O_8$ was used in PANI synthesis due to the low aniline conversion with other oxidants (as for instance ferric chloride). For the sake of simplicity and comparison purposes, the same oxidant was used in polypyrrole synthesis.

For the synthesis of PANI, 14.8 g of $K_2S_2O_8$ were dissolved in 300 mL of HCl (0.2 M); 4 mL of aniline ($C_6H_5NH_2$, $M_m = 93.13$ g·mol^{-1}) were added drop wise, and the solution was stirred for 12 h at room temperature. As soon as the aniline mixed with the oxidant solution it turned to dark green color, characteristic of the emeraldine salt form of PANI. The precipitated PANI powder was filtered, washed with a solution of HCl (0.2 M) until yellowish washing waters turned uncolored, and then dried at 80 ºC for 12 h.

For the PPy synthesis, 36.0 g of oxidant ($K_2S_2O_8$) were dissolved in 1000 mL of ultrapure water. Then, 4 mL of pyrrole (C_4H_5N, $M_m = 67.09$ g·mol^{-1}) were added drop wise and the solution was stirred for 6 h at room temperature. As soon as the pyrrole mixed with the oxidant solution it turned to its characteristic black color, this indicating the formation of PPy. The precipitated PPy powder was filtered, washed with distilled water and dried at 50 ºC for 12 h.

The oxidative chemical polymerization of tiophene in aqueous media is complicated due to the poor solubility of PT in water, the low oxidizing activity of the catalysts and an extremely low conversion. In this work, a combination of anhydrous $FeCl_3$ as catalyst and H_2O_2 as oxidant was used to guarantee high conversion (ca. 99%) of thiophene monomers with only trace amounts of $FeCl_3$ ($FeCl_3/H_2O_2$ ratio was 0.00422). In this way, continuous regeneration of the Fe^{3+} catalyst through Fe^{2+} oxidation by H_2O_2 is assured[11] (Scheme 1). The experimental procedure was as follows: 1.9 mL of thiophene monomer (C_4H_4S, $M_m =$ 84.14 g·mol^{-1}) was dissolved in 60 mL of double distilled water and added to a three necked glass reactor fitted with a reflux condenser, a nitrogen gas inlet, an ingredient inlet and a mechanical stirrer. Hydrogen peroxide (7.5 mL, 50 % aq. solution) was added to the reactant mixture solution. $FeCl_3$ (16.0 mg) was dissolved in 5 mL of double deionized water and slowly added to the reactant mixture solution with a syringe. This mixture was then stirred at 300 rpm for 12 h at 50 ºC. The initial colorless solution turned to yellowish and finally brown, indicating the polymerization process. The dark brown PT precipitate was washed with double distilled water, filtered and dried at 50ºC for 24h.



Scheme 1. Polymerization of conducting PT with $FeCl_3/H_2O_2$**.**

PT was also synthesized using surfactants of different nature: sodium dodecyl sulfate (SDS) as anionic surfactant, cetyltrimethylammonium bromide (CTAB) as cationic surfactant and polyethylene glycol terc-octyphenil ether (Triton X) as non-ionic surfactant (Scheme S4). In these syntheses, the same experimental procedure was used but 0.1 g of surfactant were dissolved in 60 mL of deionized water and added to the glass reactor before the addition of the tiophene monomer.

2.2. Materials characterization

The electrical conductivity of the prepared materials was calculated from the resistance data. Electrical resistance of polymers was determined in a four-points probe home-made equipment which consisted in a cylindrical Teflon sample holder, connected to a 2000 Multimeter (Madrid, Spain) through copper electrodes.

The textural characterization of polymers was carried out by N_2 adsorption at -196 ºC with a Coulter Omnisorp 100CX equipment. Samples were previously outgassed at 150 ºC for 4 h.

ATR-IR spectra were recorded on a Tensor 27 spectrophotometer (Bruker optics, Billerica, MA USA) in the 600-4000 cm^{-1} range using a zinc selenide crystal. 200 scans and a resolution of 4 cm^{-1} were used.

X-ray photoelectron spectroscopy (XPS) analysis was used to obtain information on the chemical properties of the polymer surface. A K-Alpha spectrometer (Thermo-Scientific) spectrometer with an Al K_α achromatic X-ray source (1486.6 eV) operating at 50 keV pass energy and 300 W was used. The pressure inside the analysis chamber was held below $5\cdot10^{-9}$ mbar during the course of the analysis. The measurements were taken using a take-off angle of 45 º. Survey scans were taken in the range 0-1350 eV, and high resolution scans were obtained on all significant peaks in the survey spectra. The intensities were estimated by calculating the integral of each peak, after subtraction of the S-shaped background, and by fitting the experimental curve to a combination of Lorentzian (30%) and Gaussian (70%) lines. Binding energies (B.E.) were referenced to the C 1s photopeak position for C-C and C-H species at 284.6 eV, which provided binding energy values with an accuracy of ± 0.2 eV.

X-Ray diffraction (XRD) patterns of polymers were obtained with a D8-Advance (Bruker) X-ray diffractometer equipped with Göebel mirror and a Cu anode which provides K_α radiation (λ = 1.5406 Å). The samples were scanned from $2\theta = 6$ ° to 90 ° at the step scan mode (step size 1 °, step time 3 s).

Transmission electron microscopy (TEM) images were taken with a JEM-2010 (JEOL Ltd., Tokyo, Japan) equipment operating at 120 kV. Sample material was mounted on a holey carbon film supported on a Cu grid by drying a droplet of an aqueous suspension of ground sample on the grid. EDX coupled to the TEM microscope provided elemental analysis of the samples.

Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) analysis were carried out in a SDT 2960 system (*TA Instruments*, Delaware, NC USA). TGA allowed to determine the thermal stability of the polymers in air. A heating ramp of 10 ºC·min^{-1} air flow of 100 mL·min^{-1} were used. The weight of the samples was between 3-4 mg.

2.3. Nitrate removal

The nitrate removal ability of the three synthesized polymers was evaluated in an aqueous solution of sodium nitrate at room temperature. A semi-batch reactor equipped with a magnetic stirrer (700 rpm) was fed with 592.5 mL of deionized water and 300 mg of polymer. During the reaction tests CO_2 was passed for 15 min through the reactor with a flow rate of 75 mL·min^{-1} in order to buffer the solution to pH ≈ 5. Afterwards, 7.5 mL of a solution of $NaNO_3$ was added in such a way that the initial concentration of NO_3^- in the reactor was 100 mg·L^{-1}. Aliquots (1 mL) were withdrawn at different times from the reactor and immediately filtered for determination of nitrate, nitrite and ammonium concentrations by ion chromatography using in a Metrohm 850 ProfIC AnCat-MCS equipment. Nitrate and nitrite anions were determined in a Metrosep ASSUPP-7 column (250 mm x 4 mm) and ammonium cation was determined in a Metrosep C3 column (250 mm x 4 mm).

2. Results and Discussion

2.1. Characterization of conducting polymers

Synthesized polymers were characterized by FTIR. PPy (Figure S1a, Table S1) shows absorption bands at 1562, 1197 and 920 cm^{-1} which are characteristic of C=N-C moieties. Besides, the band at 1714 cm^{-1} (C=O stretching) is assigned to surface oxygenated groups created as a consequence of the reaction of the polymeric chain with water within the polymer network, as polypyrrole is hygroscopic. Spectrum of PANI (Figure S1b) shows typical bands of the polymeric chain[12-13] (Table S1). The absorption bands at 1580 and 1484 cm^{-1} correspond to the absorption of quinoid and benzenoid rings, respectively, characteristic of emeraldine (Scheme S3). The relative intensities of these bands provide an indication of the PANI oxidation states.[1,13] Spectrum of PT shows adsorbed water at 3073 cm^{-1}. The bands at 1668 and 1400 cm^{-1} correspond to the asymmetric and symmetric stretching vibration modes of the tiophene ring. The bands at 874 and 704 cm^{-1} are assigned to C-S bending.

Synthesized PPy, PANI and PT showed electrical conductivities of 2.5 x 10^{-1}, 4.78 and 2.71 x 10^{-4} S·cm^{-1}, respectively. The N_2 adsorption isotherms at -196 ºC were Type II in all cases, which are characteristic of non-porous solids. The BET surface areas obtained from the adsorption isotherms were 11 m^2·g^{-1} for PPy, 39 m^2·g^{-1} for PANI and 20 m^2·g^{-1} for PT.

The thermal stability of the polymers in air was assessed by TGA experiments (Figure S2). PANI and PPy showed a first weight loss (around 8-9 % of its initial mass) between 30 and 100 ºC, which corresponds to the loss of water trapped in the polymers and non-reacted monomers. PPy showed a second weight loss which can be assigned to the degradation of the polymer. In PANI, degradation proceeded in two steps; the first one, with a 10 % weight loss and centered at around 250 ºC, could be assigned to the thermal degradation of the cross linked chains; the second one, centered at 500 ºC, can be assigned to the decomposition of the lineal part of the chains. Total burning of the polymers was produced at 730 ºC for PPy and 630 ºC for PANI. In PT there was a first weight loss at around 100 ºC, that corresponds to the loss of water and non-reacted monomers. Then, degradation of PT occurred above 200 ºC.

XRD diffraction patterns of PPy, PANI and PT (Figure 1) are characteristic of amorphous polymers. The bands centered at $2\theta = 17\text{-}18$ º for PPy and $2\theta = 18\text{-}20$ º for PANI correspond to the periodicity along the polymeric chain. Another band centered at $2\theta = 25$ º for PPy and $2\theta = 27\text{-}28$ º for PANI corresponds to the periodicity perpendicular to the polymer chain.[12] The third band situated at $2\theta = 42$ º in both polymers is also typical of the polymer phase.[13] PT shows only a broad band around 23º due to its molecular π-π stacking structure.[14]

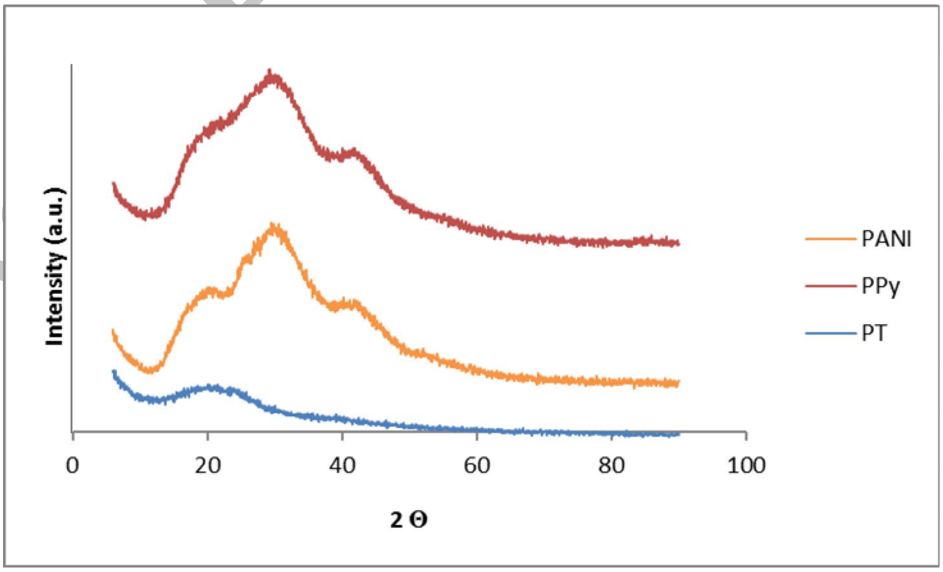


Figure 1. XRD patterns of synthesized polymers.

2.2. Nitrate removal by conducting polymers

The capability of PPy, PANI and PT conducting polymers of removing of nitrate from water was evaluated. The mechanism for nitrate removal may proceed by i) ion exchange between the counter-anion of the oxidized polymeric chain and nitrate, and/or ii) reduction of nitrate anchored to the polymeric chain by electrons donated by the conducting polymer.[7] The chemical nature of the conducting polymer plays a definitive role. Whereas electron transfer is produced through the nitrogen atom (located within the ring in PPy or outside the ring in PANI), PT possesses an S atom in its chemical structure within the tiophene ring. This seems to definitively affect the ability of the polymers to produce the abatement of nitrate.

Legislation establishes that the maximum permitted levels of nitrate, nitrite and ammonium in drinking water are 50, 0.5 and 0.5 $mg \cdot L^{-1}$ respectively).[15,16] Figure 2 shows that only PPy and PANI were able to produce a decrease of nitrate concentration below 50 $mg \cdot L^{-1}$. This decrease of nitrate concentration measured in the aqueous solution in contact with the polymers was produced within the first 5 minutes, and then it was maintained with time. Table 1 shows that a considerably high nitrate concentration is remaining in water after 300 min in the presence of PT.

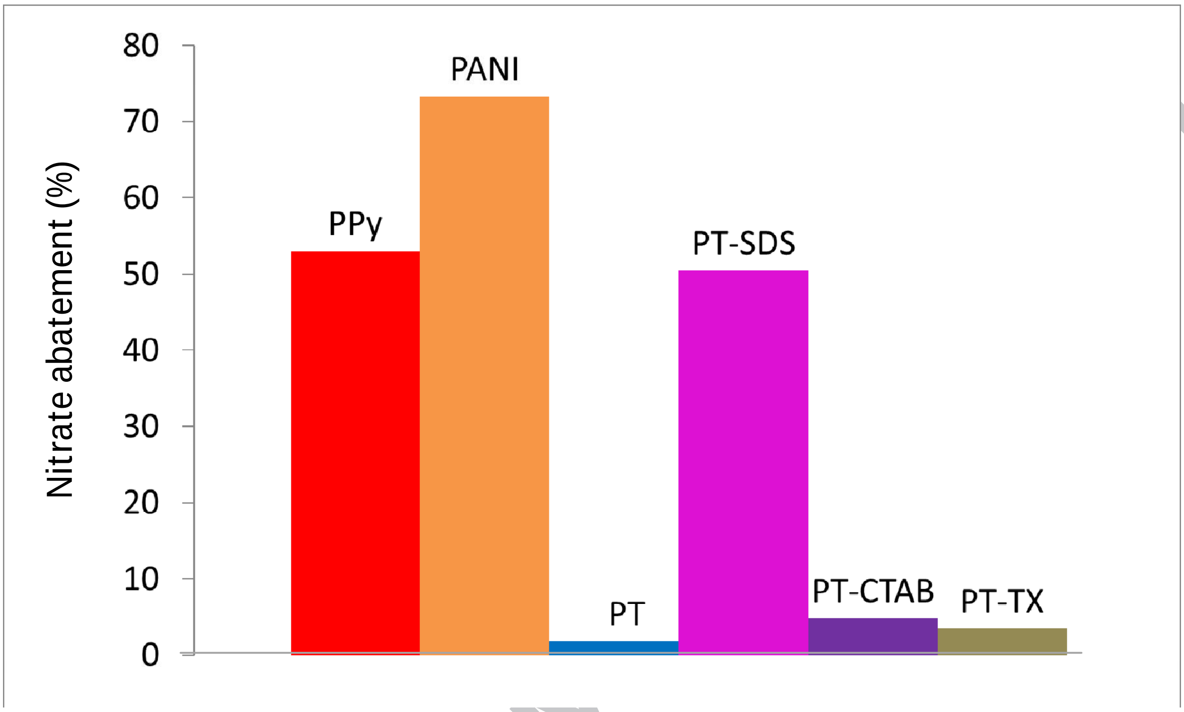


Figure 2. Nitrate abatement produced by the different synthesized conducting polymers.

Table 1. Nitrate, nitrite and ammonium concentrations (mg·L^{-1}) after 300 minutes in contact with the polymers.

(mg·L^{-1})	PPy	PANI	PT	PT-SDS	PT-CTAB	PT-TX
$[NO_3^-]$	47.00	26.70	98.22	49.54	95.23	96.57
$[NO_2^-]$	0.05	0.01	0.65	0.67	0.61	0.60
$[NH_4^+]$	4.09	0	1.39	6.06	2.28	1.75
$[Cl^-]$	1.66	12.41	1.43	12.41	5.48	1.59

When comparing the N-containing polymers, it could be observed that the decrease of nitrate concentration was much more important with PANI than with PPy. It was not possible to measure N_2 production; however, a considerable ammonium production was detected with PPy, which supports the idea of nitrate being reduced by electrons provided by the polymer. It must be taken into account that ion exchange between Cl^- and/or SO_4^{2-} present in these doped polymers and NO_3^- may be taking place. However, if nitrate would remain anchored to the polymeric chain as NO_3^- by a simple electrostatic interaction, with no further reduction process, it would be necessary to treat or to disposal the nitrate saturated polymers, which is also an environmental concern. In the case of PPy there was ammonium production; so at least some of the initially retained nitrate was suffering reduction by the electrons provided by the polymeric chain. However, neither nitrite nor ammonium was measured in the aqueous solution in contact with PANI, which may be due to nitrate being only exchanged by sulfate anions in PANI with no further redox process.

On the other hand, the S-containing PT was not effective in successfully removing nitrate from the solution, although the redox process was taking place to some extent as there was some nitrite and ammonium production (Table 1).

XPS was helpful to elucidate the mechanism of nitrate abatement produced by PPy and PANI. Surface composition from XPS analysis (Table S2) showed C from the polymeric chain and O from surface oxidation due to the contact of the polymers with the aqueous media during the polymerization reaction. Nitrogen was obviously detected in PPy and PANI and sulfur in PT.

Sulfur was also detected in N-containing polymers (PPy and PANI) but in a considerably lower amount compared to PT. This sulfur comes from the oxidant added in excess (potassium peroxydisulfate). K was not detected, but S 2p doublets at 168.6 (S 2p 3/2) and 169.9 eV (S 2p ½) in PPy, and at 168.3 (S 2p 3/2) and 169.6 eV (S 2p ½) in PANI can be assigned to sulfate (SO_4^{2-}) produced as a result of reduction of peroxydisulfate ($S_2O_8^{2-}$) when it is anchored to the polymeric chain of PPy and PANI as a counter-anion, during the course of the polymerization. This results in an oxidized polymeric chain with oxidized nitrogen groups ($-N^+-$) as assessed by the deconvolution of the N 1s level band (Figure 3, Table S3). However, the degree of oxidation was different in PPy and PANI. The polypyrrole chain showed a considerable higher percentage of oxidized nitrogen ($-N^+-$) compared to PANI, where mainly amine groups (-NH-) are present.

A noticeable percentage of chlorine as chloride anion (Cl 2p3/2 at 197.14 and Cl 2p1/2 198.64 eV) was detected in PANI, as polymerization was carried out in aqueous HCl medium. This chloride incorporates to the polymer as a counter-ion together with SO_4^{2-}. In PPy, some chlorine was also detected by XPS. As polymerization of polypyrrole was carried out in water and HCl was not added, the small amount of Cl^- detected has to come from water contamination.

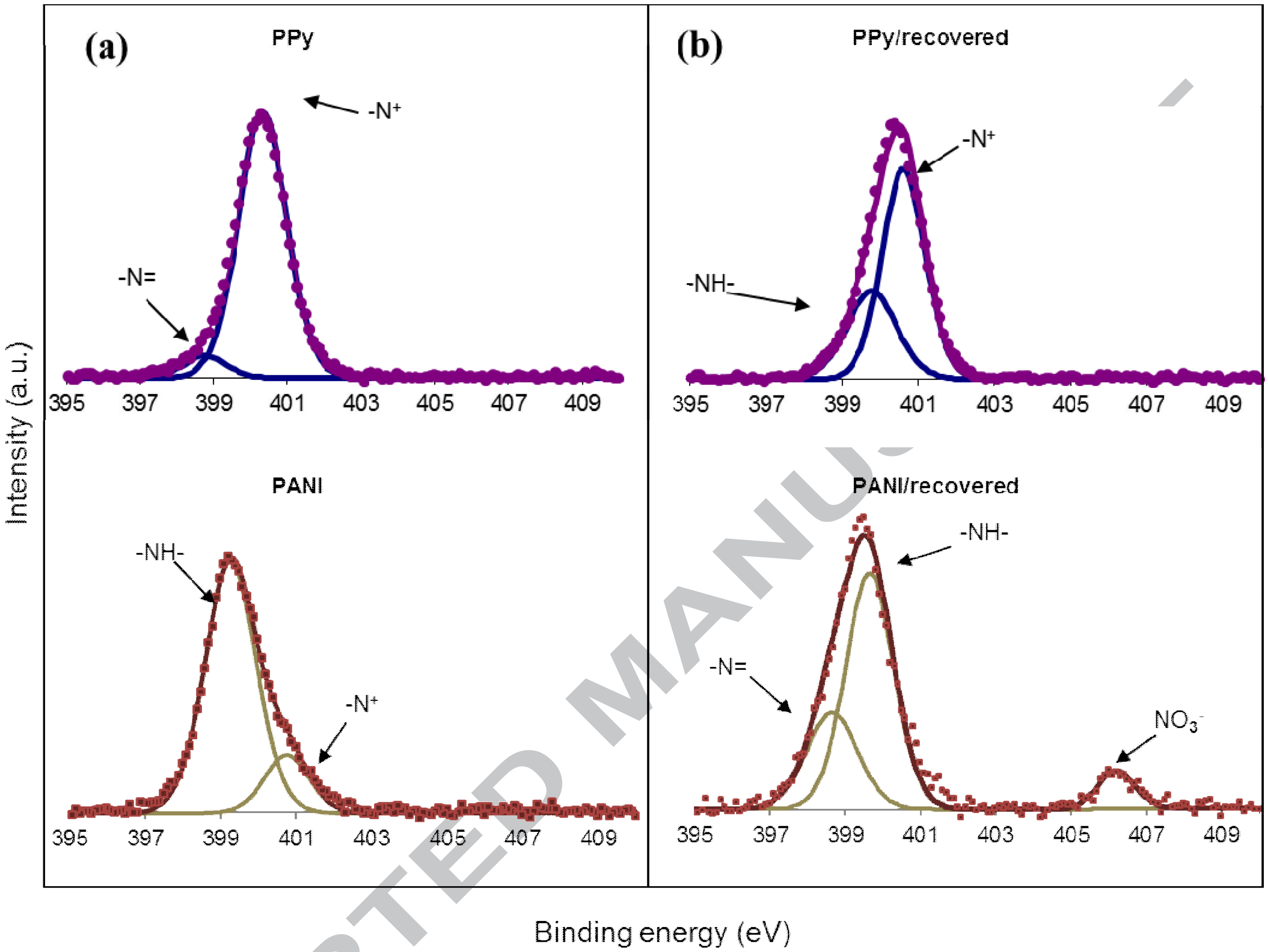


Figure 3. XPS N 1s curve fit of PPy and PANI: (a) pristine and (b) recovered after 300 min in contact with the aqueous nitrate solution.

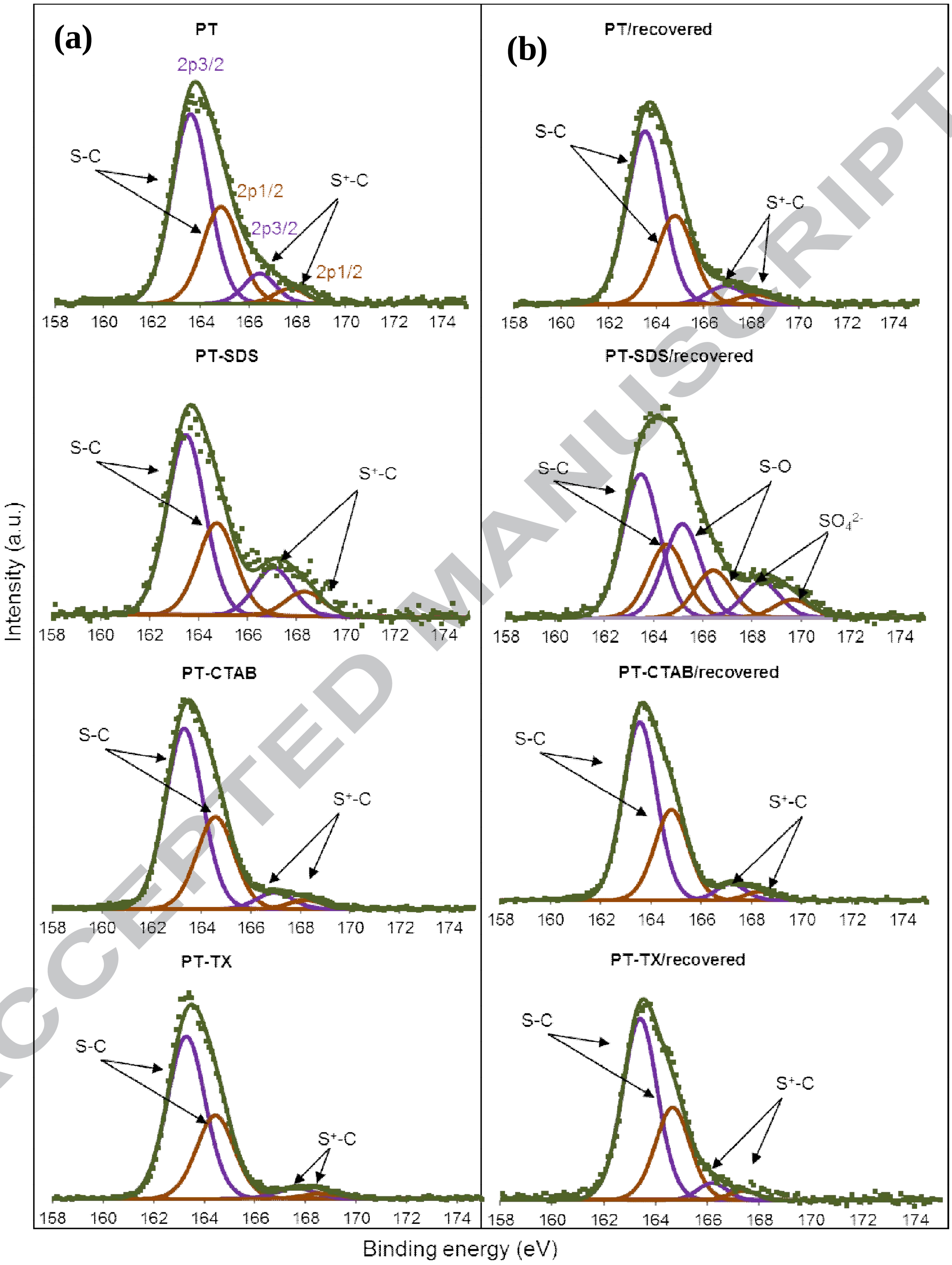


Figure 4. XPS S 2p curve fit of PT: (a) pristine and (b) recovered after 300 min in contact with the aqueous nitrate solution.

The oxidation degree of the pristine PT can be evaluated from the analysis of the XPS S 2p curve fit (Figure 4a), which shows the contribution of the reduced S-C moieties at 163.6 eV (S 2p3/2) and 164.8 eV (S 2p1/2). Only 12 % (Table S4), of the detected sulfur was oxidized as S^+-C, as shown by the presence of the doublet at 166.4 eV (S 2p3/2) and 167.7 eV (S 2p1/2). This positive oxidation state exists in water as hydrated cations, and then undergo reactions between the cations and water to neutralize their positive charges. PT synthesis in aqueous medium requires the use of a catalyst/oxidant combination to assure an appropriate yield. In this system, tiophene monomers are oxidized to cationic radicals, which react among them to produce PT. As only a trace of anhydrous $FeCl_3$ was used, neither Fe nor Cl is detected by XPS. Consequently, due to the low percentage of oxidized S^+-C moieties in PT (compared to the percentage of oxidized N^+ moieties in PPy and PANI, which are charge-compensated by Cl^- or SO_4^{2-} counter-ions), nitrate abatement from water is very poorly produced by PT. Nevertheless, the measured concentrations of nitrite and ammonium anions suggest that electron transfer from the PT chain to nitrate was indeed produced to some extent.

The capability of the conducting polymers of switching between different oxidation states imparts these polymers the capability of acting as a source or a drain of electrons, depending on the redox process in which they are involved. Therefore, it is possible that nitrate is reduced by these conducting polymers to nitrogen (desired) or ammonium (non desired), what is confirmed by the redox potentials of polymers and nitrogen-containing species involved in the nitrate reduction process: polypyrrole (PPy^+/PPy, E^o = +0.15 V); polyaniline (emeraldine/ leucoemeraldine, E^o = +0.342 V; pernigraniline/emeraldine, E^o = +0.942 V);[5] polytiophene (PT^+/PT, E^o = +0.7 V)[2] and nitrate (NO_3^-/N_2, E^o = +1.246 V; NO_3^-/NH_4^+, E^o = +0.875 V).

Upon reduction of nitrate, the polymeric chain is expected to become oxidized during the course of the reaction. In this way, PPy and PANI which were recovered after 300 min in contact with nitrate solution were analyzed by XPS.

Table S2 shows an important decrease of Cl and S contents and an increase of N content in recovered PANI. Whereas pristine PANI showed -NH- and $-N^+$ contributions of emeraldine salt, recovered PANI showed amine (–NH-) and imine (–N=) contributions of emeraldine base, as well as an important contribution at 406 eV of nitrate (NO_3^-) (Table S3, Figure 3). A considerable amount of chlorine (12.41 $mg{\cdot}L^1$) was detected by ion chromatography in the aliquots extracted from the aqueous nitrate solution in contact with PANI (Table 1). These findings evidence the occurrence of ion exchange between NO_3^- and counter-anions present in the doped PANI (Cl^- and SO_4^{2-}).

However, no nitrate contribution was observed in the N 1s spectra of PPy, and the oxidation of the polypyrrole chain in contact with the nitrate aqueous solution was evidenced. Imine contribution (=N-) at 398.8 eV in pristine PPy was not present in recovered PPy, as imine groups have been oxidized to -NH- amine groups (Figure 3).

Therefore, it can be concluded that removal of NO_3^- from water proceeds by ion exchange in a first step, which may be followed by a redox process. The ion exchange is predominant in PANI, but nitrate in completely reduced by PPy after been exchanged by sulfate anion. The different location of nitrogen outside the aromatic cycle in PANI and inside the cycle in PPy could have some influence in the extension of each mechanism, ion exchange and redox process. On the other hand, PT does not show any relevant change in the oxidation state of its polymeric chain, as it is evidenced by the contribution of reduced S-C and oxidized S^+-C moieties (Figure 4, Table S4). Consequently, no satisfactory nitrate removal is obtained with PT.

2.3. Use of surfactants in polytiophene synthesis.

The oxidative polymerization of tiophene in aqueous media is complicated due to poor water solubility of PT, the low oxidizing activity of the catalysts and an extremely low conversion.[17] A synthesis route which includes a $FeCl_3/H_2O_2$ catalyst/oxidant combination system has been used to assure a good yield.[11] However, this synthesized PT, which is mainly in a reduced state, did not provide good results in the abatement of nitrate from water.

The preparation of PT in colloidal form using surfactants is an attractive alternative to overcome its poor water solubility. The surfactant molecules form micelles in the reactant solution which affect the molecular and supramolecular structure of PT by altering the locus of polymerization.[14] In the presence of surfactants, the polymerization mechanism of tiophene with $H_2O_2/FeCl_3$ has been reported[11,18] to be determined by several steps: (i) s*tabilization step*: the formation of stable tiophene monomer swollen micelles; (ii) *diffusion step*: the metal cations (Fe^{3+}) diffuse from the aqueous phase into the micelles; (iii) *initiation step*: tiophene monomers are oxidized by the Fe^{3+} cations followed by the formation of cationic tiophene monomeric radicals; (iv) *propagation step*: tiophene cationic radicals are coupled to form dimers, the dimers are further oxidized to form cationic radicals and the coupling reaction continue to gradually form polymer chains and, (v) *regeneration step*: oxidation of Fe^{2+} by H_2O_2. The oxidant anions (Cl^-) may interfere with the diffusion process of the Fe^{3+} metal cations from aqueous phase to micelles by electrostatic attraction, or may interact with cationic radicals affecting their propagation reaction.

In this study, PT was also synthesized using surfactants of different nature: sodium dodecyl sulfate (SDS) as anionic surfactant, cetyltrimethylammonium bromide (CTAB) as cationic surfactant, and polyethylene glycol terc-octyphenil ether (Triton X) as non-ionic surfactant. The effect of the surfactants used in the synthesis on the capability of PT of removing nitrate from water was evaluated.

Synthesized polytiophenes were analyzed by ATR-IR. Figure 5 shows bands at 2925 and 2854 cm^{-1} due to C-H stretching from the surfactants, which are more important in PT-SDS. This reveals that a certain amount of the surfactants is retained by PT after washing.

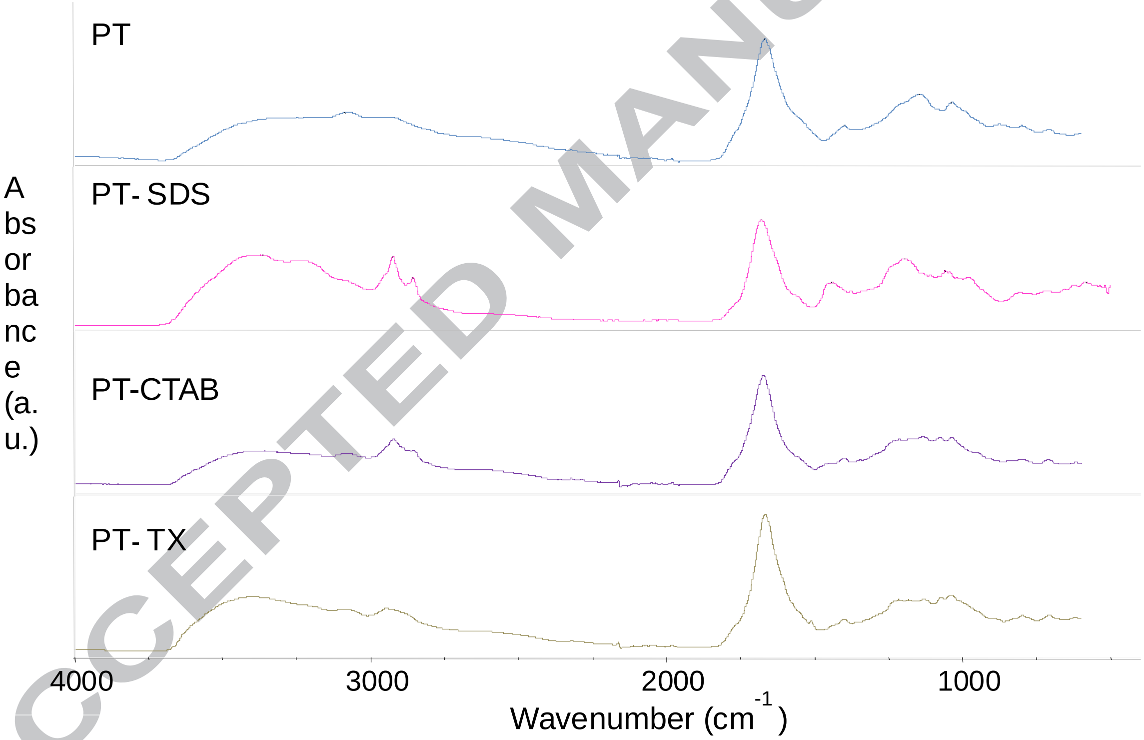
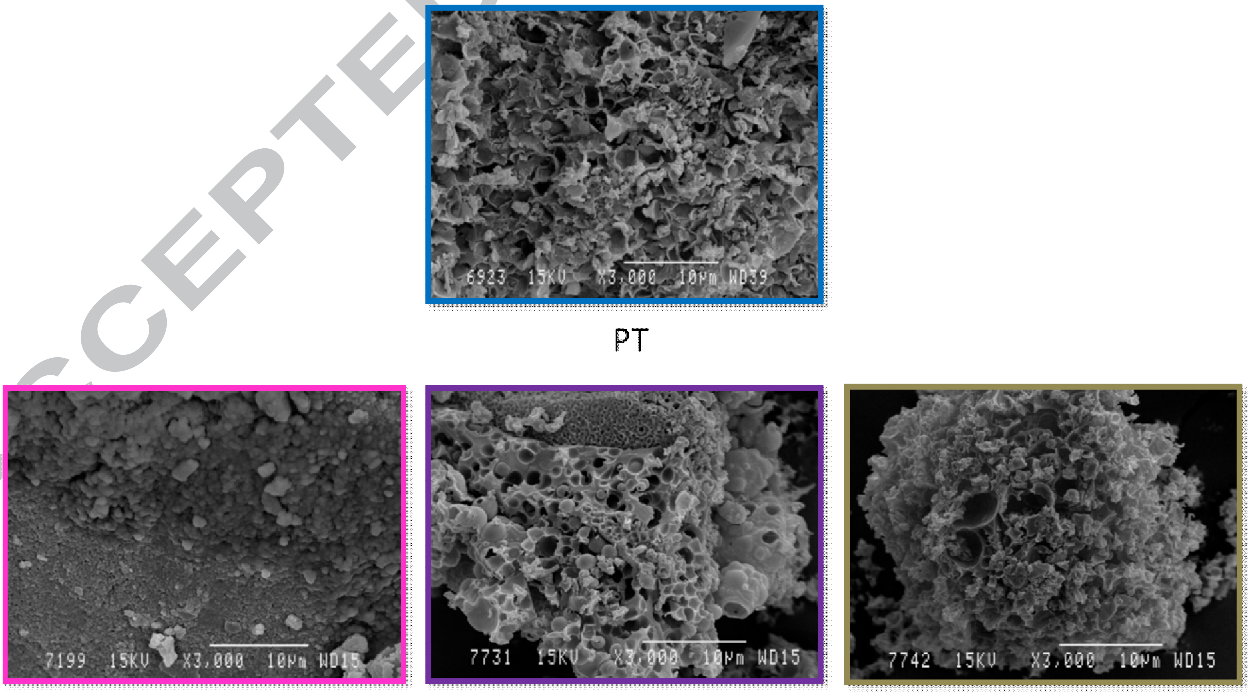


Figure 5. ATR-IR spectra of — PT ; PT synthesized with: — SDS; — CTAB and — TX.

SEM micrographs (Figure 6) also show a change in the morphology of PT by the presence of the anionic SDS surfactant. PT-SDS shows a spherical morphology instead of the colliflower-like structure exhibited by its counterparts. In aqueous medium, the molecules of surfactant form micelles spontaneously due to its amphiphilic nature, with the hydrophilic parts extending and the hydrophobic segments aggregating inside. These micelles become loci of polymerization of tiophene monomers, usually accommodated inside. As the polymerization proceeds, the hydrophobic segments of surfactants adsorb onto the PT chains to form colloid particles which stabilize themselves through electrostatic repulsion (ionic surfactants) or steric repulsion between the adsorbed layers of the non-ionic surfactant. When a critical polymeric chain length is achieved, precipitation of the polymer is produced.[18]



PT

PT-SDS

PT-CTAB

PT-TX

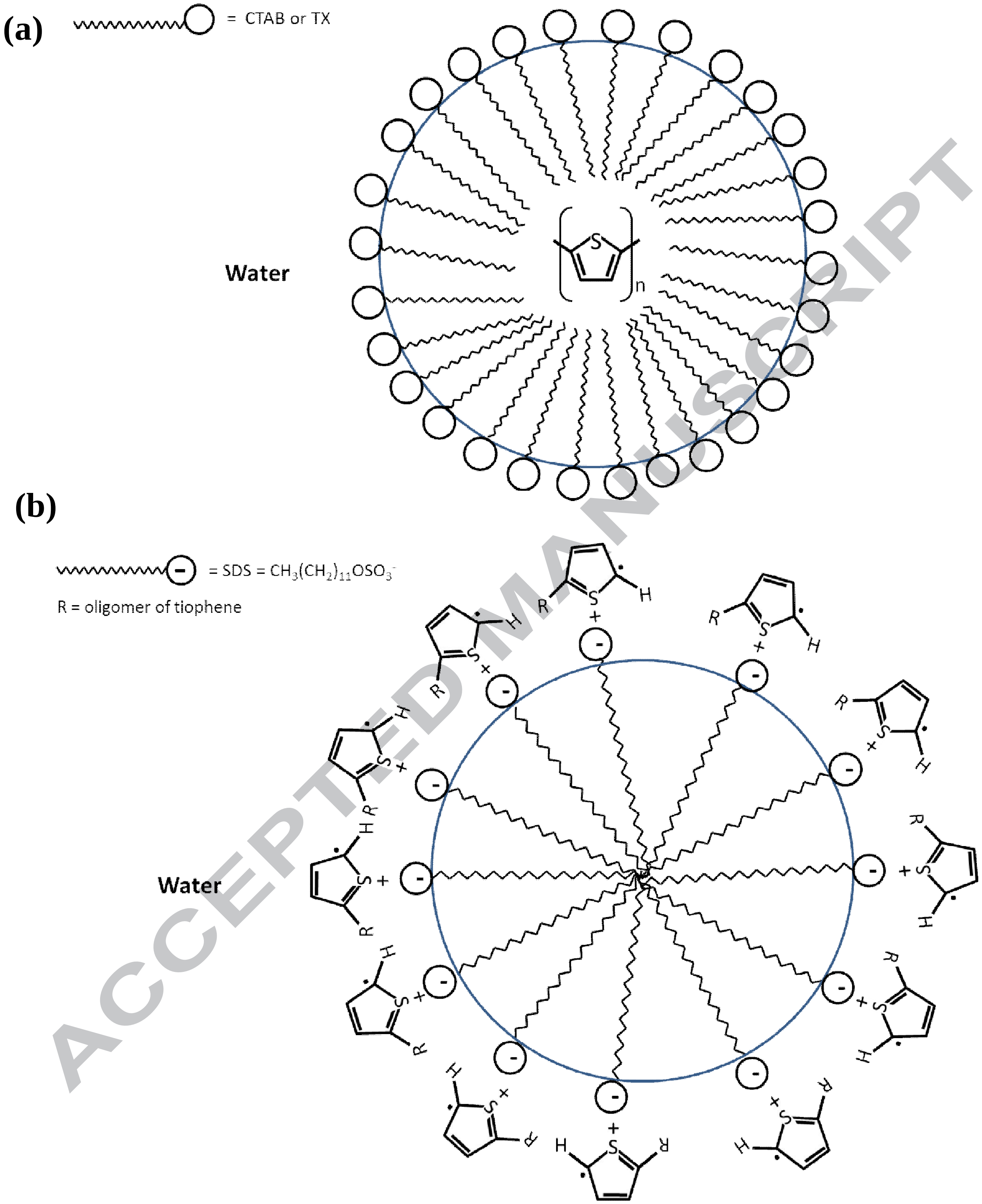
Figure 6. SEM micrographs of ▬ PT and PT synthesized with ▬ SDS; ▬ CTAB; ▬ TX.

Lee et al.[11] established that the mechanism of micelle formation depends on the nature of the surfactant. Thus, when tiophene polymerization with $FeCl_3/H_2O_2$ (Scheme 1), is carried out in the presence of a cationic surfactant (CTAB), an electrostatic repulsion between the $(CH_3)_3N^+$ groups of the CTAB surfactant and Fe^{3+} cations is produced. Thus, Fe^{3+} ions are drawn into the micelle where they catalyze the polymerization of tiophene (Scheme 2a) which had previously diffused into the inner part of the micelle due to hydrophobic-hydrophobic interactions.

In the case of the non-ionic surfactant (TX), polymerization of tiophene also proceeds inside the micelle (Scheme 2a), as Fe^{3+} ions can be attracted to the lone pair electrons of oxygen atoms present in the polyethylene glycol chain of the non-ionic TX surfactant and be drawn into the micelle to get into contact with the tiophene monomer.[19] Thus, with both CTAB and TX surfactants, Fe^{3+} ions dissolved in the aqueous medium are drawn into the droplet, where they catalyze oxidative polymerization of tiophene.

However, in the case of the anionic surfactant SDS, electrostatic interactions between the OSO_3^- groups from the surfactant and the Fe^{3+} cations are produced. In this case, polymerization of tiophene (Scheme 1) would proceed preferentially at the surface of the micelle [11, 20] (Scheme 2b). In this case, OSO_3^- groups from SDS and Cl^- from $FeCl_3$ may also act as dopants of polytiophene. Consequently, both SDS and $FeCl_3$ should be detected on polytiophene synthesized with SDS (PT-SDS).

Actually, TEM micrographs (Figure S3) show black spots of $FeCl_3$ only when tiophene was polymerized in the presence of SDS. Fe^{3+} ions dissolved in the aqueous medium are drawn into the micelle to come into contact with the swollen tiophene monomers and there, Fe^{3+} ions catalyze tiophene polymerization. In these cases, the micelle acts as a microreactor and the polymerization reaction is produced within the micelle.



Scheme 2. Scheme showing polymerization of tiophene in the presence of (a) CTAB or TX; (b) sodium dodecyl sulfate (SDS).

The incorporation of SDS surfactant into the conducting polymer affects its thermal stability and conductivity. Thus, TGA analysis (Figure S4) shows that there is an increase of thermal stability of PT in PT-SDS. With the addition of CTAB and TX there is a slight decrease of thermal stability probably due to the lower molecular weight of the PT synthesized inside the micelles.

The electrical conductivity of polytiophene was not affected by the introduction of the anionic surfactant ($3.46 \cdot 10^{-4}$ $S \cdot cm^{-1}$ in PT-SDS vs. $2.71 \cdot 10^{-4}$ $S \cdot cm^{-1}$ in PT) but it was significantly decreased with the cationic ($1.0 \cdot 10^{-6}$ $S \cdot cm^{-1}$ in PT-CTAB) and the non-ionic surfactants ($7.7 \cdot 10^{-5}$ $S \cdot cm^{-1}$ in PT-TX). This may be due to the different mechanism of micelle formations. When polymerization of tiophene takes place at the surface of SDS conductivity is not affected, but when polymerization proceeds at the core of the microreactor there is no space enough for the chains of polytiophene (PT-CTAB and PT-TX) to expand, so there will be in a shorter conjugation length which results in a decrease of conductivity.[20,21]

The presence of $FeCl_3$ on PT-SDS particles, which was detected by TEM, was also confirmed by XRD. The diffraction pattern of PT-SDS shows several peaks (Figure 7). The peak at $2\theta = 41$ ° corresponds to the SDS surfactant, and the rest of them correspond to $FeCl_{3.}$[22]

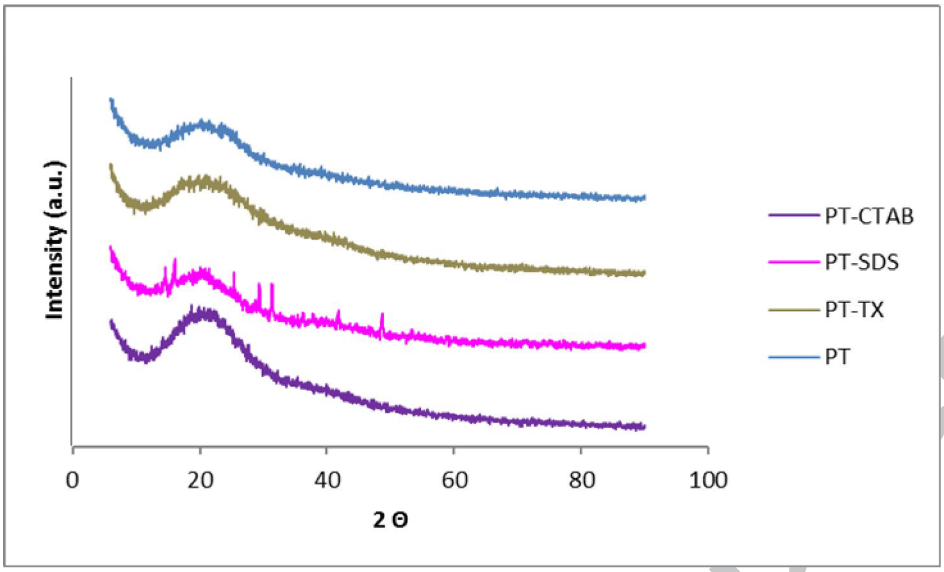


Figure 7. XRD patterns of ▬ politiophene and polytiophene synthesized with ▬ SDS; ▬ CTAB; ▬ Triton-X.

The chlorine anion from the oxidant ($FeCl_3$) was also detected by XPS (Table S2). Chlorine, as Cl^-, was identified by the Cl 2p doublet at 199.1 eV (Cl 2p3/2) and 200.7 eV (Cl 2p1/2). This chloride anion may also act as a dopant in the final synthesized polytiophene. Thus, as in PT-SDS $FeCl_3$ is located at the surface of polytiophene particles, Cl^- anion is more accessible and easily exchanged by the nitrate anion (NO_3^-) from water. In a second step, reduction of nitrate by electrons coming from conducting polytiophene might take place. Table 1 shows a considerably high concentration of Cl^- anion in the solution at the reactor, similar to that of PANI, when aqueous solution was in contact with PT-SDS. This confirms exchange between nitrates and chlorides. As a result, PT-SDS greatly increases its effectivity in removing nitrate from water (Figure 2). Nitrate concentration falls down the maximum required levels (50 mg $\cdot L^{-1}$). However, there is a production of nitrite and ammonium, which are determined by ion chromatography, in concentrations above the maximum permitted levels established by European legislation (0.5 mg$\cdot L^{-1}$, Table 1). Analysis of the S2p XPS level (Figure 3) shows the presence of S-O and SO_4^{2-} moieties from the surfactant. No nitrogen was detected by XPS (Table S2), which indicates that nitrate is not being retained by PT. However, reduction of nitrate is in fact being produced (nitrite and ammonium are detected) by electrons coming from PT.

4. Conclusions

Redox and ion exchange properties of PPy and PANI doped with $K_2S_2O_8$ have a determinant role in the removal of nitrates from water. However, the nature of each polymer greatly influences the reaction mechanism. Whereas ion exchange between Cl^- and SO_4^{2-} counter-ions and NO_3^- from water is the main responsible for the effective nitrate removal in PANI, as assessed by FTIR and XPS, the mechanism for nitrate removal is based in an electron transfer from PPy to nitrate through N located in the pyrrolic ring.

On the other hand, PT is not able to exchange nitrate unless it is synthesized using an anionic surfactant (sodium dodecyl sulfate, SDS). In this case, the electrostatic attraction between ($-OSO_3^-$) groups from the SDS surfactant and Fe^{3+} ions from $FeCl_3$ results in the doping of the oxidized PT growing chain with chloride and sulfate anions. As a result, ion exchange between counter-anions and nitrate is enhanced, and ulterior reduction of nitrate by electrons of tiophene is produced.

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Notes

The authors declare no competing financial interest

ACKNOWLEDGEMENT

Financial support from Generalitat Valenciana, Spain (PROMETEOII/2014/004) is gratefully acknowledged.

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GRAPHICAL ABSTRACT