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Fate of inorganic nitrogen species under homogeneous Fenton combined with electro-oxidation/reduction treatments in synthetic solutions and reclaimed municipal wastewater

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HIGHLIGHTS

- Nitrite could be removed during the electrolysis in synthetic media and reclaimed wastewater.
- Nitrate could not be released in reclaimed wastewater unlike in synthetic media.
- Ammonium cation accumulated in synthetic solution while it decreased in real samples.
- Chlorine species interfered directly on NH_4^+ decay.

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ABSTRACT

The fate of inorganic nitrogen species has been studied for the first time in electro-Fenton (EF) conditions in acid media. A redox cycle is first obtained and validated with a kinetic model in synthetic solution and highlights the removal of nitrite that is quickly oxidized into nitrate while the reduction conditions are sufficient to reduce nitrate into ammonium cation. However, NH_4^+ and gaseous nitrogen accumulate in such solution. The study in reclaimed municipal wastewater emphasize the removal of NH_4^+ with formation of chloramines in the presence of initial chloride ions, a species widely present in wastewater effluent. Contrastingly, NO_3^- remain constant all along the electrolysis even after 2.1 Ah L^{-1}. The oxidation conditions were not sufficient to produce perchlorate while chlorate accumulated in solution. Therefore, it limits the use of EF for direct use for drinking water purpose but could be considered as complementary treatment for wastewater reuse applications.

1. Introduction

The occurrence of compounds such as pesticides, pharmaceuticals and personal care products at very low concentration (from ng L^{-1} to µg L^{-1}) in the different natural water bodies is frequently highlighted in literature (Richardson and Kimura, 2016). These micropollutants may generate hazardous effects towards environment and cause a potential risk for human health event at such low concentrations (Kovalova et al., 2013). One of the main sources in the aquatic environment of these biorecalcitrant contaminants comes from the discharge of reclaimed wastewater: wastewater treatment plants (WWTP) are not conceived to completely remove them. Advanced physico-chemical technologies have therefore been proposed as a complementary step within the WWTP. Among them, advanced oxidation processes (AOPs) gained a lot of interest in the scientific community as they all rely on the generation of strong oxidizing agents such as hydroxyl radicals (•OH) ($E^\circ = 2.80$ V vs SHE) that can react very quickly with most of the organic xenobiotic compounds, especially the aromatic ones (10^8–10^{10} L mol^{-1} s^{-1}) (Oturan and Aaron, 2014). Excitingly, a new oxidation route of •OH has been established very recently, which permits to oxidize perhalogenocarbons by ipso-substitution (Mousset et al., 2017b). Thus it opens up many possibilities of oxidation with emerging pollutants such as fluorosurfactants. Chemical AOPs have been proposed, based on the addition of Fenton reagents (H_2O_2 and Fe^{2+}) and/or by photolysis of oxidants (H_2O_2, O_3, Fenton reagents) and/or by photocatalysis (in the presence of photocatalyst (TiO_2, etc.)). All these processes require the

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continuous addition of high amount of chemicals (acids, bases, oxidants, catalysts) that are not easy to handle and can be hazardous. Moreover, UV-based processes consume large amounts of electric energy. Electrochemical AOPs (EAOPs) have arouse increasing interests as they are able to generate continuously and *in situ* the oxidants and especially $^{\bullet}OH$ (Rodrigo et al., 2014; Sirés et al., 2014). They allow reaching very high degradation and mineralization yields in synthetic or real effluents (>99%), as compared to the (photo)-chemical AOPs (Cañizares et al., 2009; Oturan et al., 2012). EAOPs are also modular processes according to the electrode materials used and to the design of reactor which permit to generate different kinds of oxidizing/reducing species (Martinez-Huitle et al., 2015; Mousset et al., 2017a). Among these EAOPs, electro-Fenton (EF) has been widely studied as it offers the advantages to produce H_2O_2 *in situ* (Eq. (1)) and to regenerate ferric ion (Fe^{3+}) into Fe^{2+} (Eq. (2)) through reduction reactions at the cathode. Then the Fenton's reagent reacts to produce $^{\bullet}OH$ through Fenton reaction (Eq. (3)).

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (1)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (2)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad (3)$$

Numerous efforts have been devoted to (i) enhance the properties of carbon cathode materials (Zhang et al., 2015; Mousset et al., 2016a, 2017b; Ganiyu et al., 2017a), (ii) optimize the main operating parameters such as current density, catalyst and oxygen concentrations (Oturan et al., 2015; Mousset et al., 2016b; Ganiyu et al., 2017b), (iii) assess the kinetics of degradation and mineralization of a plethora of organic pollutants (Ruiz et al., 2011; Mousset et al., 2013; Garza-Campos et al., 2016; Trellu et al., 2016). However, most of EF studies have been performed in synthetic wastewater to simplify the mechanisms understanding. Therefore, the influence of inorganic species present in reclaimed wastewater has been barely studied and mainly in anodic oxidation (Kapałka et al., 2010, 2011; Lacasa et al., 2012; Pérez et al., 2012; Vidales et al., 2016; Lan et al., 2017) as described in Table 1 and only two studies have been performed with real reclaimed wastewater (Vidales et al., 2016; Lan et al., 2017). Still, there is a lack of knowledge about the inorganic nitrogen species evolution under homogeneous Fenton oxidation combined to electro-oxidation/reduction. The reduction reactions are typically important mechanisms that need to be considered.

In this context, for the first time this study proposes to monitor the fate of inorganic nitrogen species subjected to strong oxidation and reduction conditions in an EF process in both synthetic and real reclaimed wastewater. It brings new scientific insights through the following objectives: (i) depict the complete redox cycle of inorganic nitrogen species with a systematic study, including gaseous species, (ii) assess the impact of real matrix on their evolution, and (iii) highlight the possible unwanted remaining inorganic nitrogen species after the electrolysis.

2. Material and methods

2.1. Chemicals

All the chemicals were of analytical grade, and were used without any further purification. Sodium nitrite ($NaNO_2$) was purchased from Merck. Sodium carbonate ($NaHCO_3$), sodium hydrogen phosphate (Na_2HPO_4) and sodium chloride (NaCl) were supplied by VWR International. Ammonium sulfate ($(NH_4)_2SO_4$) and sulfuric acid (H_2SO_4) were provided by Thermo-Fisher Scientific. Potassium nitrate (KNO_3) and heptahydrated ferrous sulfate ($FeSO_4{\cdot}7H_2O$) were obtained from Acros Organics. In all experiments, the synthetic solutions were prepared with ultrapure water from a Purelab® water purification systems (Veolia Water) (resistivity > 18 MΩ cm at room temperature).

2.2. Synthetic and reclaimed wastewater characteristics

The fate of nitrogen species taking into account NH_4^+, NO_2^-, NO_3^- and gaseous nitrogen (N_{gas}) (by mass balance) was determined first in synthetic wastewater to better understand each mechanism independently. Then their fate was studied in reclaimed wastewater sampled at the exit of a municipal wastewater treatment plant (Reims, France) in order to assess the possible interferences with inorganic nitrogen species. The reclaimed water has been filtered (0.45 μm) first before use to avoid the presence of any potential residual particulate pollution. The main physico-chemical characteristics of the reclaimed wastewater are described in Table 2.

Table 2
Physico-chemical characteristics of the reclaimed WWTP effluent.

Parameter	Value
pH	8.01
Conductivity (mS cm^{-1})	1.09
PO_4^{3-} (mg L^{-1})	1.03
NO_3^- (mg L^{-1})	5.12
NO_2^- (mg L^{-1})	0.320
SO_4^{2-} (mg L^{-1})	60.5
Cl^- (mg L^{-1})	138
NH_4^+ (mg L^{-1})	2.10
Total inorganic carbon (mg-C L^{-1})	62.8
Total organic carbon (mg-C L^{-1})	5.83
Total nitrogen (mg-N L^{-1})	2.71

Table 1
Existing studies on the fate of inorganic nitrogen species subjected to an electrochemical treatment.

Kind of treatment	Kind of solution	Electrodes	Reference
Anodic oxidation	Synthetic solution: ammonia mixed with chloride	Cathode: Pt Anode: Ti/PtO_x-IrO_2	(Kapałka et al., 2010)
Anodic oxidation	Synthetic solution: ammonia mixed with perchlorate	Cathode: Pt Anode: Ti/IrO_2	(Kapałka et al., 2011)
Anodic oxidation	Synthetic solution: nitrate mixed with chloride	Cathode: stainless steel Anode: DSA or BDD	(Lacasa et al., 2012)
Anodic oxidation	Synthetic solution: ammonia, nitrate and nitrite mixed with chloride	Cathode: BDD Anode: BDD	(Pérez et al., 2012)
Anodic oxidation	Real reclaimed wastewater from municipality	Cathode: stainless steel Anode: BDD	(Vidales et al., 2016)
Anodic oxidation	Real reclaimed wastewater from hospital	Cathode: zirconium Anode: BDD	(Lan et al., 2017)