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Letters to the Editor

Comments on: "Nitrates removal from polluted aquifers using (Sn or Cu)/Pd catalysts in a continuous reactor" by Palomares et al. [Catalysis Today 149 (2010) 348–351]

The purpose of the article [1] in the above title is a study of the catalytic removal of nitrates in natural water from polluted aquifers by means of a continuous stirred tank reactor. This objective is laudable because the authors do not follow the usual practice of simply adding a nitrate salt to distilled water prepared in the laboratory that is commonly found in most papers on the catalytic reduction of nitrate in water. They also mention that it has been reported that this reaction is very much influenced by the presence of other ions in the media, the most important being the inhibiting effect of hydrogencarbonates, probably due to a competitive adsorption on active metallic sites. For this reason, it is interesting to test catalysts using natural waters.

Table 2 of paper [1] shows the chemical composition and source of the polluted water used in the catalytic experiments. Three of them (water A, B and C) are natural in origin while the fourth (water D) comes from an industrial source. Some comments can be made regarding the data in this table since it appears to be incomplete, in the sense that the waters (A, B, C and D) have not been properly characterized. Here follow the reasons for this assertion:

(1) Natural waters usually contain hydrogencarbonates to some extent, which depends on the aquifer terrene from which the water was extracted. We should expect that waters A, B and C in the authors' Table 2 reflect the presence of some hydrogencarbonate and therefore that it should have been reported. It is possible for the hydrogencarbonate content to be zero; however, in that case, we believe it to be of enough importance to warrant explicit mention, since, as stated by the authors in their introduction, this anion is a possible inhibitor of the catalytic reduction of nitrates. Thus, the reader might expect that this point be addressed specifically. Moreover, there is no mention of the alkaline cations such as Na^+ and K^+ which are also present in most natural waters.

(2) The incompleteness of Table 2 is also evident from the electrical balance of the water analysis presented. It is well known [2] that the accuracy of a water analysis can be estimated from an electrical balance (*E.B.*) of the major ions because the sum total of the positive charges and that of the negative charges in the water should be equal. *E.B.* is calculated using:

$$(E.B.,\ \%) = \frac{(Sum\ cations + Sum\ anions)}{(Sum\ cations - Sum\ anions)} \times 100 \qquad (1)$$

where cations and anions are expressed in meq/L and their signs must also be included. Perfect electroneutrality implies that *E.B.* equals zero. Differences in *E.B.* of up to 2% are inevitable in almost all laboratories, but with deviations in excess of 5%, the sampling and quantitative analytical procedures should be examined. Water B in Table 2 of [1] which has been used in most of the catalytic reduction tests does not meet this requirement since the *E.B. %* is 8.1%, a value higher than 5%.

(3) Another useful technique to check the quality of a particular quantitative water analysis is to compare the calculated and measured electrical conductivities [2,3]. We find it rather surprising that the chemical industrial wastewater (water D in Table 2 of [1]) can exhibit a conductivity as high as 24,000 μS/cm given the small number of ions in it. A rule of thumb commonly used as a crude approximation to estimate conductivity is:

$$\Sigma\text{anions (or } \Sigma\text{cations) (meq/L)} \times 100 = \text{conductivity } (\mu\text{S/cm}) \qquad (2)$$

The summation over all anions ($\sum$anions) comes to 21.2 meq/L in water D [1]. This results in a conductivity estimate of only 2120 μS/cm. This value is markedly smaller than the experimental value shown in the authors' Table 2, which is to be expected since the authors report that water D is very low in salt content. On the other hand, the summation over cations ($\sum$cations) comes to 0.060 meq/L for water D, which is much smaller than the corresponding value for the anions. This shows that the analysis of water D does not fulfil the necessary electroneutrality condition (*E.B.* = −99.4%) and once again demonstrates that the composition given in Table 2 cannot be complete.

There is a better way to estimate the conductivities of salt solutions that takes into account the conductances of ions. According to Ref. [3], *Standard Methods for the Examination of Water and Wastewater*, the contribution to conductivity by different types of ion is additive at infinite dilution. In general, the relative contribution of each cation and anion is calculated by multiplying equivalent conductances, λ_+^0 and λ_-^0 (in S cm^2/eq) by concentration (in eq/L) and correcting units. At finite concentrations this rule is only useful as a first approximation of the estimated value of the conductivity. In any case, there should not be much discrepancy between the experimental value of the conductivity and the estimated one. A large difference between the two could imply an error in the experimental determination. This would appear to be the cause of the discrepancy in the case of water D [1] (chemical industrial wastewater). Table 1 of the present Letter shows analytical data for water D together with its estimated conductivity as calculated from ion concentrations and conductances. This table shows that the experimental conductivity (24,000 μS/cm) is too high when compared to the calculated 1521 μS/cm. This result was foreseeable since the low ion concentration (1310 mg/L) cannot produce such a large conductivity.

Since not enough cations turned up in the chemical analysis of water D, we could venture and suppose that it contains the required amount of Na^+ to make the *E.B.* equal to zero, i.e., 21.14 meq/L. Yet, even under this assumption, with the conductance (λ_+^0) of Na^+ at 50.1 S cm^2/eq, the estimated conductivity (2580 μS/cm) does not attain the experimental value. We might then further suppose

Table 1
Parameters and calculation of conductivity for water *D*.

	Ca^{2+}	H^+	Na^+	Cl^-	$SO_4{}^{2-}$	$NO_3{}^-$
Concentration *C* (mg/L)	1.2	Not reported	Not reported	5	4.2	1,300
Concentration *C* (meq/L)	0.060	–	–	0.14	0.087	21.0
Conductances λ_+^0 or λ_-^0 (S cm^2/eq)	59.5	350	50.1	76.4	80	71.4
$(C \times \lambda_+^0)$ (μS/cm) or $(C \times \lambda_-^0)$ (μS/cm)	3.6	0	0	10.7	7.0	1,499.4
Calculated conductivity (μS/cm)	1,521[a]					

[a] Very small number as compared to the experimental value, 24,000 (μS/cm).

that the industrial chemical wastewater contains nitric acid and that the missing cation is in fact H^+ which has a higher conductivity than Na^+. However, once again, the estimated conductivity, though higher (8920 μS/cm) because the conductance of H^+ (λ_+^0) is 350 S cm^2/eq, does not match the experimental value. Our conclusion is that there must be an error in the conductivity value or in the number of ions reported.

Aside from that, we believe it necessary to comment on the following aspect: it is stated in the introduction of [1] that the disadvantage of nitrate reduction by catalysts is the formation of subproducts such as ammonia or nitrite. Therefore, the catalyst must be selective towards nitrogen to avoid the production of these by-products, since they are more toxic than the nitrates themselves. The accepted levels of nitrites and ammonia in drinking water are 0.1 and 0.5 mg/L, respectively. Since the pioneering work of Vorlop and Tacke [4] published in 1989 on nitrate removal by reduction, an abundance of papers have followed dealing with the search for selective catalysts able to convert all nitrate to nitrogen while avoiding the formation of nitrites and ammonia. To our best knowledge, this search has not yielded up satisfactory results particularly for natural waters. In our opinion [5,6], if the environmental goal is to design a large-scale treatment plant to remove nitrates from drinking water, then, based on the results of the papers published on this topic, the technique does not seem very promising.

We would also like to make some remarks regarding the results presented in [1] to corroborate the above conclusion:

(a) Multiple tests for reducing nitrate have been performed on four types of water (A, B, C and D) using a number of catalysts. The reactor nitrite concentration has not been reported in the Results and discussion section of [1] for any of those tests, in spite of the statement in the experimental section that small aliquots of sample were taken for the photometric determination of nitrate, nitrite and ammonia concentration. Thus, it is not possible for the reader to appreciate whether the tested catalysts produce a higher or lower concentration of nitrites than the accepted amount by law in drinking water. The availability of this information is crucial for evaluating the catalysts' performance as well as that of the proposed process.

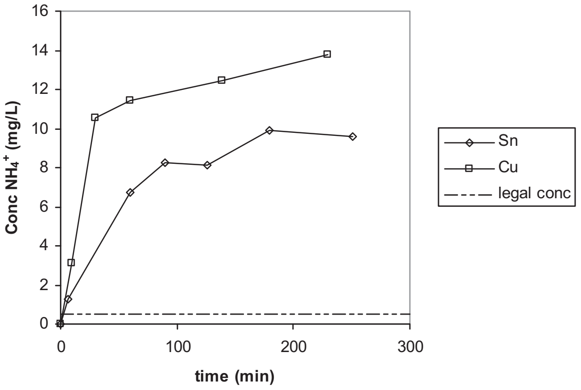

Fig. 1. Evolution of ammonia concentration with time. Data obtained from figures 3 and 4 in [1]. The dotted line represents the legal maximum for NH_4^+ concentration.

(b) As to the formation of ammonia, all tests described in Ref. [1] were carried out only on natural water B. The data presented in Fig. 3 of the publication refers to the selectivity towards ammonia in the catalytic hydrogenation of nitrates on Pd–Cu and Pd–Sn catalysts supported on alumina (Pd:metal ratio = 2). For this water source, a lower selectivity towards ammonia is obtained with the catalyst containing tin than with the catalyst containing copper. It would have been more appropriate to express the ordinate axis in Fig. 3 as concentration of $NH_4{}^+$ in mg/L instead of selectivity since the reader is left wondering whether the catalysts used can fulfill legal requirements in terms of drinking water quality. In addition, $NH_4{}^+$ selectivity is a parameter that needs further clarification since it can be defined in more than one way. We have taken it to mean

$$\text{selectivity} = \frac{\text{mol}\ NH_4^+\ \text{produced}}{\text{mol}\ NO_3^-\ \text{converted}} \times 100\% \tag{3}$$

In this case its value can be converted to ammonia concentration if the nitrate concentration in the feed stream to the reactor and its conversion (reported in Fig. 4 of [1]) are known. Fig. 3 in [1] has been reproduced here (see Fig. 1) with the ordinate axis now expressed in the desired units and with $NH_4{}^+$ selectivity replaced by $NH_4{}^+$ production. It shows that at all times the concentration of ammonia exceeds the accepted legal maximum of 0.5 mg/L (also included for comparison).

(c) Figs. 4 and 5 in [1] show NO_3^- conversion data. Fig. 4 displays data for all four types of water (A, B, C and D) and for times up to 10 h. Fig. 5 deals with only water type B and for times up to 300 h. However, such representations are not really that interesting since very high catalytic conversions of nitrates in natural water are already reported in the literature. The really interesting information is lacking, i.e., nitrite and ammonia concentration with time, which could easily have been reported since the authors state to have measured them. As noted above, the provision of this information is necessary for assessing the catalysts' performance as well as the proposed process.

References

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