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Effective catalytic removal of nitrates from drinking water: an unresolved problem?

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ABSTRACT

Over the past 29 years there have been myriad research efforts into the catalytic removal of nitrates from drinking water. In this work, 147 papers published during that period have been examined from the point of view of the ability of catalysis to produce water that is suitable for human consumption as well as amenable to industrial scale-up at reasonable working conditions of temperature and residence time. After close examination of the aforementioned articles, it is evident that this methodology has fulfilled only half its aims: it is able to reduce the nitrate concentration to guideline levels for human consumption, but it inevitably produces concentrations of ammonia and nitrites that are beyond the accepted limits for safe consumption of water. It is sometimes recommended that catalysis be combined with an ancillary technique, such as adsorption, in order to eliminate the undesirable byproducts mentioned above. However, this implies resorting to extra treatment units at the industrial scale, thus making the whole treatment process more complex and expensive. Our conclusion is

that the effective catalytic removal of nitrates from drinking water is a very difficult problem.

1. Introduction

High nitrate concentrations in surface water, and especially in groundwater, caused by chemical fertilizers, can pose a serious health risk. If babies under six months of age consume water that is high in nitrate content, this nitrate will be reduced to nitrite which combines with hemoglobin in the blood to form methemoglobin. That, in turn, leads to a health condition commonly known as "blue baby syndrome" (Shuval and Gruener, 1977).

1.1. Current treatment methods for nitrate-contaminated potable water

Currently established physico-chemical processes at the industrial scale, such as ion exchange (IX), reverse osmosis (RO), electro dialysis (ED), and biological denitrification (BD) are discussed in detail in the review carried out by (Jensen et al., 2014). These authors present a survey of nitrate treatment systems in which the advantages and disadvantages of these techniques are explored, which also takes into account geographic location. They find that IX is the methodology most commonly employed for the removal of nitrate ions in the treatment of potable water. Probably the most significant advantage of IX is the amount of knowledge gained after years of industrial experience. Standing out among the disadvantages is the costly disposal of the brine produced during the regeneration of the anion exchange resin. RO is another useful technique that separates water from nitrate and other salts through a semi-

permeable membrane by means of a pressure gradient. The main disadvantage of RO is its high capital and operational costs together with the fact that it produces a substantial amount of waste water that must be properly disposed of. On the other hand, there are very few industrial facilities that use ED to remove nitrates from contaminated drinking water. Its main disadvantages are the costs of waste disposal and inclusion of pretreatment measures to avoid fouling and scaling of the membrane. Although BD is mostly used for the treatment of wastewater (Kiran et al., 2017), there are records of denitrification of potable water at industrial scale in Europe. The main disadvantage of this technique is that posttreatment is required due to the use of denitrifying bacteria and its nutrients that cause the formation of byproducts.

1.2. Catalytic removal of nitrates from drinking water.

Given the economic and ecological disadvantages of the above mentioned techniques (IX, RO, ED and BD) for removing nitrates from drinking water, several researchers have speculated that catalytic hydrogenation of nitrates in water could become a promising alternative process. The earliest works on catalytic denitrification began to be published 29 years ago by Vorlop and other researchers (Hörold et al., 1993a; Hörold et al., 1993b; Tacke and Vorlop, 1993; Vorlop and Tacke, 1989). Their intention was to examine this technique as a means to remove nitrates from polluted water aimed at human consumption. They tested many catalysts, among others, bimetallic Pd-Cu. Their studies showed that nitrates could easily be reduced to trace amounts. They also detected that not all the nitrogen atoms from the nitrates were converted into nitrogen gas (the desirable end product), but instead, a fraction of these atoms became nitrite and

ammonia byproducts. Nitrite is formed as an intermediate byproduct that, with more reaction time, can be partially converted into ammonia. The presence of these non-desirable byproducts in drinking water is problematic because they are more toxic than the nitrates themselves. The limits of nitrates in drinking water have been established at 50 NO_3^- mg/L by the European Community and World Health Organization and at 10 $\text{NO}_3^- - \text{N}$ mg/L (nitrate nitrogen) by the U. S. Environmental Protection Agency. However, the limits of nitrites and ammonium in drinking water are even lower: 0.5 (at tap) and 0.1 NO_2^- mg/L (at works post treatment) and 0.5 NH_4^+ mg/L (European Community). Therefore, our understanding is that these studies on catalytic hydrogenation should not only aim to investigate the potential of nitrate reduction by some catalysts, but also to guarantee that the concentrations of all toxic and unwanted byproducts are below the guideline limits. At this stage, it is useful to recall, for later comparison, some of the results presented in Fig.7 from (Hörold et al., 1993b): It shows that the reduction of nitrate takes place after 15-20 minutes of reaction. It also shows the production and consumption of the intermediate product nitrite. Furthermore, it illustrates the formation of byproduct ammonium with a final concentration of around 5 mg/L (a value ten times the guideline level). Similar figures can be found in many recent papers on the same subject.

The best results from (Hörold et al., 1993b) are shown in their Table 3. There it can be seen that only the lowest hydrogen flow rate results in an ammonium concentration of 0.48 mg/L that is lower than the guideline level in drinking water (0.5 mg/L), however, at the expense of low removal of nitrates. But, if the hydrogen flow rate increases, the ammonium concentration does as well. Therefore, it can be inferred that the removal of nitrates from supplies of drinking water by catalytic reduction poses two challenges:

one, decreasing the levels of nitrates below the guideline level, 50 mg/L, and two, obtaining concentrations of the byproducts nitrite and ammonium that are also below their respective guideline limits. The results of the abovementioned works show that the problem of removing nitrates through catalytic reduction, to obtain safe drinking water, was not completely and successfully addressed in the first half of the 1990s. As a consequence, many researchers, to this day, continue to show interest in this topic, and numerous papers have been published since then.

A number of reviews are available on the denitrification of water. A first review by (Kapoor and Viraraghavan, 1997) describes in detail physico-chemical processes, but barely deals with catalytic reduction, since, at the time, this technique was in its infancy. A second review by (Shrimali and Singh, 2001) summarizes research on the topic from the 10 years prior to its publication. There is a third review more specific to catalysis (Pintar, 2003). Then, there is a fourth and more recent review already discussed above by (Jensen et al., 2014). The fifth, most recent and complete review is presented by (Martínez et al., 2017).

This paper does not intend to analyze, with respect to the denitrification of groundwater, the characteristics of the various catalysts tested in the literature (especially in catalysis journals). Conversely, the aim of the present work is very specific: we examine whether, over the past 29 years, works on catalytic nitrate reduction have overcome the two challenges mentioned above: a) elimination of nitrates and b) absence of nitrite and ammonium byproducts. In other words, this paper explores how successful the catalytic reduction of nitrates in drinking water has been with a view to its posterior application at industrial scale. We emphasize here that, already in 1989, (Vorlop and Tacke, 1989)

claimed that their intention was to obtain an effective catalytic process for purifying drinking water containing nitrates, in other words, a final water product that is potable.

2. Methodology

A total of 147 papers have been closely analysed and the results thereof are collected in Table 1. There we list, in chronological order and to the best of our knowledge, all the existing research papers on the catalytic reduction of nitrates in water, published in the period 1989-2017. There are several different columns in Table 1 detailing: the catalysts and their support, the way the research was conducted, batch or continuous setup, type of water treated (water prepared from deionised water with the addition of nitrate ions, or natural underground water, surface water, tap water, etc.). We have included a column which indicates whether the authors incorporate in their paper any comment on the environmental impact of the catalyst they have tested, particularly in their “conclusion section”, i.e., a final conclusion regarding the performance of that specific catalyst. Also, there is a column that indicates whether the ammonium concentration found in their final product meets the guideline requirement for drinking water. Table 1 allows one to quickly ascertain whether there has been real progress in obtaining drinkable water through this technique.

3. Results

The results listed in Table 1 are discussed in the order that they have been grouped in the different columns. The selected information is related to the purpose of our work: to comment and reflect upon whether the research on catalytic reduction of nitrates is fulfilling its purpose, i.e., obtaining safe drinking water.

3.1. *Chronology of the publications*

Table 1 shows all the papers that have been examined for this review, ordered by their publication date. The interest that this topic has generated over the past three decades can be better gauged if the articles are grouped into periods approximately five years in length, as shown in Fig. 1. The fact that, after three decades, researchers continue to investigate the catalytic reduction of nitrates, especially in the laboratory, indicates that the practical process for this technique has not been found yet.

3.2. *Catalysts and supports*

A close examination of all the catalysts and supports that have been tested over the past three decades also reveals the progress (or lack thereof) in this research area (see Table 1). Researchers have been looking for new catalysts and supports in an attempt to optimize the purification of water. The first bimetallic catalyst tried by the pioneering research of (Vorlop and Tacke, 1989), was made of Pd-Cu. From Table 1 it can be deduced that almost two thirds of all researchers have used this same Pd-Cu as catalyst. A comparative examination of their results show that the reduction activity of this bimetallic pair is the highest among all catalysts tested. Few papers, but not all, show that other pairs, such as Pd-Sn and Pd-In, might procure similar results than the initial pair suggested in (Vorlop and Tacke, 1989). All of this proves that there has been little progress since 1989 in the quest for new and better catalysts. Even nowadays, there are quite a number of papers that still employ the Pd-Cu catalyst. Table 1 also includes a number of papers that use Fe-based catalysts for which a hydrogen flow is not required to reduce nitrate. Fe^0 oxidizes in the presence of nitrates to form $\text{Fe}^{2+}/\text{Fe}^{3+}$ in a redox

process. The reduced nitrates form mainly ammonia. This is one of the disadvantages of using this technique. For instance, (Li et al., 2017), the last publication listed in Table 1, use Fe/Ni nanoparticles supported on biochar for nitrate degradation. The selectivity for ammonium is reported to be 83-98%. To meet the guideline limits for ammonium in drinking water, the authors propose an additional technique, adsorption by cation exchange resin, which proves effective but adds complexity (therefore more capital investment) to the denitrification process, making it less attractive at the industrial scale. As for the support of the catalyst, alumina (Al_2O_3) was initially used. By looking again at Table 1, we can see that around 40% of the research has been conducted using this support. Nevertheless, other supports have also been used, such as SiO_2 , CeO_2 , TiO_2 , Nb_2O_5 , active carbon, ionic interchange resins, etc. In any case, alumina still remains the support of choice in several of the most recent works.

3.3. *Tests in batch or continuous reactors*

The mode of reaction represents another piece of useful information that can be looked up in Table 1. It can be seen that, among the 147 papers listed, only 30 use continuous reactors to test their catalysts. The rest perform tests in the batch mode, or to be more precise, in semi-batch mode because the reductant gas, H_2 , flows to the reactor while water is kept trapped inside. The fact that, nowadays, experiments are still run in semi-batch and not in continuous mode, is an indication that the catalytic reduction has not progressed sufficiently to move on to the next practical stage: the large-scale purification of water for human consumption.

3.4. *Tests with prepared or natural water*

It is also shown in Table 1 that, out of the 147 papers examined, only 13 of them execute tests under more realistic conditions, i.e., contaminated groundwater, superficial or tap water. The remaining experiments make use of prepared water that consists of deionised water with the addition of nitrate ions. The few realistic experiments show that if, for instance, the natural water also contains bicarbonate ions, the reducing ability of the catalysts decreases. The first article stating this fact was written by (Pintar et al., 1998b) who found that the nitrate disappearance rate and nitrogen production yield decrease appreciably in the presence of hydrogencarbonates. Other authors have confirmed similar results, such as for instance (Matatov-Meytal et al., 2001), who reveal that certain salts present in water influence the activity and the selectivity of their catalyst. Also, (Chaplin et al., 2006) claim that natural groundwater samples inhibit the catalytic nitrate reduction reaction. These results show how difficult it is to transfer the laboratory technique to a realistic situation that requires the purification of water.

3.5. Examination of the “Conclusion section” of the papers listed in Table 1.

Table 1, as mentioned above, also contains a column with comments about the results discussed in the “Conclusions section” of the 147 reviewed papers. The main objective of these papers should have been to accomplish an effective catalytic process for purifying water sources contaminated by nitrate, to ultimately make them fit for human consumption. This column is subdivided into another two. The first one checks whether the authors answer the following question: Is the catalyst assessed as not effective for purifying drinking water? By looking at Table 1, it can be observed that some authors do consider the catalyst to be ineffective (although, not explicitly), while others do not even make such a relevant statement. The second column checks whether the authors state the worrying and toxic concentration levels of ammonium obtained after their

catalytic experiments. Again, some authors fail to assess the high values of ammonium (beyond the guideline toxic values) in their conclusions section, even though those are the concentration values reported in the main body of their papers. In general, most authors insist mainly on the specific characteristics of their catalyst in the conclusions section, and on some occasions, they discuss aspects pertaining to the kinetics of the nitrate reduction.

3.6. *Prospect*

Our view is that this research topic has come to a standstill. We, therefore, suggest that it be studied from a different angle. For instance, thermodynamic considerations could be used to assess if it would be possible to reduce nitrate to nitrogen without the production of the byproduct ammonium.

4. **Conclusions**

As is evident from Table 1, a good-enough catalyst for the industrial-scale production of water that is fit for human consumption has not yet been found. A number of difficulties frustrates this goal: A long reaction time (some authors claim that they need around 200 minutes, or even several hours, to substantially decrease the nitrate concentration) implies the use of an unrealistically large reactor. If a shorter residence time is used, the final concentration of nitrite in water would be higher than the admissible levels. Furthermore, this treatment plant would be a serious safety hazard due to the gaseous hydrogen used as a reactive agent to reduce the nitrates. Section 1.1 discussed the review by (Jensen et al., 2014), which mentions many locations of industrial-scale plants that employ IX, RO and ED. However, there is no existing industrial plant

devoted to chemical denitrification. For instance, (Jensen et al., 2014) indicate that RO is a feasible technique for the removal of nitrate from drinking water at the point of consumption. Indeed, there are several small commercial RO devices to purify tap water that are already in use in many homes. This clearly suggests that RO represents an *alternative* to catalysis. 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 ending up in the treated water.

It is evident that over the past 29 years there has been a profound study of the mechanisms of catalytic reduction of nitrates in water. The myriad papers published after those by Vorlop and collaborators in the early 1990s, may have reported success in the removal of nitrates, but they failed to address the concomitant and undesirable problem of the formation of toxic byproducts. Some researchers, such as (Kim et al., 2016) and (Mendow et al., 2017) use a combined catalytic-ionic exchange process with a view to reducing the content of ammonium in the final water. But, in reality, this process is more complex, requiring two or three stages, including regeneration of the ionic exchange resin, which, in turn, can produce waste streams containing concentrated brines that also require further treatment before disposal. In (Kim et al., 2016), the regeneration of the resin was performed by using a 1:1 mixture of H_2 and CO_2 , in a batch configuration that operates at 6 bar, for 6 hours at 60°C. All these extra treatment units, long reaction times and/or high temperatures obviously complicate the overall water potabilization process at the industrial scale.

At this point, we would like to stress that the novelty of our work resides in the perspective taken in this paper regarding research on drinking water denitrification via catalysis,

i.e., that its primary purpose is to “obtain potable water”. To corroborate that there has not been real progress in these 29 years of research we can examine the results obtained in the latest papers published. For instance, reference 146 in Table 1 (Hao and Zhang, 2017) report values of ammonium selectivity around 30 – 50%. Using additional data provided by the authors and assuming a 75% removal of nitrate, these values of selectivity imply that the concentration of ammonium will range between 4.5 – 7.5 mg/L which is well beyond the recommended guideline value for drinking water. Also, reference 145 in Table 1 (Wang et al., 2017) reports values between 3.5 – 5 $NH_4^+ - N$ mg/L (ammonium nitrogen) for a reaction time of 180 minutes which are again beyond the guidelines. Despite the lack of satisfactory results from the catalytic reduction, most of the 147 papers mentioned in Table 1 contain lengthy descriptions of the preparation of the catalysts, and of their supports, together with the associated methods of characterization: scanning electron microscope (SEM) images, X-ray diffraction (XRD) patterns, temperature-programmed reduction (TPR) profiles, etc. In our opinion, it only makes sense to go ahead and describe in detail the preparation of a catalyst if one is found that is good enough to yield very low concentrations of nitrates, nitrites and ammonia and, at the same time, is amenable to industrial scale-up.

To finalize, we would like to clarify that we do not question the scientific results of the papers reviewed here, or the associated interest in catalysis. We, however, believe that the effective removal of nitrates from drinking water, by catalysis, is a very difficult problem.

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Fig. 1. Number of articles on catalytic reduction of nitrates in drinking water, published during the various considered time periods.

147 papers on catalytic removal of nitrates from drinking water have been examined

No catalyst has been found to simultaneously decrease nitrate, nitrite and ammonia

To transfer this lab technique to purify water to a realistic situation, is difficult

The catalytic removal of nitrates from drinking water is still an unresolved problem

Table 1

Summary of the list of literature reviewed

#	Reference	Catalyst	Support	Experimental reactor		Water test		Conclusion section	
				Batch	Continuous	Deionised water	Tap or ground water	Is the catalyst assessed as not effective for purifying drinking water?	Is the NH ₃ level quoted?
1	(Vorlop and Tacke, 1989)	Pd-Cu	Al ₂ O ₃	X		X		X	X
2	(Tacke and Vorlop, 1993)	Pd, Pd-Cu	Al ₂ O ₃	X		X		X	X
3	(Hörold, S. et al., 1993)	Pd-Cu	Al ₂ O ₃	X		X		X	X
4	(Hörold, Sebastian et al., 1993)	Pd-Cu	Al ₂ O ₃	X		X		X	X
5	(Wärna et al., 1994)	Pd-Cu	Al ₂ O ₃	X		X			X
6	(Pintar et al., 1996)	Pd-Cu	Al ₂ O ₃	X		X			
7	(Strukul et al., 1996)	Pd-Cu	Sol-gel Al ₂ O ₃	X		X		X	X
8	(Prüsse et al., 1997b)	Pd-Cu	Al ₂ O ₃	X		X		X	X
9	(Hahnlein et al., 1997)	Pd-Cu	Al ₂ O ₃	X		X		X	X
10	(Prüsse et al., 1997a)	Pd-Cu	Al ₂ O ₃	X		X		X	X
11	(Batista et al., 1997)	Pd-Cu	Al ₂ O ₃	X		X			X
12	(Pintar et al., 1998b)	Pd-Cu	Al ₂ O ₃	X			X	X	X
13	(Pintar et al., 1998a)	Pd, Pd-Cu	Al ₂ O ₃	X		X		X	X

14	(Lüdtke et al., 1998)	Pd-Cu	Al ₂ O ₃ polyetherimide membrane		X	X		X	X
15	(Huang et al., 1998)	Iron powder		X		X		X	X
16	(Hähnlein et al., 1998)	PdCu PdZn PdIn PdSn	Al ₂ O ₃	X	X	X			X
17	(Daum and Vorlop, 1999)	Pd-Cu Pd-Sn	Al ₂ O ₃	X		X			
18	(Pintar and Batista, 1999)	PdCu	Al ₂ O ₃		X	X	X	X	X
19	(Daub et al., 1999)	PdSn	Ceramic membrane Al ₂ O ₃		X	X			
20	(Matatov-Meytal et al., 2000)	Pd	fibrous cloth	X		X		X	X
21	(Deganello et al., 2000)	Pd-Cu	pumice	X		X			
22	(Strukul et al., 2000)	Pd-Cu Pd-Sn	powders tubular membranes alumina	X	X	X		X	X
23	(Prüsse et al., 2000)	Pd-Cu Pd-Sn Pd-In	Al ₂ O ₃ Poly (vinyl alcohol)	X	X	X	X	X	
24	(Ilinitch et al., 2000)	Pd-Cu	Ceramic membrane Al ₂ O ₃	X		X			
25	(Choe et al., 2000)	Nanoscale iron		X		X			
26	(Ilinich et al., 2000)	Pd Cu Pd-Cu	Ceramic membrane Al ₂ O ₃	X		X			
27	(Pintar et al., 2001b)	Pd-Cu	Al ₂ O ₃ Combined process ion exchange		X		X	X	X
28	(Pintar et al., 2001a)	Pd-Cu	Al ₂ O ₃		X		X	X	X

			Combined process ion exchange				
29	(Epron et al., 2001)	Cu Pt Pt-Cu	Al ₂ O ₃	X	X		
30	(Berndt et al., 2001)	Pd-Sn	Al ₂ O ₃	X	X		X
31	(Matatov-Meytal et al., 2001)	Pd-Cu	glass fiber	X	X		
32	(Prüsse and Vorlop, 2001)	Pd-Cu Pd-Sn Pd-In	Al ₂ O ₃ H ₂ formic acid	X	X		
33	(Matatov-Meytal and Sheintuch, 2002)	Pd, Pd-Cu	granulated activated carbon (GAC), fibrous activated carbon cloths (ACCs) or glass fiber cloths (GFCs)	X	X		
34	(Yoshinaga et al., 2002)	Pd-Cu	AC carbón activo, SiO ₂ Al ₂ O ₃ ZrO ₂	X	X		
35	(Gavagnin et al., 2002)	Pd, Pd-Cu	SnO ₂ , ZrO ₂	X	X		
36	(Chollier-Brym et al., 2002)	Pd-Sn Pd-Cu	Al ₂ O ₃ ZrO ₂	X	X		
37	(Lemaigen et al., 2002)	Pd-In, Pd-Cu, Pd-Sn	Active carbon	X	X	X	X
38	(Epron et al., 2002a)	Pd	CeO ₂ Al ₂ O ₃	X	X	X	X
39	(Epron et al., 2002b)	Pt-Cu	Al ₂ O ₃	X	X		
40	(Chen et al., 2003)	Pd Pd-Cu	Al ₂ O ₃	X	X	X	X
41	(Gao et al., 2003)	Pd-Cu	TiO ₂ Al ₂ O ₃	X	X		
42	(Palomares et al., 2003)	Pd-Cu	Hydrotalcites Al ₂ O ₃	X	X		
43	(Roveda et al., 2003)	Pd-Sn	Acrylic resins	X	X		

44	(Matatov-Meytal et al., 2003)	Pd	ACC Activated Carbon Cloth	X	X				
45	(Gauthard et al., 2003)	Pt Pd (Cu,Ag,Au) addition	Al ₂ O ₃	X	X				
46	(Mikami et al., 2003)	Pd Pd-Cu	Active carbon	X	X				X
47	(Ilinich et al., 2003)	Pd-Cu	Macroporous polymeric membrane	X	X				
48	(Mikami et al., 2004)	Ni-Zr		X	X				
49	(Palomares et al., 2004)	Pd-Cu	Hydrotalcites Al ₂ O ₃	X	X				
50	(D'Arino et al., 2004)	Pd Pt	SnO ₂	X	X				
51	(Pintar et al., 2004)	Pd-Cu Pd-Sn	Al ₂ O ₃	X	X				
52	(Choe et al., 2004)	Fe ⁰		X	X				
53	(Huang and Zhang, 2004)	Fe ⁰		X	X				
54	(Sá and Vinek, 2005)	Pd-Cu	Al ₂ O ₃	X	X				
55	(Sá et al., 2005b)	Pd-Sn	Al ₂ O ₃	X	X				
56	(Garron et al., 2005)	Pd Pd-Sn	Al ₂ O ₃ SiO ₂	X	X				
57	(Garron and Epron, 2005)	Pd Pd-Sn	SiO ₂	X	X				X
58	(Rodríguez et al., 2005)	Pt Pt-Sn	HZSM-5	X	X				
59	(Chen et al., 2005)	fluidized zero valent iron (ZVI) reactor			X	X	X		X
60	(Sá et al., 2005a)	Pd Pd-Cu Pd-Au Pd-Ru	TiO ₂ Ak ₂ O ₃	X	X		X		X

61	(Sá et al., 2005c)	Pd Pd-Cu	Ak ₂ O ₃	X	X		
62	(Nakamura et al., 2005)	Pd.Cu	Zeolites	X	X		
63	(Gašparovičová et al., 2006)	Pd-Cu	Strong cationic resin Dowex 1x4	X	X	X	X
64	(Pintar and Batista, 2006)	Pd Pd-Cu	Al ₂ O ₃	X	X	X	X
65	(Barrabés et al., 2006)	Pt-Cu Pd-Cu	Active carbon		X	X	
66	(Nakamura et al., 2006)	Pd-Cu	Mordenite Al ₂ O ₃		X	X	X
67	(Chaplin et al., 2006)	Pd-Cu	Al ₂ O ₃		X	X	X
68	(Wang et al., 2007)	Pd-Cu	Hydrotalcita	X	X		
69	(Constantinou et al., 2007)	Pd-Cu	Al ₂ O ₃ Mn ₂ O ₃ CeO ₂ TiO ₂ Y ₂ O ₃	X	X		
70	(Gašparovičová et al., 2007)	Pd-Cu	Resin Dowex 1x4	X	X		
71	(Pintar and Batista, 2007)	Pd Pd-Cu	Al ₂ O ₃	X	X	X	X
72	(Sá et al., 2007)	Pd- Bi	SnO ₂	X	X		X
73	(Maia et al., 2007)	Pd-Cu	Nb ₂ O ₃ Al ₂ O ₃	X	X		
74	(Ranga Rao and Mishra, 2007)	Pd Pd-Cu	Al-pillared clay	X	X		
75	(Marchesini et al., 2008b)	Pd-In Pt-In	Al ₂ O ₃ SiO ₂	X	X	X	X
76	(Marchesini et al., 2008a)	Pd-In Pt-In	Al ₂ O ₃ SiO ₂	X	X		
77	(Witońska et al., 2008)	Pd-In	Al ₂ O ₃	X	X		

78	(Soares et al., 2008)	Pd–Cu, Pt–Cu, Rh–Cu, Ru–Cu, Pd–Ir, Pd–Sn, Pd–Fe, Pd–Ni, Pd–Zn, Ir–Cu, Rh–Sn, Pt–Sn and Pt–Fe,	Activated carbon	X		X		X		X	
79	(Choi and Batchelor, 2008)	Fluoride green rust modified with copper			X		X		X		X
80	(Sá and Anderson, 2008)	Pd	TiO ₂	X		X					X
81	(Wan et al., 2009)	Pd-Sn	Hydrotalcita (Al-Mg)	X		X					
82	(Soares et al., 2009)	Pd–Cu, Pt–Cu, Rh–Cu and Ir–Cu	Activated carbon	X		X					X
83	(Wang et al., 2009)	Pd-Cu	Active carbon			X		X		X	X
84	(Wehbe et al., 2009)	Pd-Cu	TiO ₂	X		X			X		X
85	(Shukla et al., 2009)	Fe	Activated carbon	X	X	X			X		X
86	(Chaplin et al., 2009)	Pd-In	Al ₂ O ₃			X		X		X	X
87	(Liou et al., 2009)	Iron deposited noble metal and copper			X			X		X	
88	(Neyertz et al., 2010)	Pd Pd-Cu Pd-In	Resin	X		X			X		X
89	(Soares, Olívia Salomé G. P. et al., 2010a)	Pd-Cu Pt-Cu	Carbons	X		X					
90	(Soares, Olívia Salomé G. P. et al., 2010b)	Pd-Cu Pt-Cu	Carbon nanotubes	X		X					

91	(Barrabés et al., 2010)	Pt	CeO ₂	X	X	X	X
92	(Palomares et al., 2010)	Pd-Cu Pd-Sn	Al ₂ O ₃	X		X	
93	(Soares, O. S. G. P. et al., 2010)	Pd-Cu Pt-Cu	Activated carbon	X	X		
94	(Wehbe et al., 2010)	Pd-Cu	Alumina tubes mesoporous mebrane	X	X	X	X
95	(Constantinou et al., 2010)	Pd-Cu	TiO ₂ -Al ₂ O ₃	X	X		
96	(Calvo et al., 2010)	Pd-Cu Rh Ni	Activated carbon	X	X		
97	(Sun et al., 2010)	Pd-Cu	Bacterial cellulose nanofibres	X	X	X	
98	(Marchesini et al., 2010)	Pt-Im Pd-In	Al ₂ O ₃ SiO ₂	X	X	X	X
99	(Soares et al., 2011a)	Pd Pd-Cu	Several metal oxides, as well as composites of metal oxides and activated carbon or carbon nanotubes,	X	X		
100	(Soares et al., 2011b)	Pd-Cu Pt-Cu Rh-Cu	Activated carbon	X	X		
101	(Palomares et al., 2011)	Pd-Sn Pd-Cu	Al ₂ O ₃ Active carbón Graphite Hydrotalcita	X		X	X
102	(Aristizábal et al., 2011)	Pt-Cu	Hydrotalcita	X	X		
103	(Theologides et al., 2011)	Pd-Cu	Mixed oxides MxOy-Al ₂ O ₃	X	X		X
104	(Devadas et al., 2011)	Pd-(Sn,In,Ag)	CeO ₂	X	X	X	X

105	(Hwang et al., 2011)	Nano zero valent iron Fe/Cu		X		X			X
106	(Trawczyński et al., 2011)	Pd-Cu	Active carbon	X		X		X	X
107	(Mendow et al., 2011)	Pd-In	Al ₂ O ₃ SiO ₂		X	X		X	X
108	(Costa et al., 2012)	Pd-Sn	Al ₂ O ₃	X		X			
109	(Wada et al., 2012)	Pd Pd-Cu	TiO ₂ ZrO ₂ CeO ₂ Al ₂ O ₃ SiO ₂	X		X			
110	(Sun et al., 2012)	Pd	Fe ₃ O ₄	X		X		X	X
111	(Soares et al., 2012b)	Pt-Sn	Activated carbon TiO ₂	X		X			
112	(Soares et al., 2012a)	Pd-Cu	Nanotubes carbon	X		X			
113	(Franch et al., 2012)	Pd-Cu Pd-Sn	Al ₂ O ₃		X		X		
114	(Soares et al., 2012c)	Pd-Cu	Multiwalled carbon nanotube	X			X	X	
115	(Choi et al., 2012)	Green rusts modified with trace metals		X		X			
116	(Pera-Titus et al., 2012)	Pd-Cu	Alumina membrane		X	X			
117	(Jung et al., 2012)	Pd-Cu	Maghemite	X		X			
118	(Marchesini et al., 2012)	Pd-In	Mixed Al ₂ O ₃ SiO ₂	X		X		X	X
119	(Chen et al., 2013)	Pd-Cu	Titanate nanotube TiO ₂	X		X		X	
120	(Bae et al., 2013)	Pd-Cu	TiO ₂	X		X		X	X
121	(Bou Orm et al., 2013)	Pd-Cu/(Mg, Nb)	TiO ₂	X		X		X	X

122	(Shin et al., 2014)	Pd	TiO ₂	X	X	X	X
123	(Zhao et al., 2014)	Cu, Ni, Pd- Cu Pt-Cu Au- Cu Ru-Cu	Al particles	X	X	X	X
124	(Rocha et al., 2014)	Pd-Sn	Al ₂ O ₃	X	X		
125	(Aristizábal et al., 2014)	Pt-Ag	Activated carbon		X		X
126	(Jung et al., 2014)	Pd-Cu	Hematite	X	X	X	X
127	(Salam et al., 2015)	Fe ⁰	Nanographene	X	X		X
128	(Garcia-Fernandez et al., 2015)	Pt Pt-Sn	Polypyrrole	X	X	X	X
129	(Soares et al., 2015)	Mono y bimetallic Pd-Cu	NaY zeolite	X	X		
130	(Hou et al., 2015)	Al-Fe alloy Catalyzed by copper		X	X		X
131	(Nakayama and Takahashi, 2015)	Pd-Cu	Al ₂ O ₃	X	X		
132	(Gao et al., 2015)	Pd-In	Mesoporous Al ₂ O ₃	X	X		
133	(Pizarro et al., 2015)	Monometalli c (Ir, Pd, Pt and Rh) and bimetallic (Pd-Cu, Pd- In and Pd- Sn) catalysts	Al-pillared clays.	X	X	X	X
134	(Lee et al., 2015)	Pd	Ceria Ceria-zirconia	X	X		
135	(Zoppas et al., 2016)	Pd -In	Activated carbon felts	X	X	X	X
136	(Kim et al., 2016)	Pd-Cu	Ion exchange	X	X	X	X

137	(Lubphoo et al., 2016)	Bimetallic (Cu–nFeO, Pd–nFeO) and trimetals (Cu–Pd)–nFeO, (Pd–Cu)–nFeO		X		X			X	X
138	(Bergquist et al., 2016)	Pd-In	Activated carbón A hybrid ion exchange-catalytic process		X		X		X	
139	(Ding et al., 2017)	PdAg Pd-Cu	Amine-functionalized SiO ₂	X			X			
140	(Hirayama and Kamiya, 2017)	Pt SnPd	TiO ₂ photocatalytic Al ₂ O ₃ nonphotocatalytic	X			X			
141	(Mendow et al., 2017)	Pd-Cu	Ion exchange resin		X			X	X	X
142	(Devard et al., 2017)	Au, In-Au, Pd-Au, Pd-In-Au	TiO ₂	X			X		X	X
143	(Madison et al., 2017)	Pd-In	Al ₂ O ₃	X	X		X			
144	(Antolín et al., 2017)	Ag, Pt, Ag-Pt	TiO ₂ Non-photocatalytic Photocatalytic	X			X		X	
145	(Wang et al., 2017)	Pd-Cu	TiO ₂	X			X		X	
146	(Hao and Zhang, 2017)	Pd-Cu, Pd-Sn, Pt-Cu, Pt-Sn, Pd, Pt, Fe ⁰	Al ₂ O ₃	X			X			

147	(Li et al., 2017)	Fe-Ni nanoparticles	Biochar	X	X	X	X
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