



Metal-free abatement of nitrate contaminant from water using a conducting polymer

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ABSTRACT

A mechanism for the reduction of aqueous nitrate with metal-free polypyrrole (PPy) is proposed. The activity and selectivity of the polymer has been compared to those of metal catalysts supported on polypyrrole, activated carbon or titania (TiO₂). The role of formic acid (FA) and hydrogen (H₂) as reductants, and carbon dioxide (CO₂) as buffer of the aqueous nitrate solution is discussed and compared to the performance of PPy by itself. The ion-exchange and the redox properties of PPy are strongly affected by the oxidation state of the nitrogen moieties in the polymeric chain. This is determined by the oxidant/dopant used in the polymer synthesis (FeCl₃ or K₂S₂O₈). The degree of oxidation of PPy can also be modified by a plasma treatment of the polymer, which determines the ability of PPy to carry out the reduction of nitrate by the electrons provided by the polymeric chain and also affects the selectivity of the nitrate reduction.

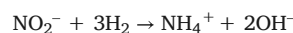
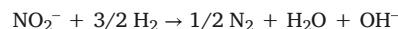
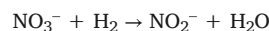
1. Introduction

Nitrates are part of the nitrogen cycle; however, the human activity unbalances the ecosystem. The increasing use of ammonia-based fertilizers results in the contamination of ground waters and aquifers [1,2]. Eutrophication, that is, the algae bloom resulting from the increased phytoplankton produced by the excess of nitrogenated nutrients in water, blocks sun light. Besides, when algae die, there is an increased oxygen consumption that results lethal for fishes. Nitrate can be reduced to nitrite in the gastrointestinal track [3], but nitrites are also added as preservatives to meat products, mainly charcutery [4]. The combination of nitrites with amines and amides results in nitrosamide and nitrosamine compounds which are potential carcinogens. Nitrite is also responsible for the oxidation of Fe²⁺ in hemoglobin to Fe³⁺, producing methemoglobin, which has an increased affinity for oxygen in blood. As a result, oxygen, which is reversibly bonded to hemoglobin, is not released to tissues when bonded to methemoglobin. This causes cyanosis, the typical blue color of infants which suffer from methemoglobinemia (known as “blue baby syndrome”) produced by their intoxication with water contaminated with nitrate and nitrite [1,5].

Physico-chemical methods as reverse osmosis and electrodialysis have a limited solution to the problem as they transfer nitrate from raw water to another phase which would also require further treatment (for instance a brine) or disposal [6,7]. Although biological denitrification transforms nitrate into molecular nitrogen, it is a slow and low efficient process which turns out in another source of contamination of water with bacteria. Otherwise, catalytic reduction of nitrate into nitrogen is a green alternative for the abatement of nitrate from water [8], which is usually carried out with molecular hydrogen [9].

Some investigations [10–13] stand for the necessary use of a bimetallic system to reduce nitrates, which is usually composed of a precious metal (Pt or Pd) and a promoter (Cu, Ni, Fe, Sn, In, Ag, etc.). The mechanism for nitrate hydrogenation with bimetallic catalysts was at first proposed by Tacke and Vorlop [14] and it is still generally accepted. The proposed mechanism includes a stepwise process which involves adsorption of nitrate on a bimetallic site, reduction to nitrite through a direct redox mechanism, desorption into the aqueous phase and re-adsorption to a monometallic site (with noble metal only) where nitrites are reduced to the end products [15]. Otherwise, the successful use of monometallic catalysts (usually Pd or Pt, but also Au and Ag) when partially reducible supports are used, has also been reported [16,17]. In this case, the initial step is believed to be catalyzed by sites on the support.

One of the main advantages of catalytic reduction is the absence of solid or liquid residues. However, it is also necessary to make sure that harmful intermediates or byproducts are avoided [18]. Catalytic reduction of nitrate with dihydrogen produces nitrite, which is further reduced to nitrogen or to ammonium:



The efficiency of some studied catalysts is not satisfactory as concentrations surpassing the maximum permitted level established by legislation of toxic nitrite or ammonium by-products instead of the desired nitrogen are obtained [19]. The European legislation [20] has established a maximum permitted level of nitrate, nitrite and ammonium

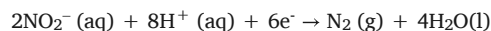
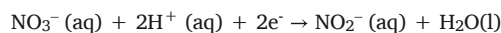
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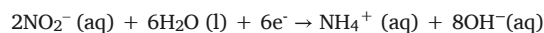
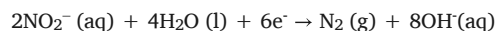
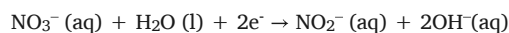
in water of 50, 0.5 and 0.5 mg·L⁻¹, respectively; US legislation is similar [21].

The selectivity of the reaction is strongly dependent of the pH of the medium [22–23]. The reactions implied in the reduction of nitrate in acid and alkaline media are described below:

In acid media:



In basic media:

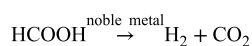


In basic media, the formation of hydroxide ions produces an undesired pH increase, which may reach unacceptable values for drinking water (c.a. 10–11). Besides, a basic pH decreases activity and selectivity towards nitrogen and increases selectivity towards ammonium [24,25]. This can be overcome by adding HCl [26] or buffering the solution with a CO₂ flow [27] at a pH value which is compatible with drinking water quality (carbonic acid/bicarbonate buffer pK_{a1} = 6.35).

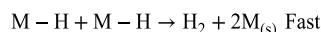
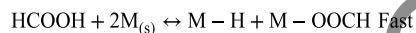
The main drawbacks concerning the use of hydrogen as reductant are its potential danger of explosion and its limited solubility in water ($SH_2^{15^\circ C} = 0.84 \text{ mM}$ at $p_{H_2} = 100\text{kPa}$), which may be insufficient for the treatment of ground waters and waste effluents from industry. Besides, introducing gaseous hydrogen in a controlled dose in contaminated aquifers is not an easy task [18].

The aim of this research work is to determine the ability of a conducting polymer, polypyrrole (PPy), for removing nitrates in water by adsorption/reduction mechanisms without the need of a metal catalyst and producing molecular nitrogen as the only product. Several reductants for aqueous nitrate will be considered as an alternative to dihydrogen. Furthermore, the reductant activity of pristine and plasma treated PPy will be investigated.

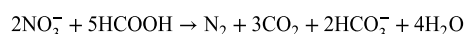
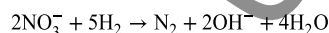
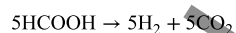
Formic acid is a precursor of H₂ and CO₂. It has been widely held [26] that formic acid decomposition requires a noble metal catalyst, such as Pt or Pd:



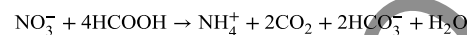
This is actually a three-step reaction, which requires two adjacent sites for a dissociative adsorption [28]:



As formic acid is highly soluble in water, it can be introduced into aqueous solutions in high doses. Furthermore it is benign and no explosive especially when dissolved in water, so it is an interesting alternative to gaseous reactants (H₂ and CO₂) [29]. Therefore, the generated H₂ would serve as reductant and CO₂ would neutralize hydroxide ion produced during nitrate reduction [30]:



Formic acid is interesting not only for the fact of being a precursor of H₂ and CO₂; it is also highly interesting due its acid and reductant character [31,32]. Its pK_a (HCCOH/COO⁻) = 3.74, provides an initial pH in a range of 3–4, instead of the pH of 10–11 obtained when molecular hydrogen is used as reductant in the reaction of reduction of aqueous nitrate. This would help to increase selectivity towards gaseous nitrogen instead of ammonium [33]:



Besides, formic acid redox potential $E^0 (\text{CO}_2)/(\text{HCOOH}) = -0.199 \text{ V/ERH}$ allows to use it as reductant by itself:



Therefore formic acid might not only act as precursor of H₂ which could act as reductant, but it can actually be the actual reductant of nitrate and nitrite in the water. Besides, formic acid might also affect the redox state of a partially reducible catalyst support, as it is the case of a conducting polymer such as polypyrrole (PPy), which is used in this work.

PPy is cheap, easy to prepare, and has a very good environmental stability. It is a conjugated polymer that has switchable oxidation states. Its synthesis can be carried out by electro-polymerization on a conductive substrate (electrode) through the application of an external potential, or by chemical polymerization in solution with the use of a chemical oxidant. The polymerization reaction of pyrrole is shown in Fig. S.1. In a first step, a neutral pyrrole monomer (Fig. S.1a) oxidizes and yields a cation radical (Fig. S.1b), which can recombine to form a bipyrrrole (dication) (Fig. S.1c). Then, the bipyrrrole suffers deprotonation producing a neutral molecule (Fig. S.1d) which undergoes further oxidation (Fig. S.1e), recombination and deprotonation steps until neutral polypyrrole (Fig. S.1f) is obtained as the final product [34,35]. Chemical polymerization is carried out with relatively strong chemical oxidants, such as iron (III) chloride and potassium peroxydisulfate, which are able to oxidize the pyrrole monomer. The oxidant also provides a counter-ion (the dopant), which is the oxidant's anion or its reduced product [36,37]. Chemical polymerization occurs in the bulk of the solution, and the resulting polypyrrole precipitates as an insoluble solid.

It has been determined [38] that there is one anion for every 3–4 pyrrole units, depending on the type and charge of the anion that is incorporated to provide electroneutrality. This represents a level of oxidation of 0.25–0.33 per pyrrole unit. As a result of the simultaneous oxidation and polymerization of the pyrrole monomer, a delocalized positive charge on the π -electron system is produced.

It has been previously reported [39] that polypyrrole can actively participate in redox processes thanks to its conducting properties. Nevertheless, the π -conjugated structure of polypyrrole is not sufficient to produce appreciable conductivity on its own; a doping process is necessary, which produces a partial charge extraction from the polymer chain. PPy chain is simultaneously doped during polymerization. Counter-ions in the reaction medium incorporate into the growing PPy chains to maintain the electrical neutrality of the polymer system (Fig. S.2) [40]. Neutral PPy behaves as a wide band gap semiconductor. During the oxidative polymerization of pyrrole, upon extraction of a negative charge from a neutral segment of a PPy chain, a positive charge is produced. The resulting unpaired spin is referred to as polaron. As a result, new intermediate states are introduced within the band gap. As oxidation continues further, another electron has to be removed from a PPy chain, that already contains a polaron, resulting in the formation of a bipolaron, which is energetically preferred. As the degree of oxidation increases, the bipolaronic energy state overlaps, resulting in the formation of narrow intermediate band structures. Formation of polarons and bipolarons as charge carriers are responsible for the increase of electrical conductivity of PPy [34–36].

It has been observed that when the intrinsic conducting polymers as PPy are put into contact with a gas or a liquid, there is an electron transfer from or towards the analyte [41]. For instance, when PPy is exposed to gases that can accept electrons such as NO₂ or I₂, electrons from the aromatic rings of PPy are removed. In this case, the doping level of this p-type conducting polymer as well as its conductivity are increased. On the contrary, when an electron donor gas as ammonia is in contact with PPy, the polymer conductivity drastically diminishes. The redox and ion-exchange properties of PPy make it suitable for its application in the removal of toxic nitrate contaminants from water, which is the main goal of this work.

2. Experimental

Although polymerization of pyrrole can be carried out chemically or electrochemically, the chemical oxidative polymerization provides a greater yield, which is interesting for industrial applications.

Pyrrole (C₄H₅N) was polymerized using either ferric chloride (FeCl₃·6H₂O) or potassium peroxydisulfate (K₂S₂O₈) as oxidants. Thus, chloride or persulfate/sulfate from the oxidants are incorporated during polymerization to the polypyrrole (PPy) and can be potentially exchanged by anions in the aqueous reaction media, such as toxic nitrate in contaminated water. This ion exchange hardly alters the polymer structure or morphology, but can alter the polymer doping level [35].

This oxidative chemical polymerization was carried out using an oxidant/pyrrole molar ratio of 2.31. The experimental procedure consisted in the drop wise addition of 1 mL of pyrrole (i.e. 0.0144 mol) to a solution of 9 g of oxidant (i.e. 0.033 mol) in 200 mL of ultrapure water. The stirring was maintained for 6 h at room temperature. The formed PPy, which exhibited its characteristic black color, was separated from the solution by filtration, then washed with deionized water and dried for 12 h at 80 °C.

In some cases, PPy was impregnated with an aqueous solution of hexachloroplatinic acid (H₂PtCl₆·6H₂O, M_m = 517.912 g·mol⁻¹ Alfa-Aesar). The target platinum loading was 2 wt%. The resulting suspension (25 mL solution·g_{Polymer}⁻¹) was maintained under stirring at room temperature for 12 h. Afterwards, the solvent was removed in a rotary evaporator (Fig. S.3b), and the platinum-impregnated PPy was dried in an oven (80 °C, 12 h). In order to produce metal platinum nanoparticles dispersed on PPy, a reductive treatment with Ar plasma was carried out (Fig. S.3c). The energetic electrons present in the plasma act as reducing agents of the platinum ions anchored to the impregnated PPy. This cold plasma radio frequency (RF) treatment (13.56 MHz) is a green and low-temperature alternative to the widely used treatment with H₂ at high temperature, which is not suitable in this case because of the limited thermal stability of PPy. The samples were repeatedly treated in a Tucano plasma system (Gambetti Kenologia, Italy) in batches of 5 min for a total of 180 min, at 200 W using an Ar flow (0.5 mbar). A manual mixing of the samples between treatments was performed for the sake of a homogeneous treatment. The temperature of the plasma treated samples remained always below 50 °C (measured using a non-contact infrared thermometer PCE Instruments, model PCE-888).

For comparison purposes, platinum nanoparticles supported on titania and activated carbon were also synthesized. Degussa P25 (80% anatase, 20% rutile) [42] with a BET surface area of 53 m²·g⁻¹, and particle size of about 100 nm, was used as the TiO₂ support. This was first calcined in air at 500 °C for 5 h and then impregnated with an aqueous solution of H₂PtCl₆·H₂O (Alfa Aesar), with the appropriate concentration to achieve a Pt content of 2 wt%. The slurry was stirred for 12 h, and the excess of solvent was removed by heating at 90 °C under vacuum in a rotary evaporator. Finally, the catalysts were dried at 110 °C for 24 h.

Activated carbon (AC) Nuchar RGC 30, from Mead-Westvaco Corp., with a BET surface area of 1535 m²·g⁻¹ and a particle size between

0.1 and 0.3 mm, was used as support. The monometallic Pt/AC catalyst was prepared by incipient wetness impregnation with an aqueous solution of H₂PtCl₆·6H₂O (Alfa Aesar). The bimetallic Pt-Sn/AC catalysts were prepared by incipient wetness co-impregnation with aqueous solutions of H₂PtCl₆·6H₂O (Alfa Aesar) and SnCl₂·2H₂O (Sigma Aldrich). The prepared catalysts were dried at room temperature for 12 h and finally dried at 120 °C overnight. A series of catalysts was prepared with a nominal Pt content of 2 wt% and a Pt:Sn atomic ratio of 1:1 and 1:5.

The electrical conductivity of the prepared materials was determined by measuring their electrical resistance using a cylindrical Teflon sample holder and a four-points probe connected to a multimeter.

N₂ adsorption (Coulter Omnisorp 100CX equipment) at -196 °C of the outgassed samples (150 °C, 4 h) was useful to determine textural properties of the prepared materials. Experimental conditions were: Nitrogen pressure: 15 Torr; equilibrium time: 120 s; heating rate: 5 °C·min⁻¹.

X-ray photoelectron spectroscopy (XPS) analyses were carried out in a K-Alpha spectrometer (Thermo-Scientific) in order to study the oxidation state of platinum loaded to the PPy support and the chemical state of nitrogen in PPy. An Al K_α achromatic X-ray source (1486.6 eV) was used and the experimental conditions were: 50 keV pass energy, 300 W and a take-off angle of 45°. The pressure inside the analysis chamber remained always below 5·10⁻⁹ mbar. The binding energies (B.E.) were calibrated with respect to the C 1 s peak (284.6 eV) of C-C and C-H, with an accuracy of ± 0.2 eV. Lorentzian (30%) and Gaussian (70%) combination was used to estimate the intensities of the peaks in the spectra.

Transmission electron microscopy (TEM) (JEM-2010, JEOL Ltd., Tokyo, Japan) was carried out at 120 kV. The experimental sample preparation procedure consisted on the deposition of a droplet of a suspension of the grounded sample in ethanol on a holey carbon film supported on a Cu grid. Elemental analysis of the samples was obtained by EDX coupled to TEM.

The capability of nitrate removal by the different metal loaded or metal free materials was assessed in a semi-batch reactor. 550 mL of ultrapure water and 500 mg of catalyst were fed to the reactor, which was maintained under stirring at 700 rpm. Depending on the experiment a flow of CO₂ (75 cm³·min⁻¹) and/or H₂ (75 cm³·min⁻¹) were passed through the reactor. When formic acid was used as reductant the reactor was fed with He at a flow rate of 250 cm³·min for 30 min, and then 186 μL of formic acid (FA) (378 mg·L⁻¹) were added.

Nitrate removal was evaluated in an aqueous solution of NaNO₃. The reaction was initiated by adding 7.5 mL of a NaNO₃ solution to the reactor, so the initial nitrate concentration was 100 mg·L⁻¹, and the flow of gases was maintained during the course of the reaction.

The withdrawal of 1 mL aliquots at different times during the course of the reaction allowed the determination of nitrate, nitrite and ammonium by ion chromatography (Metrohm 850 ProFlc AnCat-MCS equipment). Nitrate and nitrite anions were determined in a Metrosep ASSUPP-7 column (250 mm × 4 mm) and ammonium cation was determined in a Metrosep C3 column (250 mm × 4 mm).

A blank test with ultrapure water were always run for each experiment before the addition of the nitrate solution, so in the case that there were any detectable nitrate, ammonium or nitrite concentrations in the blank test, those were always automatically discounted from the measured concentrations during the course of the reaction.

Nitrate conversion (%) and selectivities to nitrite and ammonium (%) were calculated as:

$$X_{NO_3^-} = \frac{[NO_3^-]_o - [NO_3^-]_t}{[NO_3^-]_o} \cdot 100$$

where $[NO_3^-]_o$ is the initial nitrate concentration ($\text{mg}\cdot\text{L}^{-1}$) and $[NO_3^-]_t$ the nitrate concentration ($\text{mg}\cdot\text{L}^{-1}$) at time t (min).

$$S_{NO_2^-} = \frac{(n_{NO_2^-})_t}{(n_{NO_3^-})_o - (n_{NO_3^-})_t} \cdot 100 \quad \text{and} \quad S_{NH_4^+} = \frac{(n_{NH_4^+})_t}{(n_{NO_3^-})_o - (n_{NO_3^-})_t} \cdot 100$$

where $(n_{NO_3^-})_o$ is the initial amount of nitrate (mol) and $(n_{NO_3^-})_t$, $(n_{NO_2^-})_t$, $(n_{NH_4^+})_t$ are the amounts of the respective species (mol) at time t (min).

Metal leaching did not take place. This was checked by the analysis of aliquots withdrawn from the reactor using Inducted Coupled Plasma Mass Spectrometry (ICP-MS) (7700x Agilent). Experimental conditions were: RF power: 1150 W; He flow: $0.99 \text{ cm}^3\cdot\text{min}^{-1}$; liquid flow: $0.3 \text{ mL}\cdot\text{min}^{-1}$.

3. Results and discussion

A broad range of conductivity values are reported for PPy from $10^{-7} \text{ S}\cdot\text{cm}^{-1}$ to $10^2 \text{ S}\cdot\text{cm}^{-1}$ [34]. Conductivity highly depends on the synthesis conditions, the counterion and the doping level. PPy synthesized with FeCl_3 showed an electrical conductivity of $1.3 \text{ S}\cdot\text{cm}^{-1}$, which considerably diminished after supporting the platinum catalyst ($3.4 \cdot 10^{-3} \text{ S}\cdot\text{cm}^{-1}$). XPS reveals that most platinum ion (Pt^{4+}) from hexachloroplatinic acid suffers a reduction to Pt^{2+} upon anchoring to the polypyrrole chain ($\text{H}_2\text{PtCl}_6/\text{PPy}$) (Fig. 1). Previous studies [43] have shown that after impregnation with H_2PtCl_6 , platinum anchors to the pyrrolic nitrogen of the polypyrrole chain as a chloroplatinum complex. The redox potentials of platinum (VI) chlorocomplex ($E^0 [\text{PtCl}_6]^{2-}/[\text{PtCl}_4]^{2-} = +0.68 \text{ V}$) and polypyrrole ($E^0 \text{ PPy}^+/\text{PPy} = +0.15 \text{ V}$) (Table S.1), support a possible electron transfer between PPy and platinum ion [39], which results in the partial reduction of Pt^{4+} to Pt^{2+} and the oxidation of the neutral amine ($-\text{NH}-$) functionalities to oxidized amine ($-\text{N}^+$), as assessed by XPS (Fig. S.4, Tables S.2 and S.3.). Afterwards, the high energy electrons present in the plasma are able to partially reduce platinum (II) ion present in $\text{H}_2\text{PtCl}_6/\text{PPy}$ (Table S.3) and produce well dispersed metal platinum nanoparticles, which are detected by XPS (Pt/PPy in Table S.3), and evidenced by TEM (Fig. S.4). Formation of platinum nanoparticles implies dissociation of the platinum complexes anchored to the polymeric chain through the nitrogen functionality ($-\text{N}^+ \dots [\text{PtCl}_4]^{2-}$) (Fig. S.3).

The performance of this platinum catalyst supported on polypyrrole (Pt/PPy) will be evaluated and compared with other catalysts in the reaction of reduction of nitrate from water with molecular hydrogen.

The catalytic hydrogenation of nitrate is quite different depending on the metal and the support. Fig. 1 compares two Pt:Sn catalyst supported on an activated carbon ($S_{\text{BET}} = 1535 \text{ m}^2\cdot\text{g}^{-1}$) with a monometallic Pt catalyst supported on a ceramic (TiO_2 ; $S_{\text{BET}} = 53 \text{ m}^2\cdot\text{g}^{-1}$) and a polymeric (PPy; $S_{\text{BET}} = 4 \text{ m}^2\cdot\text{g}^{-1}$).

It has been well established that the monometallic catalysts are in general inactive for nitrate reduction. This is the case of the platinum catalyst supported on activated carbon, where the presence of a promoter metal is mandatory to obtain significant nitrate conversion

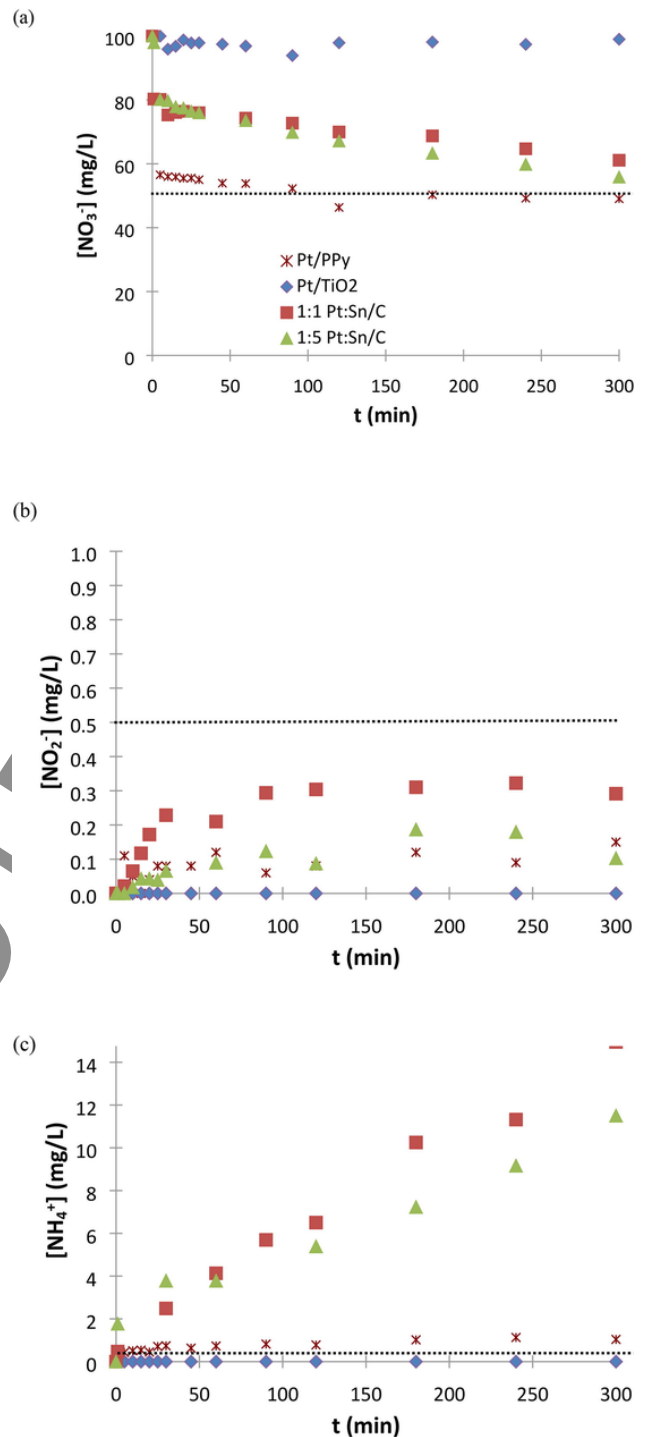


Fig. 1. (a) Nitrate, (b) nitrite and (c) ammonium concentrations ($\text{mg}\cdot\text{L}^{-1}$) as a function of time, determined by ion chromatography in the presence of platinum catalysts supported on different materials. Initial nitrate concentration is $100 \text{ mg}\cdot\text{L}^{-1}$.

[44,45]. Fig. 1 shows that the Pt-Sn catalysts supported on activated carbon are active for nitrate reduction but nitrate abatement is not enough to fulfill the water regulations, and considerable nitrite and ammonium production are produced, which surpass the permitted levels. The selectivity to these undesirable subproducts is increased with the increased noble metal concentration in the bimetallic catalyst (1:1Pt-Sn/C vs 1:5Pt-Sn/C), as reported elsewhere [10]. This can be explained on the basis that the higher the amount of the noble metal (which is very active for hydrogenation reactions) the higher number of iso-

lated noble metal surface sites, so the increased production of nitrite and ammonium.

Although some studies [17] show that Pt/TiO₂ is active for nitrate reduction using H₂ as a reducing agent, its activity and selectivity is highly dependent on the preparation procedure, especially the calcination/reduction temperatures. In the experimental conditions used in this study, the activity of Pt supported on PPy is considerable higher than the platinum catalysts supported on TiO₂ or activated carbon. Only in the case of the polymeric support, there is a considerable abatement of nitrate from the solution in the presence of H₂ and CO₂ and a Pt catalyst. This can be explained in terms of the polymeric support getting actively involved in the redox process. In less than 10 min, 56% nitrate conversion is achieved. Nevertheless, the nitrate concentration determined by ion chromatography (53.82 mg·L⁻¹ for Pt/PPy/FeCl₃ + H₂ + CO₂ in Table S.4) is still over the maximum permitted level for drinking water (50 mg·L⁻¹). Ammonium concentration (0.73 mg·L⁻¹) also exceeds the permitted limits (0.5 mg·L⁻¹) [1]. It has not been possible to measure nitrogen released to the atmosphere as a result of nitrate reduction, but ammonium production evidences that a redox process is taking place. XPS analysis of the recovered catalyst support these findings (Fig. 3). After 60 min reaction, there is a decrease of the metallic platinum amount (from 61 in Pt/PPy to 43% in Pt/PPy/H₂ + CO₂/recovered in Table S.3) and an increase of ionic platinum (from 39 to 57%, respectively).

The reduction of nitrate might be produced either by dihydrogen chemisorbed to Pt⁰ or by electrons provided by the conducting polymer (Fig. 2a). However, the electron transfer from the conducting polymer to nitrate ions is limited in the Pt/PPy compared to the metal-free PPy. In the metal-free PPy, chlorine counteranions are exchanged by nitrate, which adsorbs to PPy. Then the electron transfer from the polymer to the adsorbed nitrate is produced through the nitrogen functionalities in the polymeric chain. However, in the Pt/PPy a considerable amount of Cl⁻ enters into the coordination sphere of the platinum chlorocomplexes, anchored to the N functionalities in the polymer. This reduces the number of Cl⁻ available to be exchanged by NO₃⁻ and therefore limits the ion exchange process and also limits the electron transfer process, that is direct in the metal-free PPy, but it is platinum-mediated

in Pt/PPy, as detailed in a previous work [39]. Thus, Fig. 3a shows a more effective nitrate removal produced by the Pt-free polypyrrole.

Considering the performance of the unloaded polymer for the abatement of nitrate from water, the reductant capability of the PPy synthesized with FeCl₃ has been studied in the presence of several reductants. Superimposed graphs are obtained when the reaction is carried out using just the polymer (PPy) or when other reductants as molecular hydrogen (PPy + H₂ + CO₂) or formic acid (PPy + FA) are added to the reactor (Fig. 3). This suggests that the PPy by itself is capable of producing the reduction of nitrate in the water, and the presence of any other reductant is not necessary. This can be explained considering both the polymer ion exchange ability and its redox properties, which provide the polymer with the unique capability of reducing nitrate in the water, unlikely to other supports studied in the literature, which necessarily require the presence of a reductant (such as hydrogen), as well as a metal catalyst.

Fig. 4 shows that the decrease in the concentration of nitrate determined by ion chromatography in the aqueous solution is accompanied by the increase of chloride. This is due to the ion exchange between the chloride counter-ion of the polymeric chain and nitrate in the aqueous solution. Once exchanged, nitrate is reduced by electrons provided by the polymer chain with a consequent production of nitrogen (not measured), nitrite (Fig. 3b) and ammonium (Fig. 3c), which are detected in the solution. The low amount of nitrite and the considerable higher amount of ammonium suggest that the reduction of nitrate occurs through nitrite as an intermediate species, but this quickly undergo a subsequent reduction to ammonium or nitrogen. On the other hand, Fig. 3a and Table S.5 also show that nitrate abatement is less effective in the presence of FA. This can be explained in terms of the competition between nitrate and formate anions to exchange chloride anions. FA in solution is a source of H₂ (acts as reductant) and CO₂ (acts as a buffer). However, if some formate anions exchange chloride anions and get anchored to the polymeric chain, the H₂ production would de-

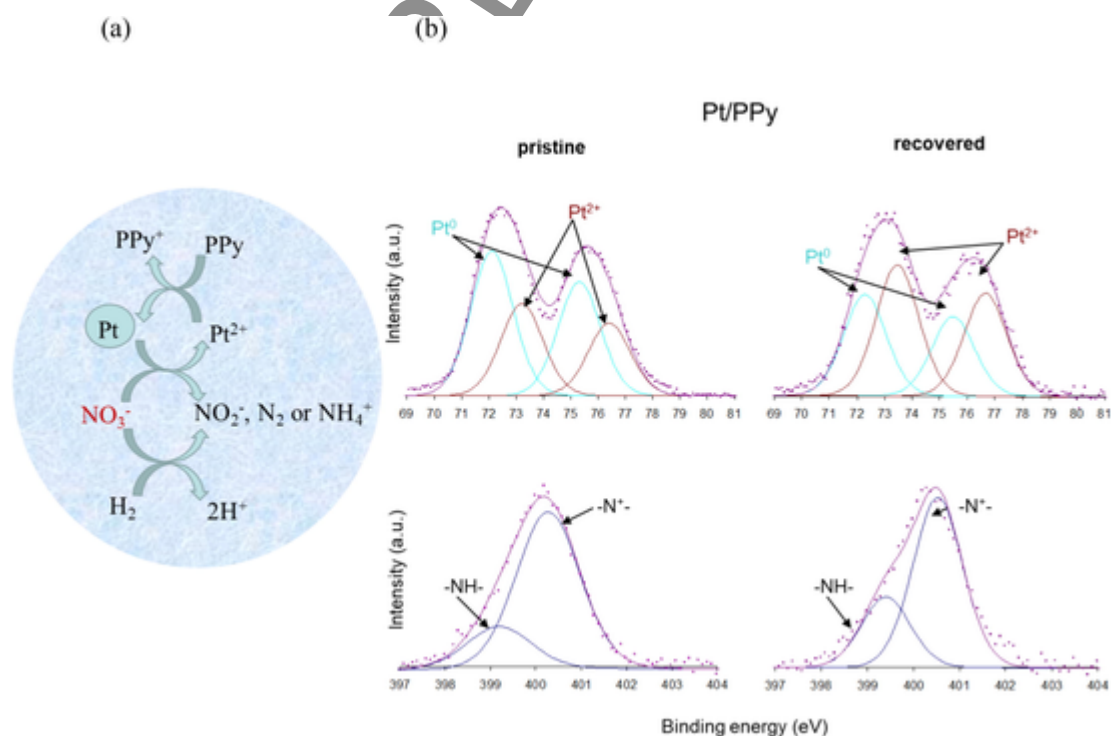


Fig. 2. (a) Scheme showing the proposed mechanism of nitrate reduction and (b) Pt 4f and N 1s curve fits (XPS) of the pristine and the recovered platinum catalyst supported on PPy.

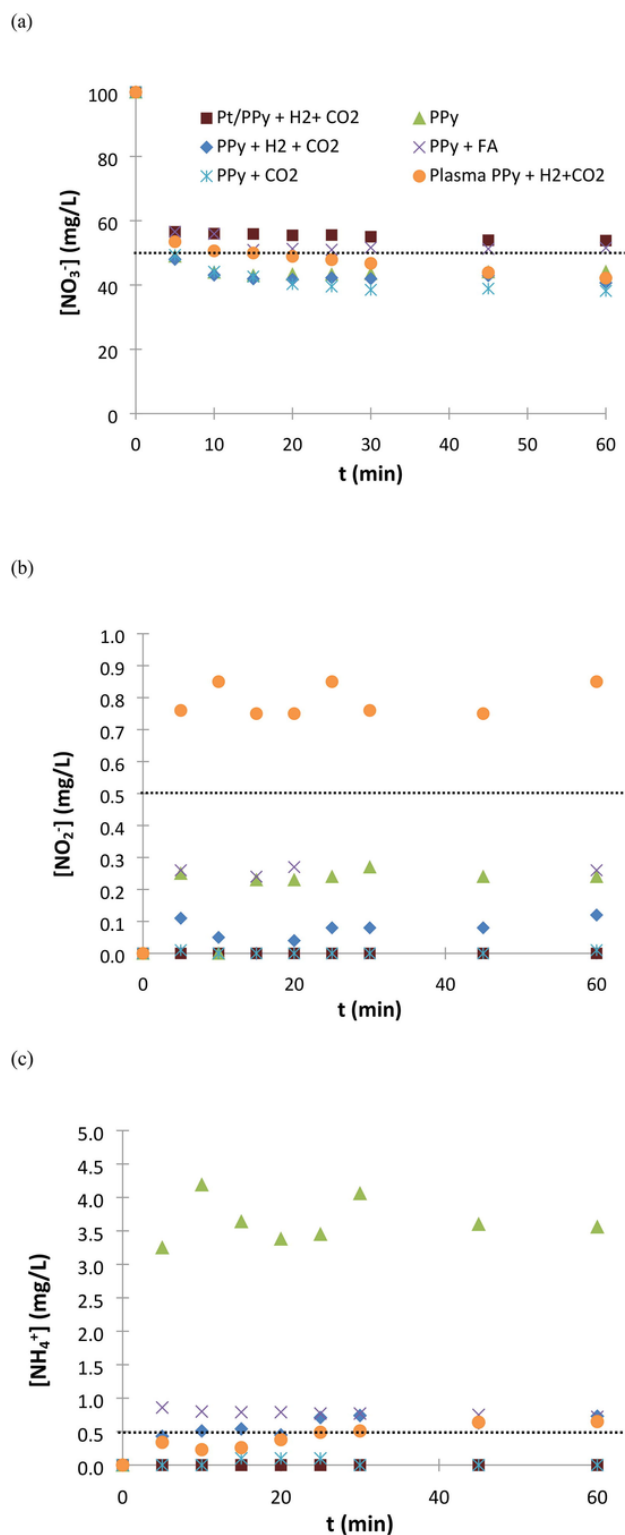


Fig. 3. (a) Nitrate, (b) nitrite and (c) ammonium concentrations ($\text{mg}\cdot\text{L}^{-1}$) as a function of time, determined by ion chromatography in the presence of platinum supported on PPy and also on metal-free PPy with different reductants. Initial nitrate concentration is $100 \text{ mg}\cdot\text{L}^{-1}$.

crease. Besides, as formiate compete with nitrate for the available sites at the polymeric chain, nitrate adsorption would also decrease. As a result, nitrate removal by PPy in the presence of FA is lowered. Nevertheless, those nitrate ions that get to anchor to the polymeric chain (Fig. 5), also suffer further reduction, mainly by the electrons provided

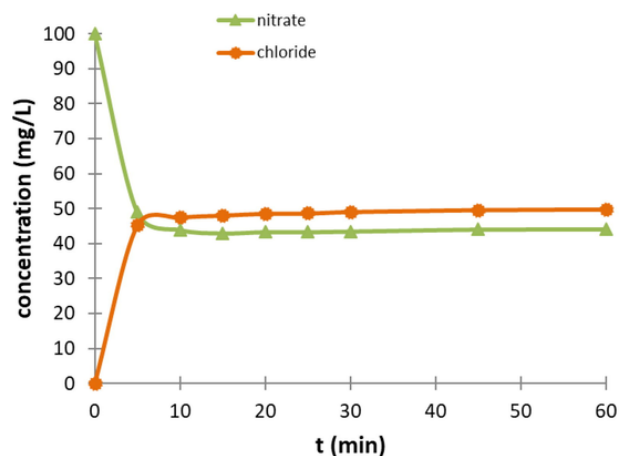


Fig. 4. Nitrate and chloride concentrations ($\text{mg}\cdot\text{L}^{-1}$) as a function of time, determined by ion chromatography using PPy in absence of any other reductant.

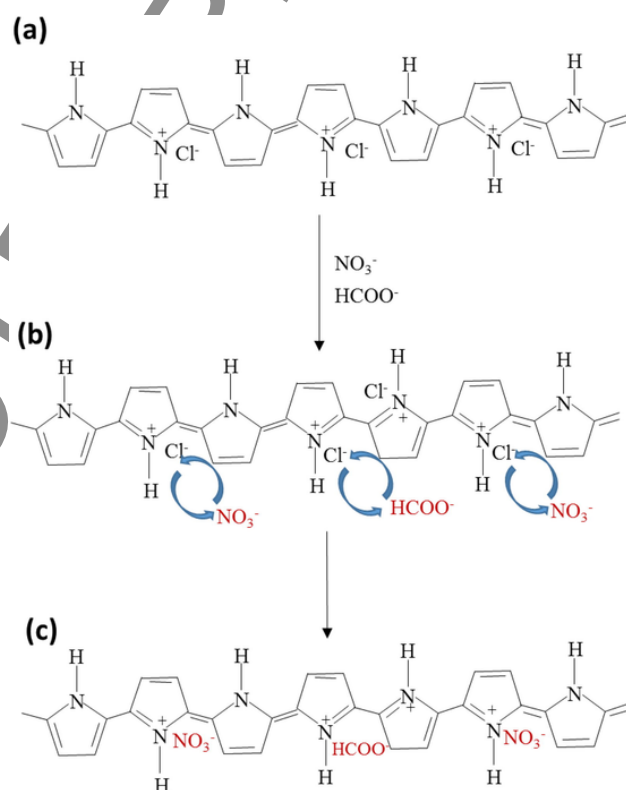


Fig. 5. Scheme showing the exchange between chlorine counter-ion of the polymeric chain and nitrate and formiate anions.

by the polymeric chain as the in situ produced H_2 is insufficient to reduce NO_3^- [46].

The ability of PPy to exchange formiate anions was evaluated from the variations in the concentration of a formic acid solution in contact with PPy, in the absence of nitrate. An increase of the concentration of chloride from 0 to $23 \text{ mg}\cdot\text{L}^{-1}$ and a decrease in the concentration of formic acid from $378 \text{ mg}\cdot\text{L}^{-1}$ to $235 \text{ mg}\cdot\text{L}^{-1}$ is observed in only 5 min, which demonstrates the ion exchange between the formiate of the solution and the chloride counter-ions of PPy. However, COO^- and NO_3^- species are not detected by XPS in the recovered polymer, so the exchanged formiate and nitrate ions are not retained by the polymeric chain.

The mechanism for nitrate abatement by PPy is produced in a two-steps pathway. First, ion exchange between PPy counter-ions (Cl^- in PPy/FeCl_3) and NO_3^- is produced, and then, electrons are supplied

to nitrate from the semioxidized polymeric chain, which is plausible from the reduction potentials of nitrate ($\text{NO}_3^-/\text{NH}_4^+$, $E^\circ = 0.875 \text{ V}$; NO_3^-/N_2 , $E^\circ = 1.246 \text{ V}$) and polypyrrole, (PPy^+/PPy , $E^\circ = 0.150 \text{ V}$) (Table S.1). In the presence of formic acid, after the competitive exchange of chloride counter-ion by nitrate and formiate from the aqueous solution, nitrate could be reduced directly by the electrons supplied by the polymeric chain, but there is also the possibility that nitrate is reduced by the H_2 evolved from the oxidation of formic acid by the polymeric chain ($E^\circ (\text{CO}_2/\text{HCOOH}) = -0.199 \text{ V}$). Thus, the PPy polymeric chain could participate either in the nitrate reduction and the formiate oxidation. This is possible thanks to the unique ability of the intrinsic conducting polymer to act as a source or a sink of electrons according to the nature of the anion anchored to the pyrrolic nitrogen (nitrate or formiate) (Fig. 5).

The changes produced in the oxidation state of the polymer chain submitted to these redox processes can be monitored by XPS. N 1s spectra can be deconvoluted into four contributions corresponding to four types of nitrogen: neutral imine ($-\text{N}=\text{}$) around 397.8 eV, neutral amine ($-\text{NH}-$) around 399.5 eV, charged amine ($-\text{N}^+$) around 401.1 eV and charged imine ($=\text{NH}^+$), around 402.0 eV. Table S.6 shows the percentages of the different nitrogen species detected on the surface the pristine polypyrrole (Pristine PPy) and also on the surface of the recovered polypyrrole after 60 min in contact with just the aqueous nitrate solution (Recovered PPy + NaNO_3); the recovered polypyrrole after contact with the nitrate solution and formic acid (Recovered PPy + NaNO_3 + FA) and the recovered polypyrrole after being in contact with the nitrate solution and H_2 and CO_2 flows (Recovered PPy + NaNO_3 + H_2 + CO_2).

Pristine PPy shows 75% of neutral amine species and 25% of positively charged nitrogen ($-\text{N}^+$), characteristic of the semi-oxidized state of the polymeric chain after the oxidative chemical polymerization with FeCl_3 . After being in contact with the aqueous solution of

formic acid and sodium nitrate, a variation of the percentages of the different N species is in the surface of the recovered PPy + NaNO_3 + FA can be noticed: 5% $-\text{N}=\text{}$; 86% $-\text{NH}-$; 9% $-\text{N}^+$. This change of the oxidation state of PPy is a consequence of the participation of the polymeric chain in both processes, i.e. the oxidation of formiate and the reduction of nitrate ions anchored to the polymeric chain. The net balance of these two processes (oxidation of formic acid and reduction of nitrate) gives rise to the nitrogen species detected by XPS in the surface of the recovered PPy from the aqueous nitrate and formiate solution.

It has been reported [26] that the oxidation of formic acid in aqueous solution requires the presence of a catalyst, which is usually a noble metal. However, in this work, it has been shown that the conductive polymer can promote the oxidation of formic acid as well as the reduction of nitrate (Fig. 6). Polarons and bipolarons in PPy (Fig. S.2), would be implied in the electron flow from and towards the polymeric chain according to the nature of the anion (nitrate or formiate) anchored through the pyrrolic nitrogen.

Table S.6 shows reduced nitrogen moieties ($=\text{N}-$) at binding energies of 398.5 eV in the recovered PPy + NaNO_3 + FA and recovered PPy + NaNO_3 + H_2 + CO_2 . However, these species are not detected in the recovered PPy + NaNO_3 . In this later case, the polymeric chain is the only reductant of nitrate and consequently, it gets more readily oxidized than in the presence of formic acid or dihydrogen. This is evidenced by the presence of oxidized nitrogen moieties ($=\text{N}^+$) in the recovered PPy + NaNO_3 . Furthermore, the absence of nitrate contribution at higher binding energies confirms that nitrate is not retained by adsorption on PPy.

Although nitrate is successfully reduced by PPy, however, a pH of 6 is obtained, this increasing selectivity to ammonium [38,47] (Table S.4). As explained in the Introduction section, the reduction of nitrate under basic conditions produces hydroxide ion. It is crucial to maintain a pH about 4 to assure a low ammonium production. This is can be achieved by buffering the aqueous solution with CO_2 . If formic acid

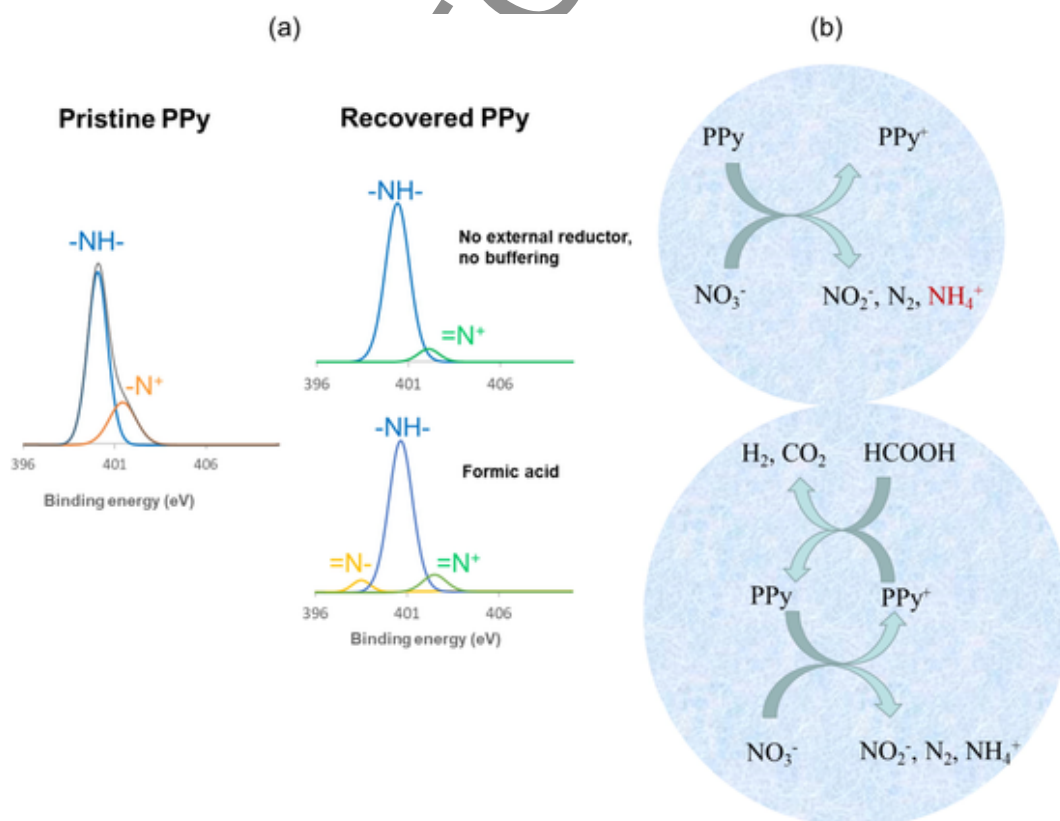


Fig. 6. (a) N 1s curve fits (XPS) of the pristine and the recovered polypyrrole by itself and in the presence of formic acid; (b) Scheme showing the proposed mechanism of nitrate reduction by polypyrrole by itself and in the presence of formic acid.

is used as a CO₂ source (as well as source of H₂), there is a more important increase in the concentration of chloride in solution (from 0 to 56.19 mg·L⁻¹) (Table S.5) compared to the chloride released to the solution when PPy is in the presence of H₂ and/or CO₂ (48.62 and 49.04 mg·L⁻¹) or just PPy (48.71 mg·L⁻¹). This is in agreement with the fact that part of the chloride ions are being exchanged by both formate and nitrate ions (Fig. 5), as mentioned above.

Once the reaction was completed, the polymer was separated from the solution by centrifugation and introduced in a stirred aqueous NaCl 1 M solution during 30 min in order to produce the desorption of the anions that could remain adsorbed [48] (nitrate, formate). Then, two subsequent runs under identical conditions were carried out. Nitrate conversions achieved with the regenerated materials were only slightly lower than those obtained during the first run (Table S.7). Ammonium and nitrite production was similar in all the three runs. However, the recycling of PPy would imply not only the regeneration of the original counterions but also the reduction of the polymeric chain to its redox state before being in contact with the nitrate solution. This is the aim of further investigations.

2 2

The ion-exchange and the redox properties of PPy are strongly affected by the oxidation state of the polymeric chain. In this study, the oxidation degree of the polymeric chain has been modified by a treatment in Argon plasma. Table S.2 shows an increase of oxygen functionalities on the surface of the PPy treated in Ar plasma at 300 w for 3 h. Plasma treatment produces the activation of the polymer surface and its ulterior contact with air results in the introduction of oxygen moieties. Thus, the XPS high resolution curve fit of the C 1 s level shows C-O and C=O contributions at 287.25 and 288.54 eV, respectively, which correspond to the O=C (532.05 eV) and 533.20 eV (O-C) contributions of the O 1 s level. Besides, analysis of the N 1 s level (Table S.6) shows a decrease of the percentage of oxidized amine moieties (-N⁺) in the plasma-treated PPy (9%) when compared to the pristine PPy (25%). This is due to the reductant ability of the high energy electrons in the plasma [43]. The decrease of N⁺ functionalities produces a considerable decrease of chlorine counter ions: 0.47% Cl in plasma treated PPy vs 2.37% Cl in pristine PPy (Table S.2). As the number of counter ions anchored to the polymeric chain, which are susceptible of being exchanged by nitrate from the solution decreases, nitrate abatement results less effective and the reduction of nitrate becomes slightly more selective to nitrite, which is furthermore released to the solution and can be detected by ion chromatography (Fig. 3).

Not only the oxidation degree of the pristine PPy, but also the nature of the counter anions that neutralize the oxidized amine functionalities of the polymeric chain determine the activity and selectivity of the reduction of nitrate by the electrons provided by the polymeric chain (Fig. 7).

In this study, pyrrole was polymerized using two different oxidants (FeCl₃ and K₂S₂O₈), which provide different counter anions. The resulting polymers, PPy/FeCl₃ and PPy/K₂S₂O₈, showed low BET surface areas of 4 and 11 m²·g⁻¹, and conductivities of 25 and 4.5 S·cm⁻¹ respectively. XRD diffraction patterns of both materials (Fig. S.5) are similar and characteristic of amorphous polymers, with a broad peak centered at 2θ = 25.0° due to the scattering from PPy chains at the interplanar spacing.

XPS characterization results can add some light to understand the different performance of the doped polymers in the abatement of nitrate from water. Oxygen is present in both polymers, but in a considerable higher amount in PPy/K₂S₂O₈ (17.97 at.% vs. 6.52 at.% in PPy/

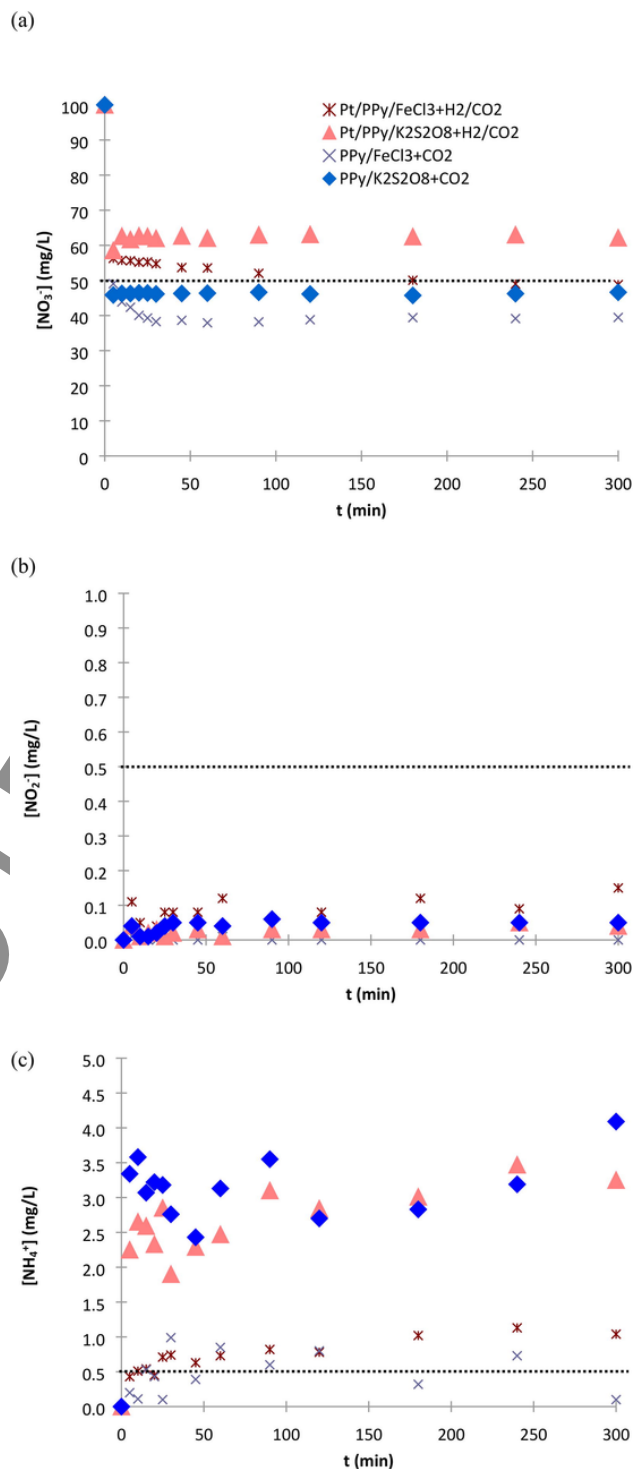


Fig. 7. Nitrate, nitrite and ammonium concentrations (mg·L⁻¹) as a function of time, determined by ion chromatography. Effect of the dopant/oxidant of PPy. In all cases, a CO₂ flow was used. H₂ flow was used only when the platinum catalyst was used. Initial nitrate concentration is 100 mg/L.

FeCl₃) (Table S.8). Oxygen moieties are detected in the curve fit of the C 1s level (Fig. 8) as C-O (286.2 eV) or C=O (287.6 eV). The binding energy at which the S 2p peak appears (168.3 eV) in PPy/K₂S₂O₈ corresponds to sulfur in the sulfate anion, this evidencing the reduction of S₂O₈²⁻ to SO₄²⁻ when it is incorporated as a counter-ion to the polymeric chain during the oxidative polymerization. When FeCl₃ is used, chloride ions are detected (Cl 2p_{3/2} at 198.5 eV). These results sup-

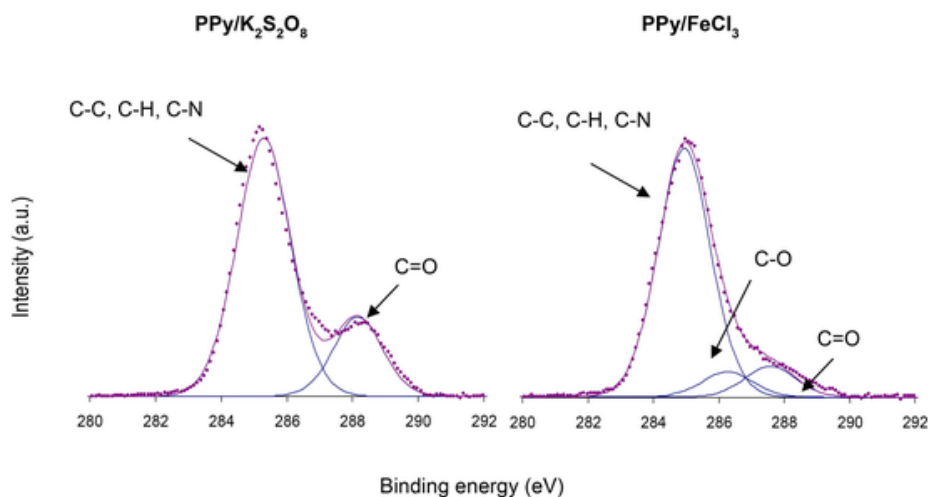


Fig. 8. XPS spectra of the C 1s level of PPy synthesized with $K_2S_2O_8$ and with $FeCl_3$.

port the ability of the oxidants to provide counter-ions to neutralize the positively charged polymeric chain. Some chlorine is also detected in PPy/ $K_2S_2O_8$ (Table S.8), which may come from water contamination, and this evidences the ion-exchange ability (some SO_4^{2-} anions replaced by some Cl^- anions) of counter-ions in the oxidized PPy chain. Cations from the oxidants do not anchor to the positively charged polymeric chain, therefore neither potassium is detected in PPy/ $K_2S_2O_8$ nor iron is detected in PPy/ $FeCl_3$.

PPy synthesized with $K_2S_2O_8$ shows 93% of positively charged nitrogen at 400.3 eV (Fig. 9, Table S.9), whereas PPy/ $FeCl_3$ results to be in a less oxidized state (65% of positively charged nitrogen). This results can be correlated with the differences in electrical conductivities, (25 and $4.5 S \cdot m^{-1}$), found for PPy/ $K_2S_2O_8$ and PPy/ $FeCl_3$, respectively.

FTIR spectra of both PPy samples show typical absorption bands (Fig. S.6): $C=C$ stretching ($1485 cm^{-1}$), $C-C$ stretching (1298

and $1102 cm^{-1}$), $=C-H$ out of plane bending ($1046 cm^{-1}$), $N-H$ bending ($801 cm^{-1}$). Characteristic bands of $C=N-C$ are slightly shifted towards higher wavenumbers in PPy/ $K_2S_2O_8$ compared to PPy/ $FeCl_3$: $C=N$ stretching (1565 vs. $1540 cm^{-1}$), $C-N$ stretching (1202 vs. $1183 cm^{-1}$) and $C=N-C$ bending (922 vs. $915 cm^{-1}$). These bands are attributed in the literature to the bipolaron bands characteristics of the doping. Besides, stretching $C=O$ absorption at $1700-1710 cm^{-1}$ in both spectra suggests the formation of oxygen moieties as a consequence of the contact of the polymeric chain with the aqueous medium during polymerization and/or by oxidation in contact with air [43].

When the metal-free polymers are put into contact with the aqueous nitrate solution in the presence of a CO_2 flow, the abatement of nitrate from the solution is more effective than that produced by the platinum supported counterparts (Fig. 7). However, the selectivity of the reaction depends on the oxidant/dopant used in the polymerization of pyr-

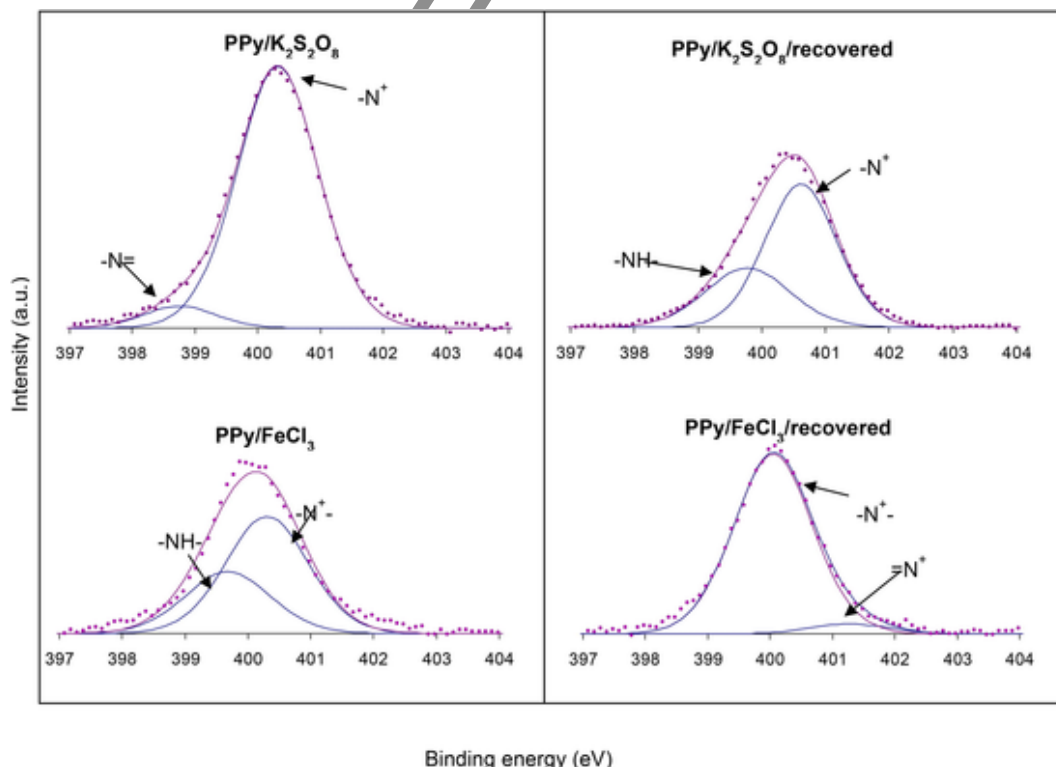


Fig. 9. N 1s curve fit of PPy synthesized with $K_2S_2O_8$ and $FeCl_3$, pristine and recovered after contact with nitrate solution for 300 min.

role. Ammonium is detected in the presence of PPy/K₂S₂O₈ (Table S.10), which reveals that nitrate is in fact being reduced. In the case of PPy/FeCl₃, neither nitrite nor ammonium ions are detected. Thus, PPy/FeCl₃ is highly selective to nitrogen, whereas selectivity to nitrogen is considerably decreased in PPy/K₂S₂O₈ due to the higher production of ammonium ($S_{NH_4^+} = 26.1\%$).

Recovered polymers were analyzed by XPS. The surface composition of the recovered PPy/K₂S₂O₈ resulted quite similar to that of the pristine polymer, except for a decrease of the amount of sulfur species (from 0.38 to 0.16 at.%) (Table S.8). Recovered PPy/FeCl₃ shows a more important decrease of the amount of chlorine species (from 2.37 to 0.60 at.%), together with a considerable increase of the surface oxygen concentration (from 6.52 to 14.39 at.%) produced by the contact with the aqueous solution.

The relative size of the chloride ionic radius (181 pm) and the thermochemical radii of NO₃⁻ (179 pm) and SO₄²⁻ (258 pm) [49] determine that exchanging of nitrate ion with chloride ion is easier than with sulfate ion [40,50,51].

Although chloride or sulfate counter-ions of PPy are exchanged by nitrate this is not detected by XPS in the recovered polymers, as no contribution to the N 1s peak at 406 eV is observed (Table S.9). This suggests that after the exchange with the polymer counter-ions, nitrate is reduced by electrons provided by the conducting polymer. As a consequence, an important oxidation is observed in recovered PPy/FeCl₃. Thus, positively charged nitrogen (-N⁺) and protonated imine (=N⁺) species are detected. Although nitrate could be reduced to nitrite in a first step, XPS analysis of recovered PPy did not show any nitrite contribution (XPS peak at 403.6 eV, Table S.9). A low concentration of nitrite was detected in the solution (0.05 mg·L⁻¹) when PPy/K₂S₂O₈ was used, being most of it reduced to ammonium (4.09 mg·L⁻¹, Table S.10) or to N₂ (not measured).

These results suggest that the initial oxidation degree of the polymer imparted by the oxidant (K₂S₂O₈ or FeCl₃) is determinant in the ability of the polymer to produce the selective reduction of nitrate by the electrons provided by the polymeric chain. The more reduced the pristine polymeric chain, the more important the electron flow to nitrate. Consequently, as PPy/FeCl₃ is initially in a more reduced state that PPy/K₂S₂O₈ abatement of nitrate in the aqueous solution is more effective with the former.

4. Conclusions

Contamination of water with nitrates is a serious environmental and health problem that requires an effective and economically viable solution. A comprehensive study of nitrate reduction with PPy-based materials has been accomplished. First, the catalytic reduction of nitrate with gaseous hydrogen has been carried out using a platinum catalyst supported on ceramic or carbonaceous materials and compared to the abatement of nitrate using a conductive polymer (PPy). Then, formic acid has been used as an alternative reducing agent to H₂ gas. The mechanism of nitrate removal from water under different experimental conditions has been studied, including the presence or absence of a Pt catalyst supported on the PPy, the pH of the solution, the reducing agent, a plasma treatment and the oxidant used in the synthesis of PPy.

From the obtained results, the following conclusions have been addressed:

1. A metal-free method of abatement of nitrates from water without the risks associated with the use of gaseous hydrogen has been developed using a conducting polymer. PPy is able to produce the abatement of nitrate by an adsorption/reduction mechanism without the need of a metal catalyst or an external reducing agent. This is due to the redox chemistry and ion exchange properties of the conducting polymer.
2. Control of pH of the solution is crucial to avoid the formation of ammonium during the nitrate reduction reaction produced by PPy. This can be achieved by either using a CO₂ flow or by using formic

acid as a source of CO₂. Although the H₂ evolved from formic acid has reductant ability, however, nitrate is mainly reduced by electrons provided by PPy.

3. The selectivity of nitrate reduction is also affected by the oxidation state of the polymeric chain, imparted either by the oxidant or by a plasma treatment. Selectivity to ammonium is low in the presence of PPy/FeCl₃, whereas the reaction is highly selective to ammonium with PPy/K₂S₂O₈. When PPy is treated in plasma, the reduction of nitrate slightly increases its selectivity to nitrite.

Author contributions

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

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2020.126228>.

References

- [1] WHO. Ammonia in Drinking-water, Background Document for Development of WHO Guidelines for Drinking-Water Quality. 2003;2:4.
- [2] K R Burow, B T Nolan, M G Rupert, N M Dubrovsky, Nitrate in groundwater of the United States, 1991–2003, *Environ. Sci Technol.* 44 (13) (2010) 4988–4997, doi:10.1021/es100546y.
- [3] I Mikami, Y Sakamoto, Y Yoshinaga, T Okuhara, Kinetic and adsorption studies on the hydrogenation of nitrate and nitrite in water using Pd-Cu on active carbon support, *Appl. Catal. B Environ.* 44 (1) (2003) 79–86, doi:10.1016/S0926-3373(03)00021-3.
- [4] V Bouvard, D Loomis, K Z Guyton, et al., Carcinogenicity of consumption of red and processed meat, *Lancet Oncol.* 16 (December) (2015) 1599–1600, doi:10.1016/S1470-2045(15)00444-1.
- [5] N. Graham, Guidelines for Drinking-Water Quality, 4th Ed. Who. 1999;1(2):183. doi:10.1016/S1462-0758(00)00006-6.
- [6] V B Jensen, J L Darby, C Seidel, C Gorman, Nitrate in potable water supplies: alternative management strategies, *Crit. Rev. Environ. Sci. Technol.* 44 (20) (2014), doi:10.1080/10643389.2013.828272.
- [7] A Bhatnagar, M Sillanpää, A review of emerging adsorbents for nitrate removal from water, *Chem. Eng. J.* 168 (2) (2011) 493–504, doi:10.1016/j.cej.2011.01.103.
- [8] K.N. Heck, S. Garcia-Segura, P. Westerhoff, M.S. Wong, Catalytic converters for Water Treatment. *Acc. Chem. Res.* 2019;52(4). doi: 10.1021/acs-accounts.8b00642
- [9] M. Hu, Y. Liu, Z. Yao, L. Ma, X. Wang, Catalytic reduction for water treatment. 2018;12(1):1-18. doi: 10.1007/s11783-017-0972-0.
- [10] O S G P Soares, J J M Órfão, J Ruiz-Martínez, J Silvestre-Albergo, A Sepúlveda-Escribano, M F R Pereira, Pd-Cu/AC and Pt-Cu/AC catalysts for nitrate reduction with hydrogen: influence of calcination and reduction temperatures, *Chem. Eng. J.* 165 (1) (2010) 78–88, doi:10.1016/j.cej.2010.08.065.
- [11] I Dodouche, D P Barbosa, M do C Rangel, F Epron, Palladium-tin catalysts on conducting polymers for nitrate removal, *Appl. Catal. B Environ.* 93 (1–2) (2009) 50–55, doi:10.1016/j.apcatb.2009.09.011.
- [12] U Prüssse, K D Vorlop, Supported bimetallic palladium catalysts for water-phase nitrate reduction, *J. Mol. Catal. A Chem.* 173 (1–2) (2001) 313–328, doi:10.1016/S1381-1169(01)00156-X.
- [13] G Mendow, N S Veizaga, C A Querini, B S Sánchez, A continuous process for the catalytic reduction of water nitrate, *J. Environ. Chem. Eng.* 7 (1) (2019), doi:10.1016/j.jece.2018.11.052.
- [14] S Hörold, T Tacke, K Vorlop, Catalytic removal of nitrate and nitrite from drinking water: 1. Screening for hydrogenation catalysts and influence of

- reaction conditions on activity and selectivity, *Environ Technol.* 14 (10) (1993) 931–939, doi:10.1080/09593339309385367.
- [15] R Zhang, D Shuai, K A Guy, J R Shapley, T J Strathmann, Werth CJ. Elucidation of nitrate reduction mechanisms on a Pd-In bimetallic catalyst using isotope labeled nitrogen species, *ChemCatChem.* 5 (1) (2013), doi:10.1002/cctc.201200457.
- [16] M.J. García-Fernández, R. Buitrago-Sierra, M.M. Pastor-Blas, O.S.G.P. Soares, M.F.R. Pereira, A. Sepúlveda-Escribano, Green synthesis of polypyrrole-supported metal catalysts: Application to nitrate removal in water. *RSC Adv.* 2015;5(41). doi: 10.1039/c5ra03441h.
- [17] O.S.G.P. Soares, E.O. Jardim, Reyes-Carmona Ivarro, et al. Effect of support and pre-treatment conditions on Pt-Sn catalysts: Application to nitrate reduction in water. *J Colloid Interface Sci.* 2012;369(1):294-301. doi: 10.1016/j.jcis.2011.11.059.
- [18] M Bertoch, A M Bergquist, G Gildert, T J Strathmann, C J Werth, Catalytic nitrate removal in a trickle bed reactor: direct drinking water treatment, *J. Am. Water Works Assoc.* 109 (5) (2017) E144–E157, doi:10.5942/jawwa.2017.109.0056.
- [19] F Ruiz-Beviá, M J Fernández-Torres, Effective catalytic removal of nitrates from drinking water: an unresolved problem? *J Clean, Prod.* (2019) 217, doi:10.1016/j.jclepro.2019.01.261.
- [20] ECETOC Nitrate and drinking water. *Eur Chem Ind Ecol Toxicol Centre Brussels, Belgium.* Published online doi: ISSN 1988: 19, 0773-8072-27.
- [21] USEPA (United State Environmental Protection Agency), National Primary Drinking Water Regulations, Washington, DC, 2008, Title 40, Part 141.; 2008. https://www.epa.gov/sites/production/files/2015-11/documents/howepargulates_cfr-2003-title40-vol20-part141_0.pdf.
- [22] O S G P Soares, M F R Pereira, J J M Órfão, J L Faria, C G Silva, Photocatalytic nitrate reduction over Pd-Cu/TiO₂, *Chem. Eng. J.* 251 (2014) 123–130, doi:10.1016/j.cej.2014.04.030.
- [23] J Shi, C Long, A Li, Selective reduction of nitrate into nitrogen using Fe-Pd bimetallic nanoparticle supported on chelating resin at near-neutral pH, *Chem. Eng. J.* 286 (2016) 408–415, doi:10.1016/j.cej.2015.10.054.
- [24] U Prisse, M Hähnlein, J Daum, K-D Vorlop, Improving the catalytic nitrate reduction, *Catal. Today* 55 (2) (2000) 79–90, doi:10.1016/S0920-5861(99)00228-X.
- [25] K.D. Vorlop, U. Prüsse, Catalytic removing nitrate from water. In: Jansen, F.J., van Santen RA, ed. *Catalytic Science Series, vl. 1. Environmental Catalysis.* ven University of Technology; 1999:195-207.
- [26] A Garron, F Epron, Use of formic acid as reducing agent for application in catalytic reduction of nitrate in water, *Water Res.* 39 (13) (2005) 3073–3081, doi:10.1016/j.watres.2005.05.012.
- [27] R Gavagnin, L Biasetto, F Pinna, G Strukul, Nitrate removal in drinking waters: The effect of tin oxides in the catalytic hydrogenation of nitrate by Pd/SnO₂ catalysts, *Appl. Catal. B-Environ.* 38 (2002) 91–99, doi:10.1016/S0926-3373(02)00032-2.
- [28] D M Ruthven, R S Upadhye, The catalytic decomposition of aqueous formic acid over suspended palladium catalysts, *J Catal.* 21 (1) (1971) 39–47, doi:10.1016/0021-9517(71)90118-7.
- [29] Y Ding, W Sun, W Yang, Q Li, Formic acid as the in-situ hydrogen source for catalytic reduction of nitrate in water by PdAg alloy nanoparticles supported on amine-functionalized SiO₂, *Appl. Catal. B Environ.* (2017) 203, doi:10.1016/j.apcatb.2016.10.048.
- [30] E Choi, K Park, H Lee, M Cho, S Ahn, Formic acid as an alternative reducing agent for the catalytic nitrate reduction in aqueous media, *J. Environ. Sci.* 25 (8) (2013) 1696–1702, doi:10.1016/S1001-0742(12)60226-5.
- [31] R B Moghaddam, P G Pickup, Oxidation of formic acid at polycarbazole-supported Pt nanoparticles, *Electrochim. Acta.* 97 (2013) 326–332, doi:10.1016/j.electacta.2013.02.133.
- [32] J C Fanning, The chemical reduction of nitrate in aqueous solution, *Coord. Chem. Rev.* 199 (May) (2000) 159–179, doi:10.1016/S0010-8545(99)00143-5.
- [33] Methods E. Noble Metal-Catalyzed Ammonia Generation by Formic Acid Reduction of Nitrate in Simulated Nuclear Waste Media. 1997;31(4):984-992.
- [34] T.A. Skotheim, Lightsense Technology I, Reynolds J, University of Florida, Gainesville U, Thompson BC, University of Southern California, Department of Chemistry U. *Handbook of Conducting Polymers: Theory, Synthesis, Properties, and Characterization.* 4 th. (John R. Reynolds, Barry C. Thompson TAS, ed.). CRC Press; 2019. <https://www.crcpress.com/Handbook-of-Conducting-Polymers-Fourth-Edition---2-Volume-Set/Reynolds-Thompson-Skotheim/p/book/9781138065512>.
- [35] Malinauskas a. Chemical deposition of conducting polymers. 2001;42.
- [36] R.A. Khalkhali, Electrochemical synthesis and characterization of electroactive conducting polypyrrole polymers. *Russ J Electrochem.* 2005;41(9):950-955. doi: 10.1007/s11175-005-0162-4.
- [37] R Ansari, Polypyrrole conducting electroactive polymers: synthesis and stability studies, *J. Chem.* 3 (13) (2006) 186–201. <http://www.hindawi.com/journals/chem/2006/860413/abs/>.
- [38] R Ansari, N Khoshbakt Fahim, A Fallah Delavar, Removal of nitrite ions from aqueous solutions using conducting electroactive polymers, *Open Process Chem. J.* 2 (2013) 1–5, doi:10.2174/1875180601002010001.
- [39] M J García-Fernández, M M Pastor-Blas, F Epron, A Sepúlveda-Escribano, Proposed mechanisms for the removal of nitrate from water by platinum catalysts supported on polyaniline and polypyrrole, *Appl. Catal. B Environ.* 2018 (225) (November 2017) 162–171. doi:10.1016/j.apcatb.2017.11.064.
- [40] M Hojjat Ansari, J Basiri Parsa, Removal of nitrate from water by conducting polyaniline via electrically switching ion exchange method in a dual cell reactor: optimizing and modeling, *Sep Purif Technol.* 169 (2016) 158–170, doi:10.1016/j.seppur.2016.06.013.
- [41] H K Chitte, G N Shinde, N V Bhat, V E Walunj, Synthesis of polypyrrole using ferric chloride (FeCl₃) as oxidant together with some dopants for use in gas sensors, *J. Sens. Technol.* 1 (2) (2011) 47–56, doi:10.4236/jst.2011.12007.
- [42] B Ohtani, O O Prieto-Mahaney, D Li, R Abe, What is Degussa (Evonic) P25? Crystalline composition analysis, reconstruction from isolated pure particles and photocatalytic activity test, *J. Photochem. Photobiol. A Chem.* 216 (2–3) (2010) 179–182, doi:10.1016/j.jphotochem.2010.07.024.
- [43] R Buitrago-Sierra, M J J García-Fernández, M M M Pastor-Blas, et al., Environmentally friendly reduction of a platinum catalyst precursor supported on polypyrrole, *Green Chem.* 15 (7) (2013) 1981, doi:10.1039/c3gc40346g.
- [44] O S G P Soares, J J M Órfão, M F R Pereira, Activated carbon supported metal catalysts for nitrate and nitrite reduction in water, *Catal. Lett.* 126 (3) (2008) 253–260, doi:10.1007/s10562-008-9612-4.
- [45] G P Soares, M F R Pereira, Pd – Cu and Pt – Cu catalysts supported on carbon nanotubes for nitrate, *Ind. Eng. Chem. Res.* 49 (2010) 7183–7192, doi:10.1021/ie1001907.
- [46] S Challagulla, K Tarafder, R Ganesan, S Roy, All that glitters is not gold: a probe into photocatalytic nitrate reduction mechanism over noble metal doped and undoped TiO₂, *J. Phys. Chem. C* 121 (49) (2017) 27406–27416, doi:10.1021/acs.jpcc.7b07973.
- [47] A Garron, K Lázár, F Epron, Effect of the support on tin distribution in Pd-Sn/Al₂O₃ and Pd-Sn/SiO₂ catalysts for application in water denitration, *Appl. Catal. B Environ.* 59 (1–2) (2005) 57–69, doi:10.1016/j.apcatb.2005.01.002.
- [48] I Dodouche, D P Barbosa, M do C Rangel, F Epron, Promoting effect of electroactive polymer supports on the catalytic performances of palladium-based catalysts for nitrite reduction in water, *Appl. Catal. B Environ.* 76 (1–2) (2009) 291–299, doi:10.1016/j.apcatb.2007.06.002.
- [49] Mark Weller, Tina Overton, Jonathan Rourke and FA. *Inorganic Chemistry.* 7th ed. Oxford university Press; 2018. <https://global.oup.com/ukhe/product/inorganic-chemistry-9780198768128?cc=es&lang=en&>
- [50] H Ge, G G Wallace, Ion exchange properties of polypyrrole, *React. Polym.* 18 (2) (1992) 133–140, doi:10.1016/0923-1137(92)90251-V.
- [51] I Dodouche, F Epron, Promoting effect of electroactive polymer supports on the catalytic performances of palladium-based catalysts for nitrite reduction in water, *Appl. Catal. B Environ.* 76 (3–4) (2007) 291–299, doi:10.1016/j.apcatb.2007.06.002.