Nitrate catalytic photoreduction: insights onto inhibitory byproducts.

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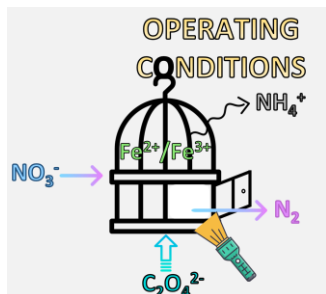
Efficient groundwater remediation technologies are necessary to ensure the access of safe drinking water in rural areas which present NO_3^- pollution due to agricultural malpractices. Amongst the multiple technologies available, photo-assisted catalytic photoreduction arises as a feasible Advanced Reduction Process to eliminate NO_3^-. This emerging technology requires an in-depth study. In this work, the generation of inhibitory byproducts is presented, as well as strategies to either minimize their generation or eliminate them after reaction.

Introduction

Contamination of groundwater with nitrates, at concentration levels above 50 mg/L, impedes the access to safe drinking water in many rural communities. The current technologies applied to solve this issue are based on separation processes, such as reverse osmosis or ionic exchange, which merely transfer the pollutant onto a more concentrated stream.

To overcome this drawback, photocatalytic nitrate reduction has arisen as a feasible technology. The Metal-Acid Light Induced (MALI) photoreduction system consists of the decomposition of a short chain acid which acts as reducing agent, usually oxalic acid, in presence of a metal catalyst that acts as electron transfer and UV-C irradiation. This can be achieved either with homogenous (Fe^{3+}) or heterogeneous catalysts (Fe_yO_x) [1,2]. Figure 1 depicts the process studied in this work.
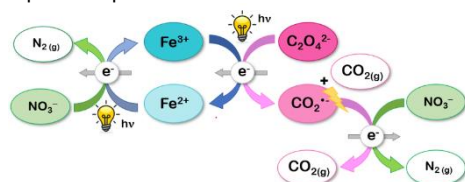

Figure 1. Homogeneous MALI nitrate reduction scheme.

Prior investigations on nitrate photoreduction using this process have reported a decrease in the reaction rate when increasing the initial NO_3^- concentration [2], as well as production of high NH_4^+ amounts [2]. This work investigates the cause of these undesired phenomena to give a roadmap on good practices to avoid them.

Material and Methods

Photoreduction assays were conducted in a 700 mL glass reactor with a magnetic stirrer set at 550 rpm to homogenize the reaction system. The reactor is equipped with a medium-pressure Hg UV lamp (150 W, Heraeus) and a quartz sleeve that maintains a constant temperature of 25 ºC throughout the reaction, facilitated by a circulating bath (Huber, Ministat 125). In a typical reaction, a solution of NO_3^- at 75 mg/L in ultrapure water is used as the starting point. After putting the solution into the reactor, an aliquot with the desired concentration of catalyst (Fe^{3+}) is added, followed by the reducing agent, typically oxalic acid. Once all the regents are introduced, the UV lamp is turned on, making this moment as initial time of the reaction.

Throughout the reaction, the concentrations of NO_3^-, NO_2^-, and NH_4^+ were monitored using ion chromatography (Metrohm). Total organic carbon (related to oxalic acid) and total nitrogen (TN) were measuring with a TOC/TN analyser (Shimadzu).

Results and Discussion

Influence on the initial concentration of nitrate was tested, keeping a mass ratio for $Fe^{3+}/NO_3^-/C_2O_4^{2-}$ at 1/15/54. This corresponds to the stoichiometric oxalic acid dosage for complete nitrate reduction towards $N_{2(g)}$, according to the following equation:

$$2 NO_3^- + 5 C_2O_4^{2-} + 12 H^+ \rightarrow N_{2(g)} + 10 CO_2 + 6 H_2O$$

Nitrate reduction, shown in Figure 1, fitted a pseudo first order kinetic model. Apparent kinetic constants are collected in Table 1.

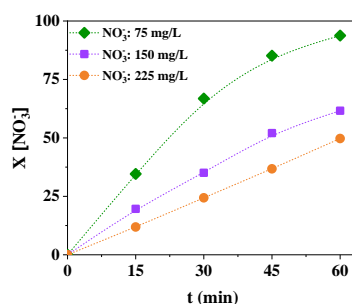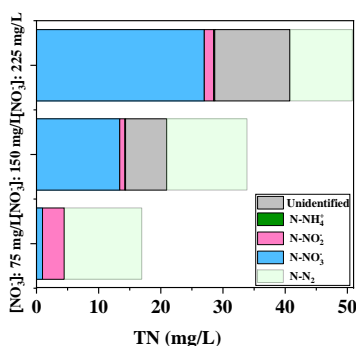**Figure 1.** Influence of initial concentration on NO_3^- photoreduction.

Table 1. Pseudo-first order rate constants for NO_3^- reduction.

$[NO_3^-]_0$ (mg/L)	$k_{app} \cdot 10^2$ (min^{-1})	r^2
75	2.92 ± 0.12	0.999
150	1.35 ± 0.08	0.998
225	0.82 ± 0.14	0.998

In first-order kinetics, the rate constant is independent of the initial concentration. In this case, as initial NO_3^- concentration is raised, the degradation rate decreases. Additionally, the nitrogen balance calculated at t: 60 min (Figure 2) shows an unidentified specie, which concentration increases along with the initial $[NO_3^-]$. Hence, it seems that there is an unidentified nitrogenated byproduct responsible for the observed inhibition. It should be noted that in all runs, NH_4^+ concentration was below 0.3 mg/L.

Figure 2. Influence of $[NO_3^-]$. Nitrogen balance at t: 60 min.

In order to get a deeper comprehension on the nature of this inhibitor, further experiments were conducted using the same molar concentrations of nitrite. In this case, reaction kinetics were similar. Nitrate reduction follows the next scheme:

$$NO_3^- \rightarrow NO_{2(g)} \rightarrow NO_2^- \rightarrow NO_{(g)} \rightarrow N_2O \rightarrow N_{2(g)} \rightarrow NH_4^+$$

Since there is no inhibition found in the case of nitrite reduction, the unidentified byproduct might be related to an Fe-NO$_x$-Oxalate complex [3], which acts as catalyst scavenger and thus, diminishes the reaction rate.

Catalyst dosing in a semicontinuous run did not have a significant impact on the reaction rate. Hence, the influence of the radiation power was evaluated. For this purpose, a medium-pressure Hg lamp modulable between 1500 and 2000 W was employed to reduce 225 mg/L of NO_3^-. Results in terms of nitrogen balance at the end of reaction, presented in Figure 3, reveal a significant reduction in the unidentified N species, from 13 mg$_N$/L with the 150 W lamp to 3 mg$_N$/L working at 2000 W.
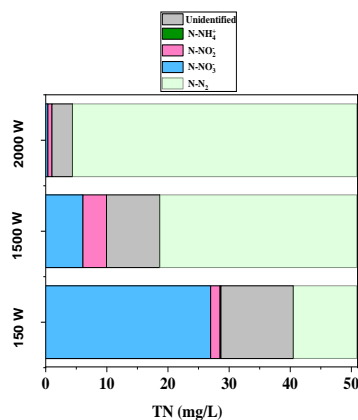
Figure 3. Influence of irradiation power. Nitrogen balance at t: 60 min.

Another strategy explored was to apply a subsequent oxidation stage using H_2O_2. This completely eliminated the unidentified N species, yielding NO_3^-, making the final effluent apt for consumption under the current European regulation.

Conclusions

Nitrate photo-assisted reduction is possible with the MALI process. Still, increase in the nitrate concentration in the inlet stream might compromise the feasibility of the process due to the generation of an inhibitory byproduct, suspected to be an iron complex, that diminishes the reaction rate. This undesired byproduct can be minimized by increasing the irradiation energy and was completely eliminated with a Fenton oxidation by adding H_2O_2 to the final effluent. Hence, NO_3^- contaminated groundwater remediation deems feasible by combining advanced reduction and oxidation photoassisted processes.

References

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[2] Z. Shi, F. Wang, Q. Xiao, S. Yu, X. Ji*, Catalysts*, 12 (2022), 348.
[3] M. Mayer, N. Vankova, F. Stolz, B. Abel, T. Heine, K. R. Asmis, Angew. Chem.Int. 61, (2022), e202117855.