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Chemical, biological and physical constrains in catalytic reduction processes for purification of drinking water

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Abstract

A review of the various development steps of a catalytic reduction process of nitrate ions in drinking water is presented. The approach followed to define and improve the catalyst at the lab scale, including kinetic study and molecular modelling, is described. The chemical engineering aspects, including diffusion and mass transfer, as well as reactor design are discussed in the light of a first pilot plant experiment in the field. The practical difficulties encountered due to the growth of micro-organisms in the reactor are also discussed in the light of process engineering rules. The results of a new field trial are presented, and some hints for future work are also given. Finally, the interest of reductive catalytic step in drinking and wastewater treatment is briefly discussed. ©1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The purification processes designed to produce drinking water from various water sources generally combine a series of physical and chemical steps to eliminate solid fraction, kill bacteria and reduce the level of chemical pollutants.

Most of the processes include a strong oxidative step, based either on the use of chlorine or sodium hypochlorite or on oxidation by ozone or hydrogen peroxide. These types of treatments intend to reduce the content of micro-organisms in water to an acceptable level, but, in the process, could also affect the chemical composition of water. For example, some traces of organochlorinated compounds could be generated if the initial organic content of the water is too high. Similarly, the oxidation of bromide ions into toxic bromate ions can also be observed. Some undesirable ions, like nitrates, remain unaffected by the oxidative treatments.

The introduction of a reductive step in drinking water treatment could lead to the destruction of some organochlorines and to the reduction of ions like nitrates and bromates. Such an approach, based on the use of a catalytic hydrogenation step, has been developed on laboratory and pilot scale.

Even though the possibility of reducing nitrate ions in water with hydrogen in the presence of noble metal catalysts has already been demonstrated [1–4], the synthesis of a stable efficient catalyst as well as the study of the diffusion limitations are essential steps in the development of an industrial process. More recent studies [5–6] also show the interest of Pd/Cu-supported catalysts in the selective reduction of nitrate to nitrogen.

In this paper, laboratory experiments, both in batch and in continuous reactors, have been carried out in

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order to optimise the catalyst composition, and to develop a pilot plant reactor and a continuous process. This has been used in field experiments to reduce to an acceptable level the nitrate content of a ground source in a rural region.

2. Development of the catalyst and catalyst optimisation

2.1. First approach

One of the major difficulties in catalytic reduction of nitrate ions in drinking water is the control of selectivity, the objective being the reduction of nitrate to nitrogen, with a limited production of nitrite and ammonium ions.

The first screening experiments at the lab scale indicated that:

- Pd and Pd/Cu alloys, supported on alumina gels, are interesting potential catalysts for the hydrogenation of nitrate in water, even if too high levels of nitrite and ammonium ions are observed. A typical catalyst is made of 1 wt.% Pd and 0.25 wt.% Cu on alumina. An alumina gel, obtained from a commercial aluminium hydroxide (Condea SB), is aged in isopropyl alcohol, dried at 150°C, treated in air at 600°C for 8 h and then impregnated by a mixture of Pd and Cu chlorides.
- The selectivity towards nitrogen formation decreases on increasing conversion. This effect, attributed to an increase in pH due to the formation of hydroxyl ions, can indeed be controlled by the buffering effect of carbon dioxide, introduced in the medium during the reaction.

2.2. Molecular modelling and mechanism

In order to get a better understanding of the chemistry of the catalytic nitrate reduction over Pd/Cu and Pd catalysts, a molecular model of the system has been developed using the modem tools of the quantum computer chemistry, as described in reference [7] and references cited therein. The resulting molecular picture has been used to explain some experimental results, and to propose some improvement of the process.

As the first step, the adsorption behaviour of the different molecular, ionic and atomic species involved in the process was studied, with a special emphasis on the influence of Pd/Cu alloy formation on chemisorption. In the second step, Langmuir scheme is applied to model the microkinetics of nitrate and nitrite dissociation on Pd, Cu and their alloys. Numerical values for adsorption, desorption, dissociation and recombination constants have been computed and the effect of water is taken into account when necessary.

This theoretical study indicated that:

- Pd alone is not very well suited to dissociate nitrate.
- Cu is not the best suited metal to decompose nitrite, but Pd alone can work.
- A Cu/Pd surface atom ratio of 5/1 seems to be optimum for a selective nitrate-to-nitrite reduction.

The nitrate decomposition occurs via a multi-step mechanism going through NO_2^-, NO and atomic nitrogen. At each step, atomic oxygen is produced that tends to be strongly adsorbed on the catalytic surface, blocking the active sites and reducing the activity. The presence of too many oxygen atoms on the surface also hinders the recombination of nitrogen atoms to form N_2. It is thus essential to continuously remove the oxygen atoms from the surface by increasing the hydrogen partial pressure. An increase in hydrogen concentration promotes cleaning of the surface, favours the formation of N_2 and consequently helps suppress ammonia formation from atomic nitrogen. A decrease in pH should have the same effect.

The rate-limiting step in the decomposition of nitrate on Cu/Pd alloys is the removal of hydroxyl groups from the copper surface. The first and rate-determining step of ammonia formation is the association of atomic nitrogen with atomic hydrogen to form an N–H bond. This formation is inhibited by the presence of a small amount of atomic oxygen. There is, however, a dynamic equilibrium between the adsorbed species and the species in solution, and the anions present in water, like Cl^-, HCO_3^- and SO_4^-, could compete with OH^- and partially modify the coverage of the catalytic surface.

Consequently, the conclusions of this theoretical approach are the following:

- To be active and selective, the catalytic surface must be essentially, but not totally, free of oxygen atoms or hydroxyl groups.
- It could be worth to use two different catalysts, one based on Pd/Cu alloys for nitrate-to-nitrite reduction, and the other based on Pd alone to reduce nitrite to nitrogen.

- An increase in hydrogen partial pressure and a decrease of the Pd/Cu ratio could be favourable to selectivity.

As described later on, the two last points have been experimentally confirmed.

2.3. Development of reproducible catalytic tests at laboratory scale

Reproducible standard tests have been developed to measure the activity and the selectivity of Pd/Cu catalysts in nitrate decomposition and of Pd catalysts in nitrite decomposition. The operating conditions are summarised below.

The water used in these tests has a well-defined ionic composition. It is prepared by addition of 260 mg/l of $CaCl_2$ and 50 mg/l of $MgCl_2$ $6H_2O$ to distilled water. The catalysts are reduced at room temperature by a solution of $NaBH_4$ in water and then washed with pure water under nitrogen atmosphere. The concentration of the reducing agent (about 10 g/l) has been chosen to ensure complete reduction of the catalysts. This was checked both through activity measure and CO adsorption on Pd catalysts.

Batch reaction tests are carried out in a stirred, double-wall glass reactor of 500 ml for 2–3 h at constant temperature (25°C). The pH is kept constant, either by addition of an acetate buffer, in the case of nitrate reduction, or by flowing CO_2 through the reaction medium, in the case of nitrite reduction. Hydrogen gas is introduced at the bottom of the reactor through a ceramic filter. Samples of 5 ml are taken regularly for analysis of nitrate, nitrite and ammonium ions.

As a standard procedure, the activity and selectivity towards ammonia formation are measured after 60 min of reaction. But, it has to be pointed out that the selectivity of the various catalysts has to be compared at similar conversion of the reactant, the amount of catalyst in the reactor and the sampling time being adjusted accordingly. In standard conditions, a solution of 50 mg/l of nitrate or nitrite is used to measure the catalyst activities, the selectivity being measured at a conversion of about 50%.

2.4. Optimisation of the catalyst support

The catalyst should be stable enough to work adequately in water for a long period of time. It implies that the catalyst carrier also resists hydrolysis and mechanical stress. An optimisation programme of the carrier synthesis has been carried out. As this optimisation cannot be made independently of the properties of the resulting catalysts, all the modified carriers were impregnated to prepare the corresponding 0.9% Pd or 0.9% Pd + 0.22% Cu catalysts, which were then tested in nitrate or nitrite reduction.

The alugel prepared, as described in Section 2.1, has been used as starting carrier for the optimisation process. Its characteristics, as well as those of some of the modified carriers, are given in Table 1. This table also presents the activity and selectivity of the corresponding catalysts, as well as some indicators of the resistance to stress and hydrolysis.

Most of the modifications studied lead to negative effects on the catalytic activity and/or selectivity of the corresponding catalysts. Interesting results have been obtained by incorporating magnesium or titanium in the alumina gel during its synthesis. Moreover, the stability against stress and hydrolysis can be significantly improved by ageing the gel in water, instead of post treating it in isopropyl alcohol, as was done previously for the preparation of the first catalysts. These new ageing conditions also improve the activity towards nitrite decomposition and reduce the selectivity towards ammonia formation in the nitrate reduction. It is to be pointed out that the specific surface area and the pore volume of the various carriers do not vary very much, indicating that the differences observed are related to the surface chemistry of the carrier.

An increase in temperature of the thermal treatment of the carrier can improve its stability towards stress and hydrolysis, but this improvement, unfortunately, leads to a decrease in the specific surface area and to a deterioration of the selectivity, so that no global advantage is obtained.

2.5. Optimisation of the impregnation process

A statistical experimental design methodology, similar to those presented in reference [8] and in the references cited therein, has been used to optimise the impregnation conditions. Eight different parameters, including type of the carrier, metal concentrations, pH and drying conditions, have been considered in the design. The main results of this study are summarised

Table 1
Optimisation of the catalyst carrier

Carrier	Properties										
	Ageing in	Thermal treatment (4 h in air)	Alumina structure	BET surface area (m^2/g)	Pore volume (cm^3/g)	Isoelectric point pH unit	Attrition by stress and hydrolysis[b]	Nitrate reduction[c]		Nitrite reduction[d]	
								A[e]	S[g]	A[f]	S[g]
Standard Condea alugel											
	IPA[a]	600°C	γ	226	0.74	8.1	0.88	3.2	35	45	7
		900°C	$\gamma+\theta$	163	0.68	8.4	0.78	2.2	47	34	8
		1100°C	$\theta+\alpha$	84	0.34	8.7	0.35	2.1	50	24	12
	water	600°C	γ	215	0.70	7.8	0.30	2.5	25	65	10
Standard Condea alugel impregnated with 1.5 wt.%											
Zr	water	600°C	γ	207	0.70	8.5	0.26	4.1	52	44	20
La	water	600°C	γ	221	0.71	9.2	0.23	2.1	54	44	18
Ti	water	600°C	γ	213	0.69	7.5	0.09	7.5	49	39	39
PO_4^{3-}	water	600°C	γ	225	0.69	6.4	0.01	2.4	50	29	15
Mg	water	600°C	γ	210	0.71	8.7	0.13	2.7	58	45	15
Standard Condea alugel cogelified with 1.5 wt.%											
Zr	IPA	600°C	γ	216	0.68	8.4	2.2	5.4	29	38	9
Ti	IPA	600°C	γ	227	0.71	7.6	1.3	3.3	53	34	9
Mg	IPA	600°C	γ	230	0.69	8.7	0.5	8.2	33	3	8

[a] Isopropylalcohol.

[b] Attrition indicator: 1 g of carrier is shaken for 35 days in 5 cm^3 of water. The extinction of the water at 500 nm wavelength is used as the attrition indicator.

[c] Nitrate reduction in standard conditions (see text) on the carrier impregnated with 0.9% Pd + 0.22% Cu.

[d] Nitrite reduction in standard conditions (see text) on the carrier impregnated with 0.9% Pd.

[e] A: activity expressed in mg NO_3^-/g cat h after 60 min of reaction.

[f] A: activity expressed in mg NO_2^-/g cat h after 60 min of reaction.

[g] S: selectivity in ammonia (unwanted product) at 50% conversion.

in Table 2, including activity and selectivity of the resulting catalysts measured according to the standard procedure described in Section 2.3.

This optimisation resulted in a significant improvement of the Pd/Cu catalyst for the nitrate decomposition, in particular, for a lower content of active metals, a higher activity and a lower level of ammonia formation. One of the major positive effects was obtained by increasing the Cu/Pd ratio (from 0.25 to 1), as foreseen by the molecular modelling approach. The catalyst mean particle size, too, has a very high influence on the global activity, indicating mass transfer limitations, which are discussed hereafter. To get an interesting activity of about 8 mg NO_3^-/(g cat h), the particle size should be smaller than 50 μm. But particles of about 500 μm could be used if the active metals are located on a thin layer of 20–30 μm on the outer shell of the particles.

The optimisation of the Pd catalyst for nitrite decomposition indicated that a high Pd dispersion is an essential parameter to get good activity and selectivity (see Table 3). This can be better achieved with a low Pd content of about 0.1 wt.%, a fast reduction step and a low temperature of drying. It has been shown that 90% selectivity towards N_2 formation could be obtained with a relatively high activity of about 40 mg NO_2^-/(g cat h).

2.6. Kinetics and mass transfer

A detailed modelling of the mass transfer phenomena occurring in the catalyst particles used in the process has been developed on the basis of experimental kinetic study carried out on several catalysts and using three-phase catalytic reactor theory [9–11].

Table 2
Optimisation of impregnation conditions: Pd/Cu deposition on carrier particles of 600 μm diameter

Carrier	Impregnation conditions and properties						
	Pd content (wt.%)	Cu content (wt.%)	Pd/Cu ratio	Pd[a] dispersion (%)	Thickness of impregnation (μm)[b]	Nitrate reduction	
						A[c]	S[d]
Alugel standard aged in water	0.74	0.29	2.55	26	86	6.4	32
	0.24	0.15	1.60	34	37	0.7	83
	0.61	0.16	3.81	15	22	7.4	38
Alugel impregnated with PO_4^{3-}	0.87	0.30	2.90	28	250	3.4	65
	0.16	0.38	0.42	25	30	1.2	28
Alugel impregnated with Ti	0.93	0.31	3.00	14	55	10.6	52
	0.23	0.39	0.59	34	38	5.5	25
	0.59	0.22	2.68	14	50	9.5	39
Alugel Condea with Ti (optimised catalyst resulting from the design of experiments study)	0.23	0.24	0.96	56	35	20	9

[a] Pd dispersion expressed by the ratio between the number of CO chemisorbed to the number of Pd atoms in the catalyst.

[b] Measured on x-ray fluorescence pattern in an electronic microscope.

[c] Activity expressed in mg NO_3^-/g cat h under standard conditions (see text).

[d] Selectivity towards ammonia formation at 50% conversion.

Table 3
Nitrite reduction catalyst: Pd/alumina Condea SB — relationship between Pd dispersion, activity and selectivity

Catalyst number	Pd content (wt.%)	Dispersion (mol CO/mol Pd)	Activity (mg NO_2/g cat h)	Selectivity towards ammonium at 50% NO_2 conversion (%)
1	0.08	0.65	19	0
2	0.24	0.60	41	3
3	0.37	0.46	43	6
4	0.65	0.39	42	9
5	0.88	0.28	39	12

The kinetic equation fitting the experimental data obtained on two different Pd/Cu catalysts working in the chemical regime (particle size less than 35 μm) is

$$r=\frac{k(C_{NO_3^-})^{n_1}.(P_{H_2})^{n_2}}{1+k_1C_{NO_2^-}C_{NH_4^+}}$$

The value of n_1 is about 0.6, while the value of n_2 is about 0.34 for a Pd/Cu ratio of 4, and is about 0.6 for a Pd/Cu ratio of 1.

The kinetic study also shows that:

- The rate of nitrate reduction is inhibited by nitrite and ammonium ions, the inhibiting effect of nitrite being larger than that of ammonium.
- An increase in the hydrogen partial pressure has a positive effect on both the activity and selectivity of the catalysts.
- A slight decrease in pH, from 6.5 to 6.1, improves the selectivity at a given conversion.
- The catalyst with the Cu/Pd ratio of about 1 is the most effective one, because its selectivity is higher for the same activity and its activity per unit weight of active metal is also much higher. These observations confirm most of the predictions made on the basis of the molecular modelling approach.

The mass transfer model shows that important diffusion limitations exist, which should be taken into account in practical conditions. Industrial catalysts with core impregnated particles larger than 300 μm work in all cases with important external and internal diffusion limitations, the effectiveness factors being smaller than 10%.

For the activity level observed on the fresh-optimised catalyst, the external and internal diffusions remain significant for catalyst particles larger than 100 μm, even if the thickness of the active layer is limited to 35 μm. In this case, the effectiveness factor is about 0.85 for both external and internal diffusion.

The limiting reactant in most cases is the nitrate ion, but not the hydrogen ion.

It should also be pointed out that the diffusion limitations strongly affect the selectivity because they increase the residence time of nitrite ions in the catalyst particles and consequently favour the formation of ammonium ions.

As a conclusion, the kinetic study clearly shows mass transfer limitations, which have to be taken into account in the design of the catalyst and of the reactor at the pilot or industrial scale. First of all, the catalyst particle size must be kept as small as possible, the concentration of active metal reduced and the impregnation limited to a very thin layer at the surface of the particles (egg's shell impregnation). As far as the reactor design is concerned, a plug-flow reactor with a very limited back mixing, will be the best solution to improve the selectivity of the process.

2.7. Scaling up

2.7.1. Lab tests scaling up

The first scaling-up approach took place at the lab scale.

- The batch-reactor used during the development study has been replaced by a fixed-bed lab reactor, in which about 300 g of an optimised Pd/Cu catalyst was continuously tested during a period of 2 months at room temperature (20–25°C). The inlet concentration in nitrate was 50 mg/l and the flow rate about 50 l/h. In this experiment, the catalyst showed stable good activity and selectivity. At a conversion rate of about 8 mg NO_3^-/g cat h, 90% of the nitrate ions are converted into nitrite ions and the rest 10% into ammonium ions.
- The optimised Pd catalyst for nitrite decomposition was also tested in a fixed-bed reactor in a similar way. A selectivity of 90% towards N_2 formation could also be observed under these conditions at a conversion rate of about 45 mg NO_2^-/g cat h.

2.7.2. Catalyst preparation

The catalysts' preparation has also been adapted to an 80 kg batch scale in a pilot plant unit for catalysts' synthesis. The carrier preparation was relatively difficult to manage and fully control. An automated unit was built, which avoids manual operations and improves the reliability of the carrier preparation. For both Pd and Pd/Cu catalysts, the same carrier was used. This is an alumina gel prepared from aluminium hydroxide (Condea SB), doped with magnesium hydroxide, aged in water, then dried at 150°C and treated in air at 600°C. This carrier has an improved stability against stress and hydrolysis.

The impregnation has been carried out on a 20 kg batch scale due to the limitations of the existing equipment. A two-step impregnation, successively using dilute solutions of Pd chloride in the presence of HCl and dilute buffered solution of Cu acetate, is carried out at room temperature. To limit the thickness of the impregnated layer, impregnation is allowed to occur for a short period of time. The reproducibility of the preparations was checked at the lab scale by applying the standard catalytic tests in batch reactor. For the four 20 kg batches prepared from the same carrier, activity and selectivity patterns are the same in the limit of the reproducibility of the tests.

The Pd/Cu catalyst for nitrate decomposition has a low metal content and a Pd/Cu ratio of about 1 (about 0.25 wt.% of each metal). The scaling-up process led to a very selective catalyst. The Pd catalyst for nitrite reduction contains only 0.2 wt.% of well-dispersed Pd to avoid ammonium formation. The dispersion, measured by CO chemisorption, is about 0.5.

3. Process development

The lab scale results obtained in the first part of the research demonstrate that it is possible to improve the overall activity and selectivity of the catalysts to reduce nitrate ions in water into molecular nitrogen at the condition of using the two-step process. In the first step, nitrate ions are mainly transformed into nitrite ions on a Pd/Cu catalyst, and in the second step, nitrite is decomposed to N_2 on a Pd catalyst, the carrier being the same for both catalysts.

3.1. Experimental field conditions in pilot trials

In order to check the feasibility of such a basic process in practical experimental conditions, the construction of a pilot plant unit was decided and implemented to purify a flow of about 7 m^3/h of ground source water in a rural area. This water contained about 80 mg NO_3^-/l, as well as dissolved oxygen and various impurities like calcium, magnesium, silicon, sulphate and phosphate ions.

The very first plant was built and trials were carried out during 1 year to study the long-term influence of the field conditions on the process and the catalysts. This was done in parallel to the catalyst optimisation study described before. The unit was constituted of a cascade of three reactors. A 60 l fixed-bed reactor is used to reduce the dissolved oxygen on a Pd catalyst (about 30 kg). Two 600 l suspended-bed reactors are used to successively reduce the nitrate ions into nitrite ions on a Pd/Cu catalyst (about 200 kg) and the nitrite ions into nitrogen on a Pd catalyst (about 150 kg). At this stage, the catalysts were not yet optimised and the effectiveness factors were lower than 10%. To kill the naturally present bacteria, the water was treated with sodium hypochlorite before entering the catalytic reactors. Hydrogen and CO_2, used for regulating the pH, were introduced in the system through saturation units. The water natural pressure in the unit was 8 bars and the mean temperature about 14°C with seasonal variations.

The following observations have been made:

- The fresh, not-optimised Pd/Cu catalyst (1 wt.% Pd and 0.25 wt.% Cu on alumina gel) can reduce the nitrate level from 80 to about 40 mg/1 by producing very small amount of nitrite and about 4 mg/1 of ammonium. After a few weeks, however, the catalytic activity decreases and a biological growth is observed in the reactors. At the same time a significant nitrite formation occurs and the ammonium concentration comes down to zero. It is obvious that, at this stage, both biological and chemical activity are present, but their respective contributions to the nitrate reduction cannot be identified.
- The catalyst for nitrite removal (1% Pd on alumina gel) is able to reduce the nitrite from about 25 mg/1 down to less than 10 mg/l with a good selectivity, 90–95% of the nitrite being reduced to N_2.
- A very important interaction is observed between the catalyst and the impurities contained in natural water. After a few weeks of operation, calcium, magnesium, silicon, sulphate and phosphate ions are observed on the surface of the catalyst. Sulphate ions are responsible for the deactivation of the catalysts, as it was shown by lab trials carried out in the presence of different type of ions. During the deactivation period, the catalytic activity is divided by a factor between 5 and 10, and then remains constant. An increase in the hydrogen partial pressure is able to improve the overall performance.
- Despite the deactivation, the chemical and mechanical stability of the catalysts is very good over the whole period. The active metal contents remain very stable and the hydrolysis of the carrier is not observed, even when the catalysts are washed or treated with hydrochloric acid to remove the adsorbed impurities.
- From the chemical engineering point of view, dead zones are observed in the reactors, which favour unwanted biological growth. Tracer experiments also showed a strong back-mixing behaviour in the suspended-beds, which does not favour the selectivity towards nitrogen, as shown by the mass transfer study.

3.2. Biological growth

One of the major difficulties faced in practical conditions is the growth of bacteria, which was not observed during the lab-scale experiments. In order to have a better understanding of the biological process involved, several trials have been designed to study the biological growth and the nature of the biological material. The results can be summarised as follows:

- The biomass observed in the pilot plant have a large variety of autotrophic bacteria, like pseudomonas, aeromonas and others, that are able to oxidise hydrogen. They do not affect the potable character of the water.
- To grow, these bacteria require anoxic conditions. They use H_2 as the source of energy, CO_2 as the source of carbon and NO_3^- as the nitrogen source. The growth rate is very slow, like in a continuous culture system.

- In the biological sample from the plant, free-flowing single cells, as well as cotton wool-like aggregates, are observed between the catalyst particles. To protect themselves against chemical aggression, by hypochlorite ions, for example, the bacteria generate alginate-type biopolymer, which form films or filaments on the surface of the catalyst particles. Microscopic investigations indicate, however, that the access to the catalyst surface remains free. The dry biomass represents only 0.3–0.5 wt.% of the catalyst.
- In order to analyse the growth of bacteria in conditions similar to those existing in the field, a continuous micropilot plant was built in the lab, which consists of a cascade of two reactors. In the first one, a fixed-bed, oxygen is removed on a Pd catalyst, and in the second one, a suspended-bed, the bacterial growth is studied in the presence of a Pd/Cu catalyst. A stable bioculture, initiated by germs coming from the field experiments, can be grown in the reactor in the absence of oxygen. The biomass grows in the second reactor between the catalyst particles, in particular, in the reactor outlet. The biomass produced under these conditions is able to selectively decompose $NO_3{}^-$ ions to $NO_2{}^-$ ions, with an activity 5–10 times higher than the activity of the Pd/Cu catalysts and with a very limited formation of ammonium (less than 1%).
- It is interesting to note that no biological growth is observed in the presence of traces of oxygen and that, in field conditions, the biomass is very limited in the third reactor containing a Pd catalyst to reduce nitrite ions to nitrogen. Even if no clear explanation of this phenomenon exists, it could be assumed that the copper present in the second reactor could play a catalytic role in the growth of the biomass.

As a conclusion, if it is possible to control the development of the biomass, this could play an interesting and positive role in the catalytic process for the selective reduction of nitrate ions to nitrogen.

3.3. Reactor technology

In a catalytic process, the reactor design and the catalyst must be adapted to each other in order to obtain the best possible performances. This is particularly true when the reaction is diffusion limited. The mass transfer phenomenon demonstrated by the kinetic study implies that a plug-flow reactor is required to reach a good selectivity. In the reactor design, this hydrodynamic condition should be taken into account, as well as the possibility of controlling the biological growth in the reactor. Both theoretical and experimental studies have been carried out to develop appropriate technical solutions. The results can be summarised as follows:

- Tracer experiments have been used to determine the residence time distribution in different reactor types (injection of KCl solutions and measurement of electrical conductivity). As previously indicated, in the pilot plant reactor the hydrodynamics behaviour is far away from a plug flow. Various modifications of the reactor design have been tested to reduce the back mixing and improve the plug flow character. Several building elements, like perforated plates, vertical honeycombs or conical mixing elements, were introduced in the cylindrical part of the reactor, but no positive effects were observed. Various trials were also carried out, in which the expansion coefficient of the suspended-bed was modified. It appears that, even with a limited expansion coefficient of 1.2, the back mixing effect is very important. The plug flow conditions can only be approached in the limiting case of an expansion coefficient of 1, i.e., a fixed-bed.
- Consequently, from the hydrodynamic point of view, a fixed-bed reactor is clearly the best solution. But to avoid excessive pressure drop in the reactor, the catalyst particle size should be kept larger than 500 μm. In these conditions, the active layer should be very thin (about 20 μm) to avoid major internal diffusion problems.
- In order to control the biological growth in the reactor, any dead zones must be avoided. The practical expertise of the pilot plant indicates that the sieves used to support the catalyst, and to retain it in the reactor, could also favour the local growth of bacteria and increase the pressure drop in the system. It is the reason why a sieve-free reactor with conical inlet and outlet has been developed and tested using the theory of suspended-bed reactor, as described in [12–14]. This concept allows a regular free flowing of the biomass through the reactor and consequently can reduce the perturbation of the catalytic system. This reactor, however, cannot avoid the problem of back mixing.

- Additional trials have been carried out to test the possible interest of an experimental deep-jet technology reactor developed by IAB Leipzig [15]. This is a perfectly mixed, loop-type reactor, in which very small catalyst particles can be used to avoid diffusion limitations and a highly efficient gas–liquid mixing can be reached. A relatively high activity towards nitrate reduction was obtained. Although the reactor is perfectly mixed from the hydrodynamic point of view, the selectivity remains reasonably good because very small catalyst particles are used, limiting the internal and external diffusion problems. A drawback of this type of reactor is the high abrasion rate of the catalyst, which implies an efficient separation technology to retain the very small particles resulting from the abrasion. Further technological development is still needed.

3.4. *New pilot trials*

To try to define the best technical compromise in the reactor design, in the new pilot trials, two reactor types were tested in parallel. In the new pilot plant, the water first flows through a suspended bed of Pd catalyst where the traces of oxygen are destroyed. The flow is then separated in two parts: one flows through two 600 l fixed-bed reactors equipped with a back-flush system, and the second flows through two 600 l suspended-bed reactors with conical inlet and outlet. In both cases, the first reactor is filled with a Pd/Cu catalyst in order to reduce nitrate to nitrite, and the second one with a Pd catalyst to reduce nitrite to nitrogen. Each reactor contains approximately the same amount of catalyst, i.e., 180 kg.

Interestingly, these new trials show the possibility of controlling the bacterial growth with the new reactor technologies. Both with a regularly back-flushed fixed-bed reactor and with a sieve-free suspended bed, it is possible to operate continuously for several months without trouble.

As far as the operating conditions are concerned, the following observations have been made:

- In the first suspended-bed reactor used to remove dissolved oxygen on a Pd catalyst, the presence of hydrodynamic preferential pathways in the suspended-bed reduces the practical efficiency of oxygen removal. As a consequence, the water flowing through the second reactor still contains oxygen, which decreases the overall activity of the Pd/Cu catalyst for nitrate reduction. To avoid this problem, a fixed-bed reactor should also be used at this first stage.
- The apparent activity of the Pd/Cu catalyst is higher in the fixed-bed reactor than in the suspended-bed, with 20 kg of catalyst in fixed-bed giving the same conversion as 30 kg of catalyst in suspended-bed. Nitrite formation is higher and ammonium formation is lower in the fixed-bed than in the suspended-bed. An increase of hydrogen partial pressure improves selectivity. These observations fully confirm the theoretical analysis of the kinetic and mass transfer study. The overall effectiveness of the catalyst has been estimated to be about 70% in the fixed-bed reactor.
- The Pd catalyst used, having not been fully optimised, the ammonium formation in the third reactor, where nitrite is reduced into nitrogen, is still too high to be acceptable to fulfil the drinking water regulation (maximum allowed ammonium concentration is 0.5 mg/l).
- As previously observed, calcium, magnesium, silicon and sulphate ions are fixed on the catalyst surface after some weeks of operation. This leads to a reduction in the catalytic activity by a factor of 2–2.5. Washing the catalyst by a dilute HCl solution can restore the initial activity.

3.5. *Further improvement possibilities*

3.5.1. *Fully catalytic process*

The multidisciplinary approach presented here and used to develop and improve a catalytic process for nitrate reduction can be considered as a successful one, both from the technical and scientific point of view. Better chemical, biological and technical knowledge has been developed, which opens the door for further improvements and leads to the following conclusions:

- The technical feasibility of a fully catalytic process for nitrate reduction in drinking water has been demonstrated. Such a process is based on a cascade of three fixed-bed reactors, equipped with a back-flush system, which should be regularly operated (at least once a week) in order to get a good control over the biological growth. The first reactor is filled with a Pd catalyst to reduce the oxygen dissolved in water. The second reactor contains an eggshell-impregnated Pd/Cu catalyst with a metal content of about 0.25 wt.% Pd and 0.25 wt.% Cu. In this reactor, a hydrodynamic plug flow should exist to obtain the right activity and selectivity in the nitrate-to-nitrite conversion. The third reactor is filled with an eggshell-impregnated Pd catalyst, characterised by a. high dispersion of Pd. This reactor should also work under plug flow conditions to reach the required selectivity.

- As the biological growth can be controlled by regularly back-flushing the reactors, disinfecting the water at the inlet of the unit does not seem compulsory any more.
- In the second reactor, the pH should to be regulated between 6.1 and 6.5, for example, by a continuous introduction of CO_2. The hydrogen partial pressure should also be kept constant along the reactor, for example, by using a multiple inlet system.
- As the activity of the catalysts is reduced after few weeks of operation due to the presence of various impurities in the water, it is important to design the reactor volumes by taking into account the activity of the aged catalysts. Further optimisation of the Pd/Cu catalyst is needed to minimise the negative effect on activity and selectivity of some anions (like sulphate) present in natural water.

There is a major drawback of a fully catalytic process. Even for a very good global selectivity of 95 mol % in the two reduction steps, the maximum nitrate abatement should be limited to about 10 mg/1, if the maximal authorised level of 0.5 mg of NH_4^+ per litre in potable water should be respected.

3.5.2. Process combining catalysis and biology

A second feasible process for nitrate reduction in drinking water could be a mixed process, which combines the two catalytic steps and a biological step. Like in the fully catalytic process, the first reactor is a fixed-bed reactor, with a back-flush system, filled with a Pd catalyst to destroy the dissolved oxygen. The second reactor is the suspended-bed type, where a specific biomass, able to selectively reduce nitrate to nitrite, is allowed to grow in anoxic conditions on a porous carrier to be purposely developed. Thanks to the new reactor concept with a conical inlet and outlet, a stationary state can be reached and maintained. The activity of this well-adapted biomass is so high that the residence time in the reactor (and consequently the reactor volume) can be very low, compared with a classical biological process. The third reactor is the fixed-bed type, with a back-flush system, filled with a well-dispersed Pd catalyst, which is able to reduce nitrite to nitrogen. In this case, again, there is no need for disinfecting the water at the inlet of the unit.

The basic idea of such a mixed process is to take advantage of the selectivity of the biology by selecting the appropriate anoxic conditions to control the growth of the biomass, instead of trying to suppress it completely. This approach needs further development to better define the optimal conditions of development of this specific biology. It should, however, be pointed out that, at least at the lab scale, the appropriate biomass could be successfully inoculated in a bio-free reactor, an abatement of more than 50 mg NO_3^- being easily obtained with a very high selectivity. Moreover, by introducing a very selective biochemical step, the requirements on the catalytic properties of the Pd catalyst in the third reactor are becoming less stringent. This is the solution that should be technically favoured in future development.

4. Further applications of catalytic reduction in water

The development of catalytic reduction processes applicable to water requires a multidisciplinary approach, which combines key knowledge on catalysis, chemical engineering, physical modelling and biochemistry.

- The expertise gained in the present study was also used in the reduction of traces of halogenated organic compounds in groundwater sources. These compounds could be catalytically dehalogenated by hydrogen on a Pt catalyst or Pd catalyst supported on active coal. In this case, an organic carrier favours the adsorption of organic substances and enhances the catalytic hydrogenation. Even trace amounts of halogenated organic material can be easily removed. As an example, a flow of about 10 l/h of groundwater has been successfully treated in a small pilot unit, during one month, to reduce the total AOX content [16] from 2 to less than 0.1 mg/l.

- The same type of catalysts as those used to reduce nitrate to nitrogen are also able to reduce the bromate ions into bromide ions with a very good efficiency. This process could be applied both in the purification of drinking water, in which bromate ions should be avoided, and in the treatment of wastewater from industrial processes. The reduction of chlorate ions to chloride ions is more difficult, but possible at a slightly higher reaction temperature (50°C) in the presence of an improved catalyst. In this case, an application to drinking water purification is not economically feasible, the warming of the water being expensive. In some industrial processes, however, such a reduction reaction could be an interesting purification tool of wastewater.
- The same principle has been applied to drastically reduce the AOX level of wastewater from industrial units [17]. After a modification of the catalyst carrier to increase its stability towards the salinity and pH conditions of the effluent, pilot experiments showed a very interesting potential of such an approach. The AOX level can be reduced from more than 1000 mg/l to less than 50 mg/l in economically acceptable conditions. In this case, the catalytic reduction appears to be more environmental friendly than the classical reduction processes using chemical reducing agents, like sodium hyposulphite, because the total ionic load after the treatment is less important.

5. Conclusion

The technical feasibility of catalytic reduction processes in drinking water treatment has been demonstrated and a multidisciplinary approach has been presented to develop and improve this type of process.

Compared with catalytic gas-phase reactions, the reduction processes in water are submitted to constrains linked to the presence of micro-organisms, which could interfere with the catalytic reaction and cause drastic modifications in the hydrodynamic behaviour of the reactors by producing an uncontrolled amount of biomass in the system. Several solutions have been proposed to solve this problem.

The diffusion and mass transfer conditions in the water phase are also very different from those encountered in the gas phase, even if a similar theoretical approach could be applied. These conditions of course affect the type of reactor to be used as well as the characteristics of the catalyst.

Kinetic and mechanistic aspects are also important to investigate. Both molecular modelling and kinetics experiments are very useful and should be used to define a realistic process. Even if this process gives very positive results at the lab scale, only pilot experiments in practical field conditions can take into account the effects of impurities present in the water. An adaptation of the reaction conditions to the type of water to be treated is required for each application.

Finally, several examples have been given to demonstrate the interest of catalytic reduction processes, both in drinking water and wastewater treatment, in particular for the destruction of halogenated organic compounds.

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References

[1] K.D. Vorlop, Th. Tacke, Chem.-Ing.-Techn. 61 (1989) 836–838.
[2] Th. Tacke, Ph.D Thesis, Technische Universität Carolo-Wilhelmina, Braunschweig, Germany, 1991.
[3] M. Sell, M. Bischoff, D. Bonse, Vom Wasser 79 (1992) 129–144.
[4] Solvay Umweltchemie GmbH, European Patent No. 89 116245.5, 1989.
[5] A. Pintar, J. Batista, J. Levec, T. Kajiuchi, Appl. Catal. B: Environ. 11 (1996) 81–98.
[6] A. Pintar, J. Levec, Slovenian Patent Application P-9500357, 21 November 1995.
[7] A. Klesing, D. Labrenz, R.A. van Santen, J. Chem. Soc. Faraday Trans. 94 (1998) 3229–3235.
[8] G.E.P. Box, P.Y.T. Liu, J. Qual. Technol. 31 (1999) 1–54.
[9] M. Crine, G.A. L'Homme, Advances in tricked bed reactor modelling, in: L.K. Doraiswany (Ed.), Recent Advances in the Engineering Analysis of Chemically Reacting Systems, Wiley Eastern, New Delhi, 1984, pp. 430–461.

[10] H.S. Fogler, Elements of Chemical Reaction Engineering, Prentice-Hall, Englewood Cliffs, NJ, 1992.
[11] L.D. Schmidt, The Engineering of Chemical Reactions, Oxford University Press, 1998.
[12] J.F. Richardson, W.N. Zaki, Trans. Instn. Chem. Engrs. 32 (1954) 35–53.
[13] A. Kaskas, Berechnung der stationären und instationären Bewegung von Kugeln in ruhenden und strömenden Medien, Dipl. Arbeit, Technische Universität Berlin, 1964.
[14] E. Truckenbrodt, Fluidmechanik, Springer, Berlin, 1989.
[15] IAB, Ingenieurbetrieb Anlagenbau Leipzig GmbH, Postfach 747, 04007 Leipzig, Germany.
[16] AOX: Adsorbable organohalogens compounds measured according to DIN 38409 Part 14, 1985.
[17] Solvay Deutschland GmbH, European Patent 94 909897.4, 1994.