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REMOVAL OF NITRATES FROM INDUSTRIAL WASTEWATER

Nitrates in water result mainly from the organic pollution caused by urban agglomerations. However, other important nitrate-sources are fertilizers used in agriculture, discharges from certain industries, as well as some combustion processes. Typically, wastewater undergoes a complex series of mechanical, physical, chemical and biological treatments, which point at the elimination of pollutants for the subsequent restitution of purified water to the environment or for reutilization. While anions that form insoluble compounds are removable by precipitation, nitrates are water-soluble and their abatement from aqueous media requires specific approaches. Obviously, among the existing solutions, those that do not involve the production of additional waste materials should be preferred.

Nitrogen occurs naturally under oxidation states comprised between +5 (e.g., nitric anhydride, N_2O_5, and nitrates, NO_3^-) and -3 (ammonia, NH_3, and ammonium ions, NH_4^+). Differing from the other elements of its group, presenting oxidation states limited to ±3 and ±5, nitrogen can form a larger variety of compounds; Tab. 1 lists some exclusively inorganic species.

Human activities have increased environmental nitrate concentrations, causing introduction of large quantities of nitrates into ground and surface waters. While agriculture is a major source, due to the increasing use of nitrogen-containing fertilizers, concentrated livestock and poultry farming, nitrates come also from the industrial production of glass, explosives, as well as from various chemical production and separation processes.

Nitrogen is a fundamental component of living organisms; unfortunately, animals are not able to metabolize the atmospheric molecular nitrogen (N_2), and their nitrogen sources must be phyto-organic. Food is usually the major source of nitrogen, in the form of nitrates: a typical diet provides an average of 75 to 100 milligrams per day of nitrate. Vegetables, particularly spinach, celery, beets, lettuce, and root vegetables are responsible for most of the dietary intake.

Much anthropogenic nitrogen is lost into air, water and soil, causing a cascade of problems for human health and the environment.

Tab. 1 - Inorganic nitrogen compounds.

Oxidation states	Examples
+5	N_2O_5, nitrates, NO_2X, HNO_3
+4	$N_2O_4 \Leftrightarrow 2\ NO_2$
+3	N_2O_3, HNO_2, nitrites, NOX, HX_3
+2	NO, nitrohydroxylamine
+1	N_2O, hyponitrites
0	N_2
-1/3	HN_3, azides
-1	NH_2OH, hydroxylammonium salts
-2	NH_2NH_2, hydrazinium salts, hydrazides
-3	NH_3, ammonium salts

In particular, nitrates are a health hazard because of their metabolic reduction to nitrites. Once ingested, their conversion takes place readily by oral bacteria in the saliva of people of all age groups, but in particular in the gastrointestinal tract of infants. Nitrites are then absorbed in the blood, causing the conversion of hemoglobin into methemoglobin: since the latter is unable to bind oxygen, the capacity of the blood to transport oxygen is decreased, resulting in cyanosis and, eventually, in asphyxia [1]. The concentration of nitric nitrogen in drinking water is usually less than 10 mg/L, in the absence of bacterial contamination. In areas where nitrate contamination is higher, steps must be taken to lower it in order to avoid nitrate-induced methemoglobinemia in infants. Ten mg/L of nitric nitrogen has been adopted by the U.S. Environmental Protection Agency as standard level in the Primary Drinking Water Regulations, chiefly to protect young infants. Young infants are able to convert approximately 10% of ingested nitrate to nitrite, compared to the 5% conversion in older children and adults. Starting from 1993, the *World Health Organization* set the maximum levels allowed in drinking water as follows [2]: 50 mg/L as nitrates and 10 mg/L as nitric nitrogen (15 mg/L NO_3^- for children); more stringent limits are present in the case of nitrites and ammonia (0.5 mg/L in both cases). The European Community directive 98/83/EC sets a still lower limit for nitrites, equal to 0.1 mg/L. While it may be technically possible to treat contaminated (ground)water, it can be difficult, expensive and not totally effective; for that reason, prevention is the best way to ensure clean water, and an effective treatment of wastewater is advisable in order to limit the environmental dispersion of contaminants. In Italy, the discharge of wastewaters in superficial waters requires that the nitrite and nitrate concentrations to be below 0.6 and 20 mg/L, respectively; the level of the latter is set slightly higher, at 30 mg/L, when water is discharged into the sewer. Except for wastewater treatment facilities that are specifically designed to remove the total nitrogen content, most of it will pass through the process into the host waters. The nitrogen content of an industrial wastewater may vary considerably, easily reaching levels as high as thousands mg/L of nitric nitrogen [3]; on the other hand, many industries are expected to produce high nitrogen-containing effluents, including those operating in meatpacking, milk processing, refineries, fertilizer manufacturing, and synthetic fiber processing.

All nitrates are soluble in water, and this creates considerable problems for their removal. A review of academic works pertaining to the electrochemical oxidation/reduction of different kinds of inorganic nitrogen has been recently published [4]; the present contribution will take into consideration a wider spectrum of techniques, specifically focusing on methods that seem to have a direct practical application.

Technologies currently adopted for the removal of nitrates comprise:

a) biological denitrification;

b) ion-exchange resins;

c) reverse osmosis;

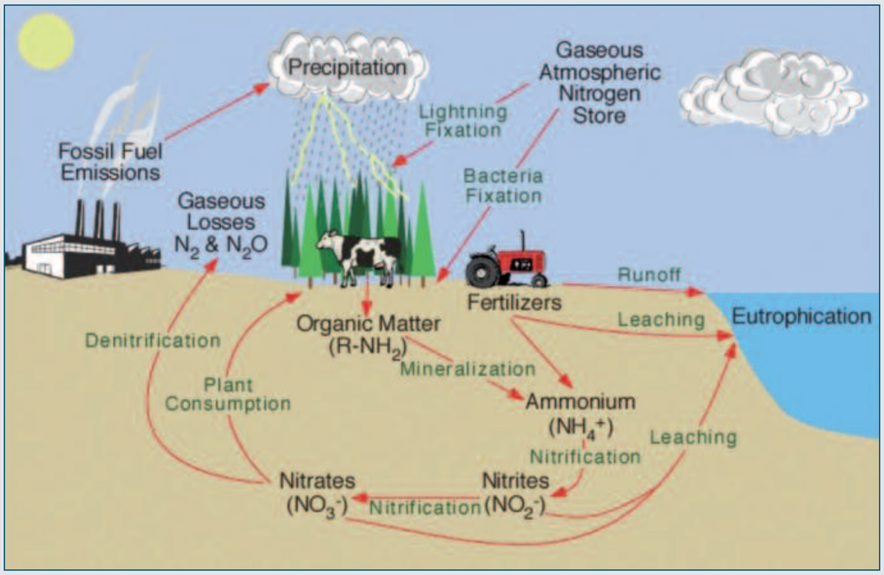
d) chemical reduction.

Each of them has specific limitations, which add to those related with the quality of wastewater to be treated, with the result that the problem has not been solved yet in a unique and satisfying way.

Biological denitrification requires regular maintenance and a steady supply of organic substrate, which may be a problem for industries that do not deal with organic materials; in addition, the process is usually slow and sometimes incomplete.

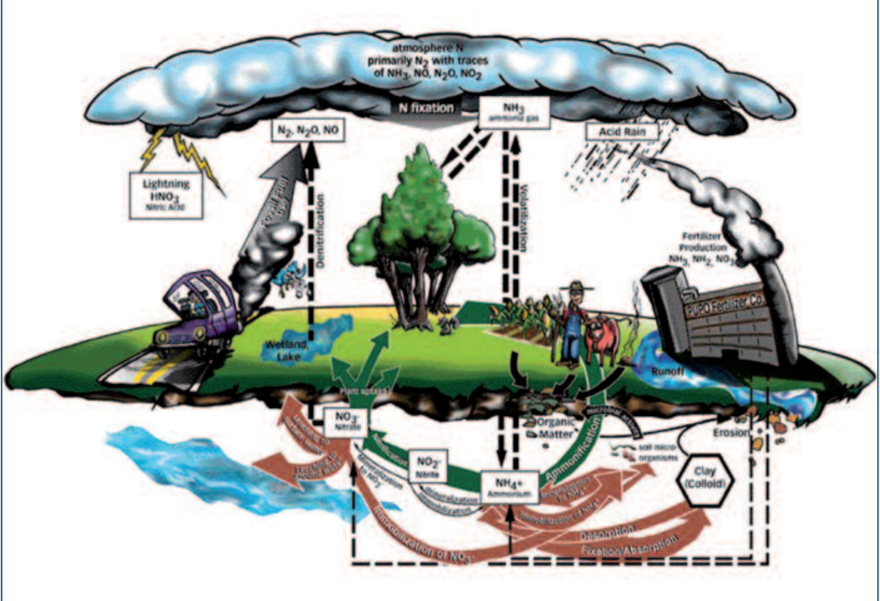
On the other hand, the use of ion-exchange resins, as well as the recourse to reverse osmosis and electrodialysis, require frequent regeneration and lead to the production of secondary solutions. These arise from the accumulation and concentration of undestroyed nitrates, and are of higher salinity, which requires them to be subsequently disposed of. In addition, both the ion exchange resins and the reverse-osmosis membranes have high initial and operational costs.

Thus, among the methods proposed and actually adopted, the chemical reduction process seems particularly interesting, since it allows higher reaction rates, an easier operation control as well as the absence of secondary pollutants in wastewater.



The chemical reduction

There are several ways to perform a chemical reduction in order to convert nitrates into nitrites, a process that essentially requires the nitrate-containing solution to be brought in contact with a metal. Further reaction reduces the nitrites into molecular nitrogen. Since nitrates are very stable, with respect to reduction, operational conditions that allow their transformation into nitrites are usually sufficient to permit subsequent reactions, also with reference to nitrites, leading mainly to the production of ammonia. For this reason, various operational solutions have recently been proposed and patented, with claims of interesting results in terms of yield and selectivity of the reaction process. Since this is a reduction reaction, it is first possible to distinguish among purely chemical processes, catalytic reduction processes, electrochemical processes, and processes that could be called "mixed", as they require the simultaneous/synergistic or subsequent action of more approaches.



Purely chemical reduction

This approach has been described in the literature as early as the end of the Nineteenth century [5]. The process takes advantage of very reactive metals, such as aluminum amalgam or zero-valence iron powder. The latter has recently come back into fashion thanks to the application of permeable reactive barriers for the decontamination of groundwater [6]. Reduction of nitrates can take place either as an indirect or direct process. The former takes place by means of nascent (H) or molecular (H_2) hydrogen, the latter by the activity of the zero-valence metal:

$$Fe^0 \rightarrow Fe^{2+} + 2e \tag{1}$$
$$2H^+ + 2e \rightarrow H_2 \tag{2}$$

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \tag{3}$$
$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \tag{4}$$
$$2Fe^0 + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^- \tag{5}$$

$$NO_3^- + 2H^+ + 2e \rightarrow NO_2^- + H_2O \tag{6}$$
$$2NO_2^- + 8H^+ + 6e \rightarrow N_2 + 4H_2O \tag{7}$$
$$NO_2^- + 8H^+ + 6e \rightarrow NH_4^+ + 2H_2O \tag{8}$$
$$3H_2 + 2NO_2^- + 2H^+ \rightarrow N_2 + 4H_2O \tag{9}$$
$$3H_2 + NO_2^- + 2H^+ \rightarrow NH_4^+ + 2H_2O \tag{10}$$

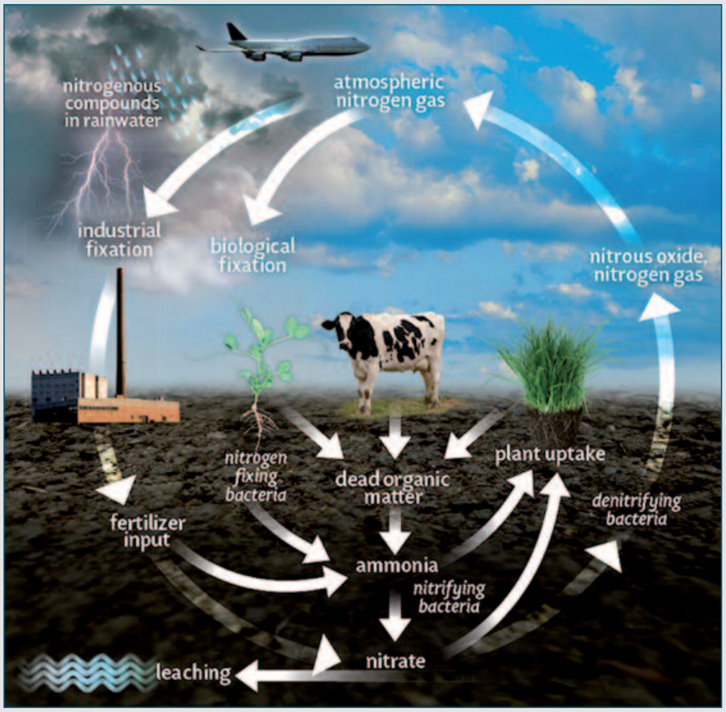
$$10Fe^0 + 6NO_3^- + 3H_2O \rightarrow 5Fe_2O_3 + 6OH^- + 3N_2 \tag{11}$$
$$Fe^0 + NO_3^- + 2H^+ \rightarrow Fe^{2+} + H_2O + NO_2^- \tag{12}$$
$$5Fe^0 + 2NO_3^- + 6H_2O \rightarrow 5Fe^{2+} + N_2 + 12OH^- \tag{13}$$
$$4Fe^0 + NO_3^- + 7H_2O \rightarrow 4Fe^{2+} + NH_4^+ + 10OH^- \tag{14}$$
$$4Fe^0 + NO_3^- + 10H^+ \rightarrow 4Fe^{2+} + NH_4^+ + 3H_2O \tag{15}$$
$$8Fe^{2+} + NO_3^- + 10H^+ \rightarrow 8Fe^{3+} + NH_4^+ + 3H_2O \tag{16}$$

Under aerobic conditions, the dissolved oxygen acts as the preferred electron acceptor (reaction 5): in that case, the primary reaction (consumption of the zero-valence metal) leads to the production of hydroxide ions, rather than to hydrogen. In the absence of oxygen, both nitrates and nitrites can be reduced directly to N_2 by Fe^0 (reactions 1, 7, 11 and 13) or indirectly by hydrogen (reactions 6 and 9). The reduction pathways can also proceed toward the synthesis of ammonia (or ammonium ions), while the dissolution of the zero-valence iron can generate Fe^{2+}, Fe^{3+}, Fe_2O_3 or Fe_3O_4, depending on reaction conditions. Generally, to maintain a favorable reducing environment, continuous additions of acid are necessary; alternatively, the environment must be buffered to guarantee a weak acidity. The reaction rates depend not only on pH but also on the nature of acids used for the pH changes; for further details on this, see ref. [7].

The different chemical reactions reported above indicate that the nitrate reduction causes a concomitant corrosion of the zero-valent iron, with plausible formation of passivating scales (oxides/hydroxides of iron) that limit the long-term reducing action. The removal of such scales is generally accomplished through acid washing or by taking advantage of the acidity of the solution to be treated; in addition, the use of ultrasound for cracking the passivating film allows a multiplication of reaction sites [8].

In any case, the reduction of nitrates by zero-valence iron (but also by the previously cited aluminum amalgam) leads to the formation of ammonia in a nearly quantitative amount.

In order to increase the selectivity towards the production of molecular nitrogen, it has been suggested to work with iron particles whose catalytic activity has been modified by the deposition of noble metals (platinum, palladium, gold) and copper: in this way, the stability of adsorbed intermediate would be changed, facilitating their recombination to N_2. Through the use of zero-valence iron modified with Pd (0.3% wt) and Cu (0.5% wt), the selective formation of N_2 achieved a



30%, which however has to be assessed against a lower reaction rate (especially for pH values ≥ 7) and only a partial conversion, i.e. incomplete reduction of nitrates, with formation of nitrites and ammonia [9].

A further method of chemical reduction, through the use of metals, requires to treat the nitrate-containing aqueous solution with zinc or cadmium (possibly in the presence of copper, silver or mercury as catalysts) [10]. This approach reduces nitrates to nitrites; after that, the nitrite-containing solution is allowed to react with an amide (e.g., urea) to produce nitrogen and carbon dioxide. For both reactions, the pH of the reaction environment seems to play a crucial role: in general, the pH should be between 1 and 6. In the first stage of the reaction (reduction of nitrates to nitrites) the aqueous solution passes in a column containing cadmium powder (granules).

Before introducing the nitrate-containing solution, the metal powder is treated by passing a $CuSO_4$ solution through the column for several times, until complete bleaching (with consequent deposition of copper on the cadmium granules). Subsequently, the nitrate-containing aqueous solution (which has been acidified to pH 1.7 with HCl) is eluted in the column, until complete conversion of nitrates to nitrites (the reaction can be followed spectrophotometrically: NO_3^- at 302 nm, NO_2^- at 354 nm). Due to the nitrate reduction, the cadmium metal is partly dissolved to Cd^{2+} ions:

$$Cd + NO_3^- + 2H^+ \rightarrow Cd^{2+} + NO_2^- + H_2O \tag{17}$$

The solution containing the nitrites is then added with urea and hydrochloric acid, stirred a few times and then left at rest, in an open container, to complete the reaction (the concentration of residual nitrites can be monitored spectrophotometrically). Nitrites should react with urea in a 2:1 ratio, i.e. every mole of removed NO_2^- should produce 1 mole of nitrogen (N_2) and 0.5 moles of CO_2; if urea is added in excess, ammonia is also found in the reaction environment.

As a final point, the solution is electrochemically treated to remove the dissolved cadmium ions (by electroplating), allowing the reuse of this material in the first stage of the process.

In a subsequent patent application [11], the approach just described has been modified through the use of an electrochemical reduction, to be performed in the presence of an amide; urea can be used again, as well as sulfamic acid, formamide or acetamide. The reaction involves once again the combination of two stages: the first stage, electrochemical, implies the reduction of nitrates to nitrites:

$$NO_3^- + 2H^+ + 2e \rightarrow NO_2^- + H_2O \tag{18}$$

the second stage, chemical, involves the reaction between the amide (H_2NA) and the NO_2^- ions:

$$NO_2^- + H_2NA \rightarrow N_2 + AO^- + H_2O \tag{19}$$

If the used amide is sulfamic acid (H_2NSO_3H), sulfates will appear among the reaction products. The described chemical reaction takes place in the volume of the solution, during the electrolytic process. To support their proposal, the authors reported several examples; anyway, the process seems questionable because it requires an amide concentration 5 times higher than that of the nitrates initially present. In addition, the current efficiency of the process did not exceed 50%, with the synthesis of hydrogen, in amounts approximately equal to that of N_2, and of nitrous oxide (N_2O), which was stripped by the electrochemically produced gases (H_2 and O_2).

In another paper, Lee and coworkers investigated the chemical reduction of nitrates by using zinc powder and sulfamic acid [12]. The best results were obtained at acidic pH (around 3), and treating solutions in which the nitrate concentration was not too high (less than 600 ppm); starting from higher nitrate contents, the rate of the process increased but a significant amount of ammonia was produced. The rate depended also on zinc concentration and on the amount of sulfamic acid; however, the latter did not seem to play a role in controlling the ammonia synthesis. A final chemical approach of some interest requires to treat the aqueous solution containing the nitrates (or any other oxidizing agents) with calcium metasulfide (obtained by reacting sulfur and calcium hydroxide) or with potassium polysulfide (obtained from sulfur and potassium carbonate) [13]. The proposed reagents do not seem to be directly available on the market, and should therefore be synthesized *ad hoc* by melting elemental sulfur (S_8) in an inert atmosphere, and then adding the desired amount of $Ca(OH)_2$ or K_2CO_3. The product that forms in the first case (reaction with calcium hydroxide) is a mixture of molecules containing a variable number of sulfur atoms (hence the name metasulfide), insoluble in water; the reaction with nitrate ions determines their conversion to nitrogen, with formation of calcium sulfate that can be removed. In the second case (reaction with K_2CO_3), the synthesized product should have a more precise stoichiometry (maybe K_2S_8) and should be soluble in water; this product is suggested for the removal of chlorine, e.g. in pools. The synthesis requires the heating of sulfur and K_2CO_3 at a temperature not exceeding 185 °C, until effervescence ceases (development of CO_2), and subsequent cooling of the mixture in absence of air and/or humidity.

Catalytic hydrogenation

This approach belongs to the chemical reduction family, since it involves the use of a reducing agent (hydrogen) in the presence of metal catalysts, usually supported on high-surface-area inert materials (e.g., alumina or silica). In some cases, also the support can show a chemical activity, typically as a result of an appropriate stress; in the case of titanium dioxide, for example, activation is attained by an appropriate UV radiation.

A process for the decontamination of water containing nitrites or nitrates through their reduction to molecular nitrogen has been described by Vorlop and coworkers [14]:

$$2NO_3^- + 5H_2 \rightarrow N_2 + 2OH^- + 4H_2O \quad (20)$$
$$2NO_2^- + 3H_2 \rightarrow N_2 + 2OH^- + 2H_2O \quad (21)$$

Both reactions involve the formation of hydroxyl ions in an amount that is equivalent to that of the nitrogen-containing ions removed from the solution. During the process, the alkalinity increase requires continuous adjustment, in order to maintain the pH between 4 and 7.

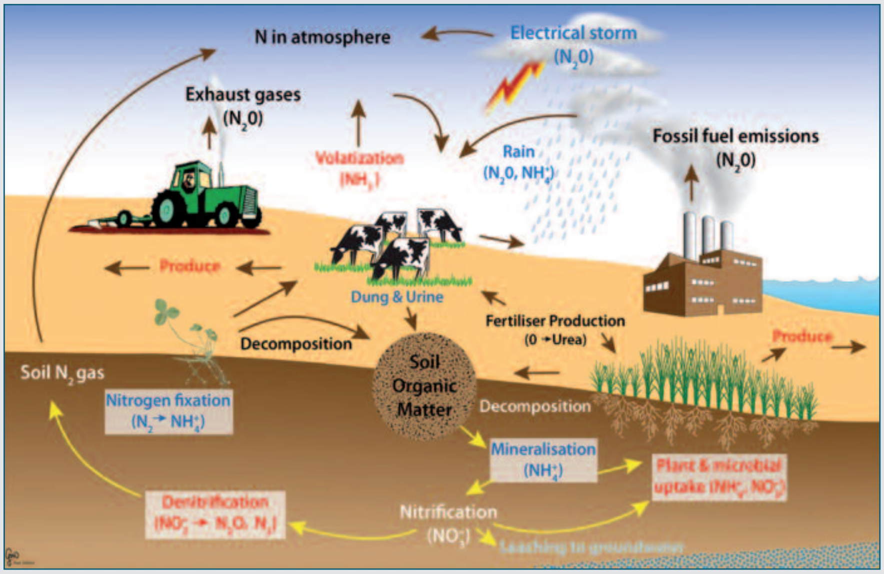
In practice, the solution is treated with hydrogen gas, in order to allow a partial dissolution. However, the solubility of hydrogen in water does not exceed 2 mg/L at atmospheric pressure and for temperatures between 10 and 25 °C. Doubling the pressure (which requires the use of special containers) allows doubling of the solubility of H_2, which obviously increases the reaction rate (greater availability of a reagent).

The patent document contains examples obtained with different catalysts, i.e. modifying either the catalytically active metal or the metal support. With regard to the former, the authors suggest to use palladium and/or rhodium, when the water contains only nitrites; the use of palladium in combination with copper-group metals (copper and silver, in particular), or even to rhodium, is recommended for nitrates. Suitable supports are activated carbon and porous ceramic materials such as aluminum oxide (γ-Al_2O_3), silica (SiO_2) and alumino-silicates.

The patent application describes the removal of nitrites through examples 1, 2, 3 and 6, while examples 4, 5 and 7 relate to the treatment of solutions containing nitrates. In the first case, the most appropriate catalyst appears to be palladium (5% wt) supported on γ-Al_2O_3, while, for the treatment of nitrates, the use of a mixture of palladium (2% wt) and copper (~0.5% wt) is suggested, on the same support (γ-Al_2O_3). Examples pertaining to continuous mode processes recommend to work with solutions at a pH of 6 and at a temperature of 10 °C, in order to maximize the dissolution of hydrogen in water. In the case of nitrates (example 7), the specific rate of conversion was equal to 19 mg NO_3^- per hour and gram of catalyst.

A very similar approach is described in a Japanese patent application [15], which concerns the abatement of nitric acid by catalytic reduction; the catalyst is a mixture of Pt:Cu:Sn at a molar (or atomic) ratio of 100:25:4, on alumina, prepared from a commercial Pt-alumina product (Wako Pure Chem, Pt: 5%).

Two L of nitric acid solution at 10,000 mg/L (pH=0.8) are treated with 1 g of catalyst and shook for 120 minutes under bubbling hydrogen (1L per minute). A detailed analysis of obtained results, in terms of formed products and selectivity, is unfortunately not reported in the patent application. Four different bimetallic catalysts, supported on activated carbon, are described and compared in a Portuguese research [16]. Among the studied formulations, the rhodium-copper (1%-1%) couple seems to be the most catalytically active, leading to a 90% conversion of nitrates after 5 hours of reaction (35% N_2, 59% NH_4^+, 6% NO_2^-); unfortunately, the process lacks in selectivity. Under the experimental conditions of a *batch* reactor at atmospheric pressure, thermostated at room temperature, 790 mL of de-ionized water +400 mg of catalyst were placed under magnetic stirring at 700 rpm. Then, a mixture of H_2+CO_2 (1:1) was bubbled at a flow rate of 200 Ncm³/min for 15', to remove air and adjust the pH to ~5.5. Subsequently, 10 mL of $NaNO_3$ were added to the system, in such a way to obtain a synthetic waste with an initial concentration of 100 ppm of NO_3^-. Another scientific report makes a comparison between catalytic and photocatalytic reductions, mentioning the use of a bimetallic catalyst supported on titanium dioxide (Pd-Cu/TiO_2, 4.2% Pd-1.2% Cu) [17]. The study observed the reaction in the presence of the following media: H_2, formic acid (which acts as a reducing agent), the mixture of both, and with UV irradiation.



Formic acid is the reducing agent (instead of H_2) for nitrates: in presence of a noble metal, it tends to decompose to H_2+CO_2, thus representing an *in situ* source of hydrogen while allowing for a pH buffering (thanks to the action of CO_2). In the presence of HCOOH, the reduction of nitrates (0.8 mmol/L) is initially fast but then decelerates, ceasing at a 50% conversion only; nitrites are not synthesized, and the production of ammonium ions remains low (0.03 mmol/L). In the presence of hydrogen, on the contrary, the reaction is initially slow but then proceeds rapidly, allowing a total reduction of nitrates; nitrites are synthesized and then eliminated, with formation of about 0.08 mmol/L of ammonium ions. Finally, the use of a H_2+HCOOH mixture allowed for intermediate results: elimination of nitrates, no formation of nitrites and synthesis of about 0.07 mmol/L of ammonium ions.

The work is of interest, especially as far as the action of formic acid is concerned, since it seems to inhibit the formation of nitrites; the HCOOH/NO_3^- stoichiometric ratio required for a selective reduction to N_2 at acidic pH should be equal to 5/2:

$$2NO_3^- + 2H^+ + 5HCOOH \rightarrow N_2 + 5CO_2 + 6H_2O \qquad (22)$$

However, other studies have shown that optimum activity is obtained only for larger ratios, equal to 5 at least. In the above described work, the authors operated with an even larger amount of formic acid (ratio of 25), in order to have a concentration of HCOOH relatively constant during the reaction; though this may make sense in an academic research context, it does not appear acceptable for a real application.

Photocatalytic reduction

The last example has introduced the photocatalytic approach. This methodology exploits the properties of certain materials to absorb electromagnetic radiations bringing active sites to an excited state condition, from which they have then to decay by means of charge transfer or light emission phenomena. The used materials include inorganic semiconductors or very large and complex organic molecules. In the context of inorganic photo-chemistry, titanium dioxide is one of the best-known and most studied materials. The light-induced charge separation allows the formation of free electrons, creating so-called "electronic holes": the latter are responsible for subsequent oxidation reactions (in order to compensate for the formed electronic gap), while the former may induce photo-catalytic reduction processes.

A specific example is the reduction of nitrates to molecular nitrogen, in the presence of substances that operate as *hole-scavengers* (for allowing the reduction reaction, the oxidizing capacity of the system has to be "neutralized"). The process requires the presence of suitable metal centers, acting as active sites, and that of "sacrificial" electron donors such as methanol, ethanol, EDTA, oxalic acid, formic acid, sucrose, or others [18]. What happens has already been briefly mentioned above: in the case of formic acid, the photocatalytic process leads to the formation of CO_2 and nascent hydrogen, and the latter allow the reduction reaction. In acidic media (pH≈2.5), the use of formic acid allows a 98% conversion of nitrates, with a 100% selectivity to molecular nitrogen formation; as the pH shifts to less acidic values, both the conversion yield and the selectivity change, with formation of nitrites and ammonium ions. The following experimental conditions were investigated: 250 mL of solution containing 440 mg/L nitrates, 0.25 g of catalyst (1% wt Ag/TiO_2), 0.04 mol/L *hole scavenger* and 30 minutes of irradiation (125 W, mercury lamp - see Fig. 1). The authors propose this approach in case of small water treatment plants, in particular through the use of solar irradiation.

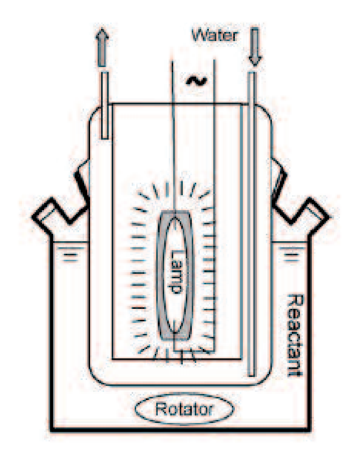


Fig. 1 - Scheme of a reactor for photocatalytic experiments (from [18])

A subsequent investigation, comparing Cu/TiO_2, Fe/TiO_2 and titanium dioxide modified with silver, has confirmed the higher photocatalytic activity of the latter [19]. The authors of this study used a *batch* reactor containing 660 mL of water and 250 mg of catalyst. The solution, degassed with N_2 and treated with ultrasound for 15', was heated to 34 °C and pre-irradiated for 30' with a mercury lamp (110 W); after adding the nitrates (100 ppm) and the *hole-scavenger* (0.04 M), the reaction was monitored by sampling every 15', for a total time of 3 hours. Formic acid proved to be still the best chemical agent, in comparison with acetic acid and the sodium salts of both. A complete reduction of nitrates, with a 100% selectivity, was attained, after an initial induction period (approximately 30'), the rate of the reaction catalyzed by 1% wt Ag/TiO_2 resulting in 287 μmoles (~18 mg NO_3^-) per minute and per gram of catalyst.

Electrochemical reduction

Among the mentioned chemical reduction methods, patent application US 6,436,275 requires to perform a process first stage through the use of a particular reducing agent: the electron [11]. The electrochemical approach may in fact represent a quite effective de-polluting way, which adds the electric parameter to the usual chemical variables (pressure, temperature, concentration of one or more reagents...) and, exploiting it, the ability to inject energy into the system, modifying the stability of reagents and products, as well as that of any other transient species. As known, in aqueous media a sufficiently negative polarization for the working electrode (cathode) results in the reduction of protons to hydrogen (acidic media), or in the reduction of water to hydrogen and hydroxyl anions (alkaline media). These processes take place at potentials close to zero (*vs.* RHE) on cathodes with high catalytic activity (such as platinum, $i_0 = 10^{-4}$-10^{-2} A/cm^2), while they may require quite significant overpotentials if the material at which the reduction reaction takes place does not exhibit stabilizing properties for the hydrogen radicals that are created as a result of proton discharge. Mercury is among the metals that exhibit a very low exchange current density for the hydrogen evolution reaction (i_0 = 10^{-12}-10^{-10} A/cm^2); others scarcely active materials are cadmium, lead, zinc, tin, silver and bismuth [20].

Owing to its low catalytic activity towards the hydrogen evolution reaction, bismuth was chosen as electrode material (cathode) in an investigation on the electrochemical reduction of nitrates [21]. The paper reports that many byproducts are formed, such as NO_2, NO_2^-, NO, N_2O, NH_2OH, NH_3 NH_2NH_2; in addition, both the selectivity to N_2 and the reaction rate are generally low. The same authors have been working on the subject since 2005, showing that good selectivities (N_2: 85-92%) and good reaction rates are possible when using tin cathodes. The rate of the process seems to depend on the concentration and on the crystallographic dimension of both the cation ($Li^+<Na^+<K^+<Cs^+$) and the anion ($F^-<Cl^-<Br^-<I^-$) of the supporting electrolyte. Unfortunately, the reduction of nitrates at tin cathodes requires a quite negative electrode potential (-2.8V *vs.* Ag/AgCl), at which tin forms hydrides or metal alloys with the cation of the supporting electrolyte: as a consequence, this “cathodic corrosion” cause the pollution of the solution subjected to treatment.

At bismuth cathodes, the selectivity to N_2 is around 58-65%, with a 95% conversion of nitrates and formation of 1.8-2.6% of nitrites; production yields of NO and NH_3 depend on the applied potential: NO increases from 7.2 to 22% and NH_3 decreases from 19 to 3.8%, when the electrode potential is changed from -2.2 to -2.9V *vs.* Ag/AgCl. Anyway, the authors assert that bismuth is a promising cathode material for the reduction of nitrates, especially in the light of its lower corrosivity and lower toxicity (compared to tin).

High catalytic activities were observed with tin cathodes modified with noble metals (Rh, Ru, Ir, Pd and Pt); however, reaction products were strongly dependent on the nature of the electrode material [22]. For an electrode potential of -0.2V *vs.* Ag/AgCl, the main product of NO_3^- reduction at Sn/Rh was N_2O (59%); other species were NH_3^+OH (22%) and NH_4^+ (19%). At Sn/Ru, mainly hydrogenated substances were formed (NH_3^+OH: 46%, NH_4^+: 41%), while Sn/Pd led to a 78% N_2O (NH_3^+OH: 9%, NO_2^-: 13%). Finally, Sn/Ir and Sn/Pt led to a distribution of substantially similar products (N_2: 17%, NO_2^-: 17%, N_2O: 11%, NH_3^+OH: 56% at the former electrode, N_2: 26%, NO_2^-: 10%, N_2O: 7%, NH_3^+OH: 46%, NH_4^+: 41% at the latter).

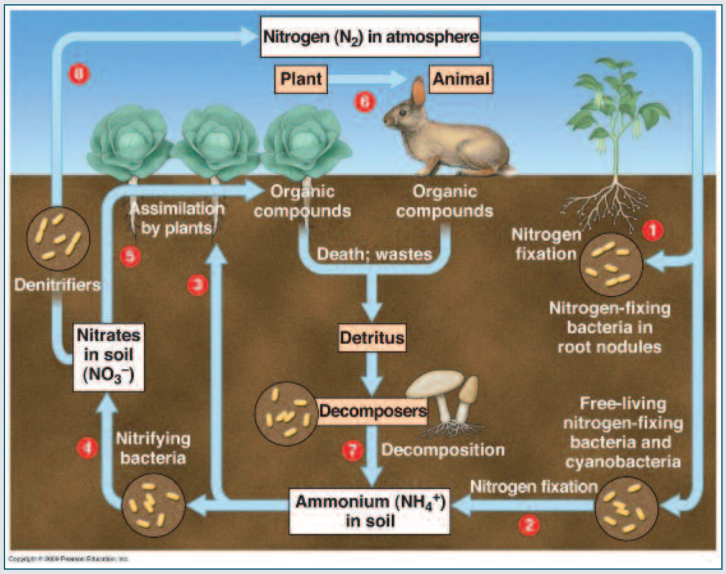
Both the formation and variety of byproducts limit the applicability of the method; however, since a few cathode materials exhibit some selectivity toward N_2, re-oxidation of undesired species, and repetition of the reduction process, may succeed in the removal of nitrates with simultaneous minimization of byproducts. This approach has been investigated in an undivided cell, using a Ti/IrO_2-Pt anode, different cathodes (Fe, Cu and Ti) and in presence of NaCl as a mediator of oxidation [23].

The best performances were obtained working with an iron cathode, both in absence and in the presence of NaCl in solution; the presence of the oxidation mediator (0.5 g/L) allowed to reduce the formation of both nitrites and ammonia, leading to a 87% nitrate conversion in 3 hours, with 100% selectivity towards the formation of N_2. All tests were carried out in a 200 mL electrolysis cell, with an initial nitrate concentration of 100 mg/L and in the presence of 0.5 g/L of Na_2SO_4 as the supporting electrolyte; anode and cathode were spaced 8 mm and presented geometric surfaces of 40 cm^2 each.

The role of pH, electrode potentials (at both the anode and the cathode) and cathode/anode surface area ratio were highlighted in a subsequent work by Reyter *et al.* [24]; experiments were carried out using a copper cathode and a Ti/IrO_2 anode. Under optimized conditions, the simultaneous reduction of nitrate and oxidation of ammonium allowed a 100% selectivity to nitrogen; however, the authors stated that further investigation is required, e.g. to increase the rate of nitrate removal.

More recently, the same authors published the outcomes of their further investigations, which were focused on a cathode material optimization: copper, nickel and cupronickel alloys were considered [25]. Significant improvement in the nitrate removal was obtained with a $Cu_{70}Ni_{30}$ cathode, which showed good corrosion resistance as well as high efficiency and selectivity for the reduction of nitrate to ammonia. Among the investigated materials, $Cu_{70}Ni_{30}$ allowed the highest current efficiency: about 75% at the beginning of the electrolysis (after 30’), with a decrease to 42% after 3 hours (when the reactant concentration was reduced from 600 to less than 100 ppm).

A different approach has been described by Reynes and Hadjiev [26]. The process involves an electrochemical treatment at a pH between 2 and 5 (preferably around 3), in the presence of a zinc salt (Zn^{2+} at a concentration ≥0.5 g/L), which will be subsequently removed (e.g., by electrodialysis). The treatment can be carried out using graphite electrodes, or graphite anodes and zinc cathodes. In order to reduce the concentration of forming ammonia, an oxidation with ClO_2 (at pH values close to 2) is provided after the electrochemical treatment. As



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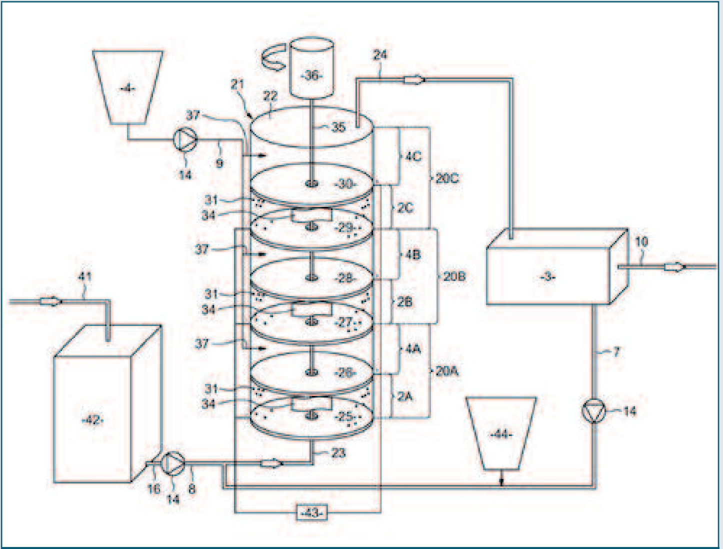

Fig. 2 - Schematic representation of a processing device for carrying out a mixed electrochemical/chemical treatment of nitrate-containing liquid media (from [26])

shown in Fig. 2, the authors suggest a tubular structure, in which the electrochemical reduction and chemical re-oxidation stages are mutually spaced so as to allow a complete removal of the nitrates initially present. Na_2SO_4 (0.01 M) is used as supporting electrolyte.

Other approaches

For the sake of completeness, it is worth mentioning the use of ion-exchange resins, adsorption with adsorbent materials, as well as the initially quoted biological approach.

Ion-exchange resins were recently tested for the removal of nitrates from landfill leachates. These were previously subjected to electrochemical oxidation for the removal of COD and ammonia [27]. Since the oxidation of NH_3 and/or NH_4^+ led to N_2 and, in part, to NO_3^-, the use of selective anion exchange resins can be a suitable approach, given the concomitant presence of sulfates and chlorides. The selectivity of *Purolite A 300* resin proved to be quite low (a predictable outcome, given that it is a strong non-selective base) but still able to provide performance comparable with those of *Purolite A 520E* resin, which was specifically designed for nitrate removal. Regeneration of both resins can be accomplished by washing with NaCl 4.8% wt: the first one requires a regenerating solution volume 15 times larger than the volume of the resin (time required ≈ 20'), while 10BV (bed volume) seems sufficient for the second resin, with similar treatment times. The removal efficiencies ranged between 92 and 100%. The nitrate-rich solutions produced during the regeneration phase show concentrations varying between 4.5 and 5.2 g/L of NO_3^-. This corresponds to a 5-fold increase, compared to the solution initially treated. In the case of the non-selective resin, a lower sequestering capacity for nitrates was confirmed by the presence of 1.6 g/L of sulfate in the produced eluates. Concerning the adsorption, a comprehensive review by Bhatnagar and Sillanpää has recently appeared [28]; among the materials considered in the review, which took into consideration 25 different sorbents, double layered hydroxides/hydrotalcite-type compounds and modified chitosan showed the highest nitrate uptake. The initial nitrate concentration, as well as the presence and concentration of other competing ions, are two factors playing a major role for the selection of a suitable sorbent; in addition, an adjustment of water pH may be required. Actually, the task is made even more tricky by the doubtful reusability of spent adsorbents.

To consider the biological denitrification, the treatment of effluents from the salmon industry by anaerobic digestion can be discussed [29]. It involves the exploitation of tubular reactors with immobilized biofilm. Nitrate reduction efficiency was close to 98% (starting from concentrations ranging between 20 and 280 mg/L NO_3^-), but nitrogen removal varied from 50 to 88%, depending on COD content (lower efficiencies were obtained for higher levels of organic matter), with production of ammonia on account of the anaerobic digestion.

The use of three-dimensional bio-electrochemical reactors was also proposed, to increase the denitrification yield [30]. With reference to Fig. 3, the reactor consists of (a) a central anode (∅ 45x200 mm) in β-PbO_2 modified with a fluorinated resin, as to increases its corrosion resistance, (b) a peripheral cylindrical cathode made of carbon fibers (*ACF*, ∅ 130x160 mm) with an active area of 500 cm^2 (important for microorganisms immobilization), and (c) a 3D bed of activated carbon (*AC*) with a volume of about 500 cm^3 placed between the above two electrode devices. To complete the system, a cellulose acetate membrane is placed near the anode to prevent the movement of oxygen toward the cathode chamber (*AC+ACF*).

Finally, denitrifying microorganisms are immobilized on both the cathode surface and the *AC* bed. The paper does not provide information about the specific surface of the coal. Working with a current of 23 mA and a 200 mL/min solution flow (30 mg/L N-NO_3^-, 26 mg/L TOC, pH 7.5, T = 35 °C), denitrification rate reached 0.288 mg of nitric nitrogen per cm^2 per day (99.8% removal), with current efficiencies of nearly 250% (thanks to the reducing action of synthesized hydrogen plus the activity of denitrifying microorganisms). The figure per unit area has probably to be referred to the *ACF* cathode only. Similar to the above discussed utilization of ion-exchange resins - the analogy consists in the production of an effluent (75-80% of the initially treated volume) substantially free from nitrates, and in the disposal of a concentrated solution (20-25% of the initial volume) - is the approach described in ref. [31] and schematized in Fig. 4. The method, called capacitive deionization, is based on the physical principle of electrostatic capacitors. It intelligently exploits

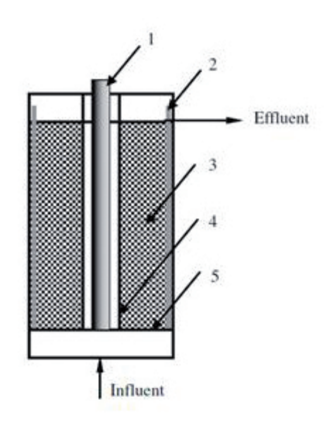

Fig. 3 - Schematic representation of a 3D reactor: (1) anode; (2) ACF; (3) AC; (4) membrane; (5) hydraulic distribution board (from [30])

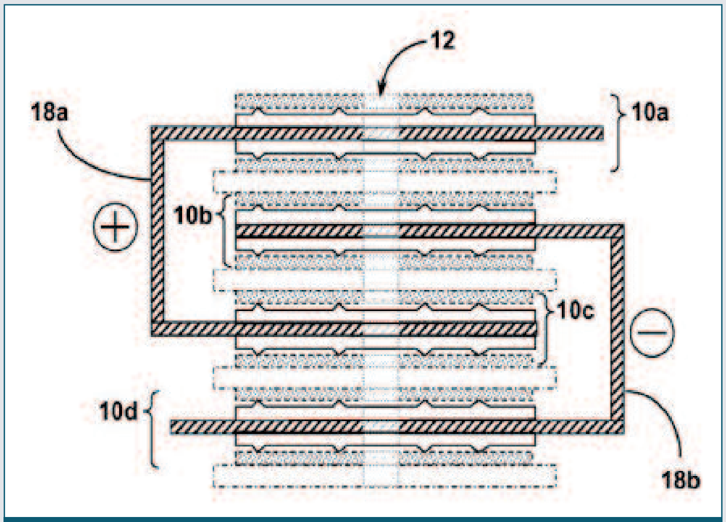

Fig. 4 - Partially schematic cross-sectional view of a number of the subassemblies of the invention, stacked and connected in series (from [31]).

the parallel between a physical capacitor (two metal plates separated by a dielectric) and the interphase phenomena that arise at the surface of a polarized electrode, immersed in an electrolyte solution (formation of an electrical double layer, with adsorption of charged material at the electrode-solution interphase). Being a "heterogeneous" approach, in the sense that an active role for the electrode surface is expected, the technology is, at the same time, both simple (charging and discharging of a capacitor) and quite advanced (use of materials with high surface area, use of ion-exchange membranes, use of operational controls by computer). However, for allowing the abatement of nitrates, a preliminary chemical treatment is required, in order to remove from water the ionic content due to metal cations and "precipitable" anions. Let us recall here that the problem of nitrates is their substantial complete solubility in water.

The reference to the concept of "*substantial complete solubility in water*" is not accidental. It provides the possibility to discuss a further resolution to the issue of this technical review. "Nitron" is an organic compound ($C_{20}H_{16}N_4$) consisting of one cycle of 5 atoms (3 nitrogen and 2 carbon atoms), with phenyl substituents (see Fig. 5). It is chemically a base (such as the amines) and forms with nitric acid an adduct that is practically insoluble in water.

The molecule (CAS: 2218-94-2) is cited in the literature under different names: *1,4-diphenyl-3-phenylamino-1,2,4-triazolium hydroxide*, *3,5,6-triphenyl-2,3,-5,6-tetraazabicyclo [2.1.1]hex-1-ene*, *4,5-dihydro-2,4-diphenyl-5-(phenylimino)-1H-1,2,4-triazolium hydroxide*. It can be purchased, for example from Sigma Aldrich (Fluka) and Alfa Aesar, at costs that vary depending on quantity (1 g: 18 €, 50 g: 260 €). The use of *nitron* for the gravimetric (quantitative) determination of nitrates was originally suggested by Busch in 1905 [32].

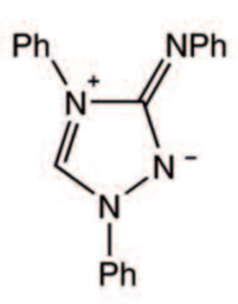

Fig. 5 - Chemical formula of Nitron

The compound has a molecular weight of 312.2 daltons, while the HNO_3-adduct reaches 375.2 daltons. Consequently, the "salt" weighs six times more than the free acid, with the result that any weighing error on the precipitate influences for 1/6 on the determination of the quantity of HNO_3, or for 1/27 only on the amount of nitrogen.

The product is soluble in alcohol, benzene, chloroform, acetone, acetic acid and ethyl acetate, slightly soluble in other ethers and practically insoluble in water; in addition to HNO_3, insoluble adducts are formed with HBr, HI, HNO_2, H_2CrO_4, $HClO_3$ and $HClO_4$. Visser (1907) reported that also oxalic and salicylic acids form insoluble precipitates with *nitron* in water, while soluble salts are formed with sulfuric acid, hydrochloric acid, formic acid, acetic acid, boric acid, benzoic acid, tartaric acid, citric acid and phosphoric acid [33].

The reagent, dissolved in 5% acetic acid (1 g of *nitron* in 10 mL of acid), is stored in a dark bottle until use, as the solution decomposes when exposed to light. Therefore, it should be prepared in small amounts when necessary. The use of the reagent requires the addition of sulfuric acid to the solution containing the nitrates (max 1.875 g/L) and heated to boiling temperature, and then the addition of a volume of *nitron* equal to 1/7-1/8 of the solution volume to be treated (e.g.: 80 mL of solution + 12-15 drops of H_2SO_4 + 10-12 mL *nitron*). After stirring, wait for 30 to 45 minutes.

During cooling, needle-like crystals of *nitron*-nitrate segregate. Since the procedure aims at a quantitative analysis, it is suggested to place the container in an ice bath for half an hour, before filtering the crystals using a ceramic filter (*Gooch*) under slight vacuum.

The precipitate is washed with 10 mL of cold water (to be used in two successive portions) and then dried at 105 °C for one hour prior to weighing. To ensure a complete recovery of nitrates, the solution can be re-heated to boiling, added with a small amount of reagent, and then cooled as described. Obviously, an approach having a de-polluting character (as opposed to the above analytical one) may pass over a complete recovery (removal may be limited as to respect the legislation limits), with obvious simplifications and reduction of operating times. As anticipated, *nitron* is relatively expensive but can be easily recovered from the precipitates.

These should be treated with diluted ammonia and heated to 60 °C (while not explicitly reported, a conversion of the nitrate salt into a hydroxide is likely to occur); the solid mass is then left to "digest" in 5% acetic acid until complete dissolution. Nitrates dissolve in the ammonia solution as ammonium salts, which could be recovered and used e.g. in agriculture (such as fertilizers and soil conditioners).

Nitrate removal "by precipitation" looks relatively simple, and the recovery of the reagent is expected to allow repeating the process indefinitely, albeit with minimal losses of substance.

The approach seems feasible, and economic and practical assessments should be made basing on the volume of solution to be treated. Furthermore, the reagent can be synthesized (a synthetic route is described in ref. [34]), in case the acquisition on the market would not seem economically feasible.

Tab. 2 - Removal of nitrate by different approaches: M indicates a noble-metal (i.e., Ru, Rh, Pd, Ir, or Pt); initial nitrate concentration is always referred as mg/L of nitric nitrogen; the total ion concentration limit for capacitive deionization is based on an economic evaluation.

Ref.	Approach	Reducing agent(s)	Initial pH	Initial NO_3^- (mg-N/L)	Reaction	Reaction rate (best conditions)	Denitrification (best conditions)	N_2 selectivity (best conditions)	Byproducts
[7]	Chemical reduction	Fe powder	2, 3, 4	50 - 400	pseudo-first order	K_{obs}: 0.0353 min^{-1}	Complete	NA	NA
[8]	Chemical reduction	Fe powder + ultrasounds	2, 4	22	NA	NA	Not complete	NA	NA
[9]	Chemical reduction	(Pt, Pd, or Au)-Cu on Fe	5 - 8.5	40	pseudo-first order	K_{obs}: 0.0422 min^{-1}	Complete	4.4 - 28.9%	NH_4^+ (19-40 mg-N/L) NO_2^- (1.0-4.8 mg-N/L)
[10]	Chemical reduction	Cu (catalyst) + Cd (reactant) + amide	< 5	225	NA	NA	Complete	NA	NO_2^-, Cd^{2+}
[11]	Electrochemical/ Chemical reduction	DC + sulfamic acid	< 8	250	NA	NA	NA	25.5%	Traces of NO and N_2O
[12]	Chemical reduction	Zn powder + sulfamic acid	2 - 3.5	65 - 225	NA	NA	Almost complete	NA	NH_3 (8-25%)
[13]	Chemical reduction	Metasulfides	Very alkaline	NA	NA	NA	Complete	100%	NA
[14]	Catalytic hydrogenation	H_2, M-Cu on Al_2O_3	4 - 7	22	NA	0.37 mg NO_3^- $(min \cdot g_{catalyst})^{-1}$	NA	NA	NH_4^+ (0.3 mg/L)
[15]	Catalytic hydrogenation	H_2, Pt-Cu-Sn on Al_2O_3	< 2	2250	NA	0.82 mg NO_3^- $(min \cdot g_{catalyst})^{-1}$	NA	NA	NA
[16]	Catalytic hydrogenation	H_2, M-Cu on Al_2O_3	5.5	22	NA	NA	Not complete	75%	NO_2^-, NH_4^+
[17]	Photocatalytic hydrogenation	H_2, + HCOOH, Pd-Cu/TiO_2, UV	~ 4	11	NA	~ 3 mg NO_3^- $(min \cdot g_{catalyst})^{-1}$	98%	86%	NH_4^+ (1.2 mg/L)
[18]	Photocatalytic reduction	HCOOH, Ag/TiO_2, UV	< 3	100	NA	~ 3.67 mg NO_3^- $(min \cdot g_{catalyst})^{-1}$	98%	100%	NH_4^+ (0.14 mg-N/L) NO_2^- (0.4 mg-N/L)
[19]	Photocatalytic reduction	HCOOH, Ag/TiO_2, UV	< 3	22	NA	~ 4.33 mg NO_3^- $(min \cdot g_{catalyst})^{-1}$	Complete	100%	NH_4^+
[21]	Electrochemical reduction	DC, cathode: Bi	< 7	700	complex	0.2 mM min^{-1}	95%	58 - 65%	N_2O (7-22%) NH_4^+ (3.8-19%) NO_2^- (1.8-2.6%)
[22]	Electrochemical reduction	DC, cathode: M-Sn	~ 1	140	complex	NA	60%	87%	NH_3^+OH, NH_4^+, N_2O, NO_2^-
[23]	Electrochemical reduction	DC, cathode: Fe, Cu or Ti, anode: IrO_2-Pt, NaCl	~ 7	100	complex	< 0.1 mM min^{-1}	87%	100%	NO_2^-, NH_3
[24]	Electrochemical reduction	DC, cathode: Cu, anode: IrO_2, NaCl	12	1,400	complex	≈ 0.02 mM min^{-1}	30%	100%	NO_2^-, NH_3
[25]	Electrochemical reduction	DC, cathode: $Cu_{70}Ni_{30}$, anode: IrO_2, NaCl	12	140	complex	< 0.15 mM min^{-1}	70%	100%	Not detected
[26]	Electrochemical/ Chemical reduction	DC, cathode: Zn, anode: C, ClO_2	< 4	33	complex	< 0.1 mM min^{-1}	87%	NA	NH_4^+ (11.5 mg/L)
[27]	Ion-exchange	Organic resin	~ 7	225	---	~ 40 mg NO_3^- g^{-1}	> 90%	---	---
[27]	Adsorption	Various materials	---	up to 700	---	up to 100 mg NO_3^- g^{-1}	---	---	---
[28]	Biological denitrification	Biofilm	~ 7	up to 65	---	≈ 0.02 mM d^{-1}	88%	---	---
[29]	Bio-electrochemical	DC, cathode: C, biofilm	7.5	30	---	0.28 mg NO_3^- cm^{-2} d^{-1}	99.8%	---	NO_2^- (0.08 mg/L)
[30]	Capacitive deionization	(electrostatic approach)		< 6,000 (total ions)	---	~ 20 mg L^{-1} min^{-1}	80% (total ions)	---	---

Conclusions

In concluding this technical review, the impression is that the problem of nitrate removal from wastewater has potentially multiple solutions (a summary of potential approaches is presented in Tab. 2). Quite diluted solutions can be treated successfully with a capacitive deionizer, but the same approach would not be effective with more concentrated solutions: several units in series would be necessary, with large volumes of waste to be disposed (hence, the process loses any attractiveness). The chemical [13] and electrochemical [23-26] reduction methods seem promising, and their implementation quite easy; unfortunately, they are not readily feasible [35], and further investigation is required. On the other hand, the bio-electrochemical approach [29] and the methods based on ion-exchange resins [27] can be of interest, even if somewhat tricky. For sure, more operative lines should be available for the latter, so as to eliminate discontinuation of treatment during the resin regeneration stage. As a workable alternative, the chemical precipitation (with the use of *nitron*) deserves to be taken into account: it is obviously a discontinuous approach, requiring the availability of multiple containers for storing the solutions before the treatment, as well as those being treated; however, the common physico-chemical treatments suffer from the same limitations. Moreover, chemical precipitation would allow the treated water to be fully recovered in the system, while the initial "problem" would be converted in the synthesis of an economically exploitable product, resulting in abatement of disposal costs. A further strength of the chemical precipitation lies in the fact that it takes place in a homogeneous phase, any other solution to the problem involving the addition of solid (insoluble chemicals or electrode surfaces) or gaseous phases, which necessarily cause problems and limit the speed of the process.

Acknowledgements: The present review was prompted by *Ricerca Chimica s.n.c.*, Vighizzolo d'Este (PD), Italy. SF thanks Dr. Francis Hirsch and Dr. Elena Tamburini for proofreading the manuscript and for helpful discussions.

Born in 1972, Sergio Ferro has a PhD in Chemical Science and works as a research assistant at the University of Ferrara since November 2000. Author of about fifty papers on international journals, co-author in a couple of book chapters and in five patents, he received both national and international awards for the quality of his work (Electrochemistry Division award for the best PhD thesis, conferred by the Division of Electrochemistry of the Italian Chemical Society, in 2002; Oronzio DeNora Foundation Prize for Electrochemical Technology and Engineering, conferred by the International Society of Electrochemistry, in 2003). His research activity has been frequently focused on practical aspects, being prompted by a number of industries or public/private entities; competences include the preparation and characterization of advanced electrode materials (mainly anodes for industrial applications: oxygen and chlorine evolutions), the utilization of electrochemical methods for the remediation of soils and wastewater, and the synthesis and applicability of disinfectants.

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RIASSUNTO

Rimozione dei nitrati dagli scarichi industriali

I nitrati sono presenti nelle acque principalmente a causa dell'inquinamento organico causato dagli agglomerati urbani; tuttavia, altre importanti cause di contaminazione sono i fertilizzanti usati in agricoltura, gli scarichi provenienti da alcune industrie, ed alcuni processi di combustione. Tipicamente, le acque reflue subiscono tutta una serie di trattamenti meccanici, fisici, chimici e biologici, allo scopo di consentire l'eliminazione degli inquinanti ed una successiva restituzione dell'acqua purificata all'ambiente, oppure un suo riutilizzo. Contrariamente ad altri anioni, che formano composti insolubili e sono pertanto rimovibili per precipitazione, i nitrati sono solubili in acqua ed un loro abbattimento dalle acque richiede approcci specifici; tra le soluzioni percorribili, e che verranno qui prese in considerazione, risultano ovviamente preferibili quelle che non comportano la produzione di rifiuti supplementari.