

Letter to the Editor

## Assessment of the catalytic reduction of nitrates in water from an environmental point of view

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The catalytic hydrogenation for the removal of nitrates from water was first described in 1989 by Vorlop and Tacke [1]. There are numerous reports in the last decade aimed at the development of suitable catalysts. In a recent article, published in 2004, Palomares et al. [2] reported the catalytic hydrogenation of nitrates in water using a Pd–Cu/Mg/Al hydrotalcite. They showed that the use of calcined hydrotalcite as a support eliminates some of the problems associated with mass-transport limitations observed with Pd–Cu/Al<sub>2</sub>O<sub>3</sub> catalysts. Moreover, Palomares et al. [2] give a good overview of state-of-the-art catalytic hydrogenation of nitrates in water and a comprehensive review of the extensive literature. The aim of these papers was to study the catalytic reduction of nitrates to solve the problem of increasing nitrate concentrations in water supplies. The standards for drinking water are 50 mg/L in the European Union and 25 mg/L in the United States (guide level). This Letter to the Editor comments on conclusions drawn by the authors from their experimental results and their evaluation of the catalytic reduction of nitrates as a possibility for avoiding the contamination of drinking water. The following comments can be applied to most of the articles published on the catalytic hydrogenation of nitrates, although some of the experimental data used as examples come from [2], the most recent article.

The authors point out that “the catalyst must be selective to avoid the production of nitrite and ammonium ions, which are more toxic than the nitrates”. Therefore, it would be helpful to calculate the conversion of NO<sub>3</sub><sup>−</sup> to gaseous N<sub>2</sub>. It would also be helpful to assess the high nitrite and ammonia levels obtained in the catalytic hydrogenation of nitrate. It is well known that the accepted levels of nitrites and ammonium in drinking water are 0.1 and 0.5 mg/L, respectively. Therefore, an efficient method of nitrate reduction should

enable the complete conversion to N<sub>2</sub>, approximately 100%, with no appreciable trace of nitrite and ammonium ions.

Fig. 3A [NO<sub>3</sub><sup>−</sup> and NO<sub>2</sub><sup>−</sup> concentration profiles (mg/L) as a function of time] shows the experimental results for Pd–Cu/Al<sub>2</sub>O<sub>3</sub> and Pd–Cu/Mg/Al catalysts. Fig. 3B shows the evolution of the ammonium ion concentration as a function of nitrate conversion. It is possible to transform the data of Figs. 3A and 3B in order to show NO<sub>3</sub><sup>−</sup> (reactant), NO<sub>2</sub><sup>−</sup> (intermediate product), and NH<sub>4</sub><sup>+</sup> (final product) concentration profiles as functions of time in the same figure, as usual in studies of chemical kinetics. Furthermore, when concentration is expressed in units of millimole per liter, it is possible to formulate mass balances to calculate the quantity of gaseous N<sub>2</sub> formed at any time (mmol difference [nitrate initial – (nitrate residual + nitrite formed + ammonium formed)]/2). Fig. 1 (Pd–Cu/Al<sub>2</sub>O<sub>3</sub> catalyst) and Fig. 2 (Pd–Cu/Mg/Al hydrotalcite catalyst) show NO<sub>3</sub><sup>−</sup>, NO<sub>2</sub><sup>−</sup>, and NH<sub>4</sub><sup>+</sup> concentration profiles (mmol/L) as functions of time, as well as the gaseous N<sub>2</sub> (mmol) released from 1 L of solution.

Figs. 1 and 2 show the different behavior of the Pd–Cu/Al<sub>2</sub>O<sub>3</sub> and the Pd–Cu/Mg/Al hydrotalcite catalysts. With the Pd–Cu/Al<sub>2</sub>O<sub>3</sub> catalyst, the reduction of nitrate to gaseous N<sub>2</sub> as the final product is very low, while there is a substantial final concentration of NH<sub>4</sub><sup>+</sup>. At the same time, the intermediate product (nitrite) reaches a high, maximum concentration. However, with the Pd–Cu/Mg/Al hydrotalcite catalyst, the final N<sub>2</sub> formed is greater, the final concentration of NH<sub>4</sub><sup>+</sup> decreases, and the maximum nitrite concentration is lower. After 200 min, the conversion of nitrate to N<sub>2</sub> is 23.2% for the Pd–Cu/Al<sub>2</sub>O<sub>3</sub> catalyst and 71.2%, for the Pd–Cu/Mg/Al hydrotalcite catalyst; in both cases, however, the conversion is far below 100%.

Similar experimental results, with conversion to N<sub>2</sub> far below 100% and a substantial final concentration of NH<sub>4</sub><sup>+</sup>,

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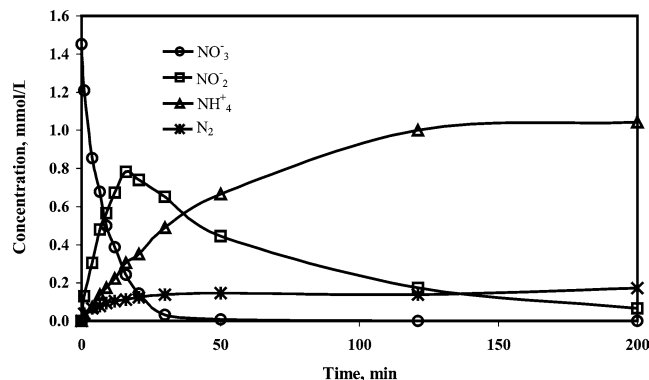


Fig. 1. Pd-Cu/Al<sub>2</sub>O<sub>3</sub> catalyst. NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup> concentration profiles (mmol/L) and gaseous N<sub>2</sub> (mmol) released from 1 L of solution as functions of time.

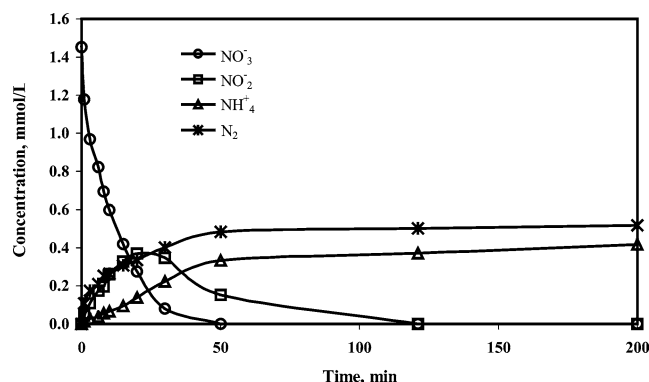


Fig. 2. Pd-Cu/Mg/Al hydrotalcite catalyst. NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup> concentration profiles (mmol/L) and gaseous N<sub>2</sub> (mmol) released from 1 L of solution as functions of time.

can be found in other recent studies on the catalytic hydrogenation of nitrates in water [3–5].

If the environmental goal is the design of a large-scale treatment plant to remove nitrates from drinking water, the analysis of the results given in the papers mentioned leads to a negative evaluation of this technique. For instance, utilizing the best catalyst, the hydrotalcite:

1. A 71.2% conversion of nitrates to N<sub>2</sub> implies a final concentration of 0.417 mmol/L NH<sub>4</sub><sup>+</sup>, which is equivalent to a very high value of 7.5 mg/L, much higher than the admissible level of 0.5 mg/L.
2. The long reaction time (200 min) implies the use of an unrealistic large reactor. Even if the residence time (30 min) is shorter, the final concentration of nitrite in water would be 16 mg/L (admissible level: 0.1 mg/L), that of the NH<sub>4</sub><sup>+</sup>, 4 mg/L, would be too high.
3. The experiments reported in article [2] were carried out in a glass reactor with a 90 mg/L solution of KNO<sub>3</sub> in distilled water. More realistic experiments with tap water have not been carried out. The concentration of anions such as SO<sub>4</sub><sup>2-</sup> and hydrogen carbonates in tap water is above 90 mg/L, which could inhibit nitrate reduction, probably due to competitive adsorption of these

anions on catalytic active sites. Fig. 2, in the paper [2], shows the infrared spectra of the Pd-Cu/Mg/Al calcined hydrotalcite that was in contact with the nitrate solution and with distilled water. In the nitrate solution, the presence of nitrates in the hydrotalcite is confirmed by the intense band at 1384 cm<sup>-1</sup>. These results can be explained by the “memory effect” of calcined hydrotalcite structures: when rehydrated, they recover the positively charged layered structure forcing the nitrate anions in the media to move to the interlayer space, thus compensating the positive charge. However, it is not known what would happen if calcined hydrotalcite were in contact with nitrate solution prepared with tap water. Anions such as sulfate and hydrogen carbonate might compete with the nitrate for the interlayer space, thus compensating the positive charge. In that case, the catalyst would be less effective in removing nitrate. In fact, Pintar et al. [6,7] reported that, when drinking water was used as a reaction medium instead of distilled water, the nitrate disappearance rate as well as the nitrogen production yield decreases appreciably in the presence of hydrogen carbonates.

4. Furthermore, this treatment plant would be a serious safety hazard because of the gaseous hydrogen used as a reactive agent to reduce nitrates.

The literature mentioned clearly shows that the authors’ assessment of the catalytic hydrogenation in comparison to conventional methods (physical-chemical or biological) for removing nitrates is too optimistic. Most authors state that the most adequate and promising way from an environmental point of view to remove nitrates is to convert them into gaseous nitrogen by liquid-phase nitrate hydrogenation on a noble metal catalyst. At present, however, reverse osmosis is used in large- and small-scale operations, to produce drinking water with low levels of nitrate. An argument against reverse osmosis is that nitrates are not converted into harmless compounds but are found in high concentrations in secondary waste, which must be treated or disposed of. The disposal of waste brine generated during reverse osmosis desalination of seawater, is indeed a problem. However, when low-saline tap water with a nitrate concentration around 90 mg/L is treated by reverse osmosis, the waste concentration is relatively low and its disposal does not present a serious problem. A number of small commercial reverse-osmosis devices are used in the home to purify tap water. In contrast, it is hard to imagine a domestic device capable of removing nitrates by means of catalytic hydrogenation because of the long reaction time, the risks associated with the use of gaseous hydrogen, and the possibility of toxic nitrite and ammonium ions in the treated water. In summary, as noted above, the comments of this Letter can be applied to most of the articles published on the catalytic hydrogenation of nitrates in water. The Letter does not question the scientific results of the papers, only the too optimistic conclusions in relation to possible applications in society.

## References

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