Short communication

Controlled deposition of Pd and In on carbon fibers by sequential electroless plating for the catalytic reduction of nitrate in water

F.M. Zoppas [a,b], F.A. Marchesini [a], A. Devard [a], A.M. Bernardes [b], E.E. Miró [a,*]

[a] *Instituto de Investigaciones en Catálisis y Petroquímica (FIQ, UNL-CONICET), Santa Fe, Argentina*
[b] *Programa de Pós-Graduação em Engenharia de Minas, Metalúrgica e de Materiais (PPGE3M-UFRGS), Porto Alegre, Brazil*

A B S T R A C T

Catalysts containing 1.8 wt.% of Pd and different In loadings were prepared by sequential electroless plating on activated carbon felts (ACF). Homogeneous structures were obtained, with In particles deposited at the top of a tiny Pd film. The catalyst with the higher In loading (Pd:In ratio of 2.0) presented high activity and good selectivity towards nitrogen, with negligible deactivation after 6 h of time-on-stream and three consecutive nitrate pulses. Besides the promising catalytic behavior, PdIn/ACF have the advantages of an open structure, which is highly accessible to the reactants, with no need of separation after the reaction.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Nitrate is considered a potentially hazardous when groundwater is used as a supply of drinking water. The maximum levels of nitrate, nitrite and ammonium species recommended in drinking water by the World Health Organization are of 44.0, 0.1 and 0.5 mg/L, respectively.

The catalytic reduction is considered as one of the most promising methods to treat water contaminated with nitrates. In this process, nitrates are reduced to nitrogen using hydrogen or other reducing agents, but undesirable compounds as ammonia and nitrite are also formed, thus the adequate control of activity and selectivity is a key issue for the effectiveness of this method [1]. The controlled deposition of bimetallic particles on different supports is an issue of great interest in designing catalysts for this process [2]. A promising method for this purpose is electroless plating (ELP), which is a catalytic process whereby a chemical reducing agent reduces a metallic salt onto specific surface sites of the catalytic surface [3]. In a previous work [4] it was demonstrated that Pd nanoparticles can be homogeneously deposited on the surface of carbon fibers, being active and selective for nitrite reduction with hydrogen. However, while Pd nanoparticles are effective for nitrite reduction, this is not the case for nitrate reduction. For this purpose, another metal must be loaded, for example Cu or In. In is a good candidate, being the optimal Pd:In ratio about 1:0.25 in a weight basis, when alumina or silica are the supports [5].

We have selected carbon fiber felts as the support for PdIn bimetallic catalysts because cloths and felts from thin μm-sized fibers allow reducing the diffusion limitations and the pressure drop in reactors; as well as combining an open macrostructure with mechanical flexibility [6,7].

The aim of this contribution is to find new ways to control the catalyst performance using a well-defined procedure for its preparation, that is the electroless plating method. To this end, carbon fiber felts were used as a support for Pd,In active phases which were homogeneously deposited by a sequential electroless plating (ELP) technique to obtain active and selective catalysts deposited on a structured support. The catalysts were tested in the nitrate reduction reaction using hydrogen as reducing agent, and the results were compared with those obtained with a conventional PdIn/Al$_2$O$_3$ catalyst [5]. They were also characterized by XRD, EDS, SEM and XPS techniques.

2. Experimental

2.1. Preparation of catalytic felts PdIn/ACF (activated carbon felt)

Commercial activated carbon felts (ACN 211-15, American Technical Trading, Inc.; area density: 180 g·cm^{-2}, surface area: 1500 m^2·g^{-1}, thickness: 2.00 mm) were used. They were treated in aqueous solutions of HCl 4.8 M for 2 h at 50 °C and then rinsed in distilled water and dried at 80 °C for 12 h. The Pd felts were prepared in two steps. First, the surfaces were activated by deposition of catalytic Pd seed nuclei using a conventional two step SnCl$_2$/PdCl$_2$ procedure [4]: substrates were immersed for 5 min in a 0.6×10^{-3} M solution of SnCl$_2$·2H$_2$O (pH 2) and then for another 5 min in a 0.1 M solution of PdCl$_2$ (pH 2); this sequence

Table 1
Plating Bath compositions.

Composition of plating baths		Samples			
		Pd	$(PdIn)_A$	$(PdIn)_B$	$(PdIn)_C$
Pd bath	$PdCl_2$ (mM)	2.5	2.5	2.5	2.5
	Na_2EDTA (mM)	25.3	25.3	25.3	25.3
	NH_4OH (7.1 M) (mL/L)	80	80	80	80
	N_2H_4 (20 mM) (mL/L)	5	5	5	5
In bath	$In(NO_3)_3$ (mM)	0	0.6	1.5	3.0
	HCl(0.4 M) (mL/L)	0	4	10	20
	N_2H_4(0.2 M) (mL/L)	0	1	1	2

was considered as an activation cycle. Electroless plating (ELP) was used to grow the Pd nuclei. The synthesis features are shown in Table 1.The felts were immersed in the Pd plating bath for 90 min at 50 °C, and a

Pd/ACF catalyst sample, with 1.8 wt.% of the noble metal determined by ICP, was obtained. The as-deposited samples were carefully rinsed with deionized water. Then, the felts were immersed in the In plating bath (10 ml/cm² felt) with the same reducing agent (N_2H_4, 0.20 M). Three samples (A, B and C) were prepared by this technique with Pd:In ratios determined by EDS of 9.5, 3.5 and 2.0, respectively. Again, the fibers were carefully rinsed with deionized water and finally dried at 80 °C.

2.2. Catalysts characterization

2.2.1. X-ray diffraction (XRD)

The XRD patterns of the films were obtained with an XD-D1 Shimadzu instrument, using CuKα radiation at 30 kV and 40 mA. The scan rate was 2°/min in the range 2θ = 10–90°.
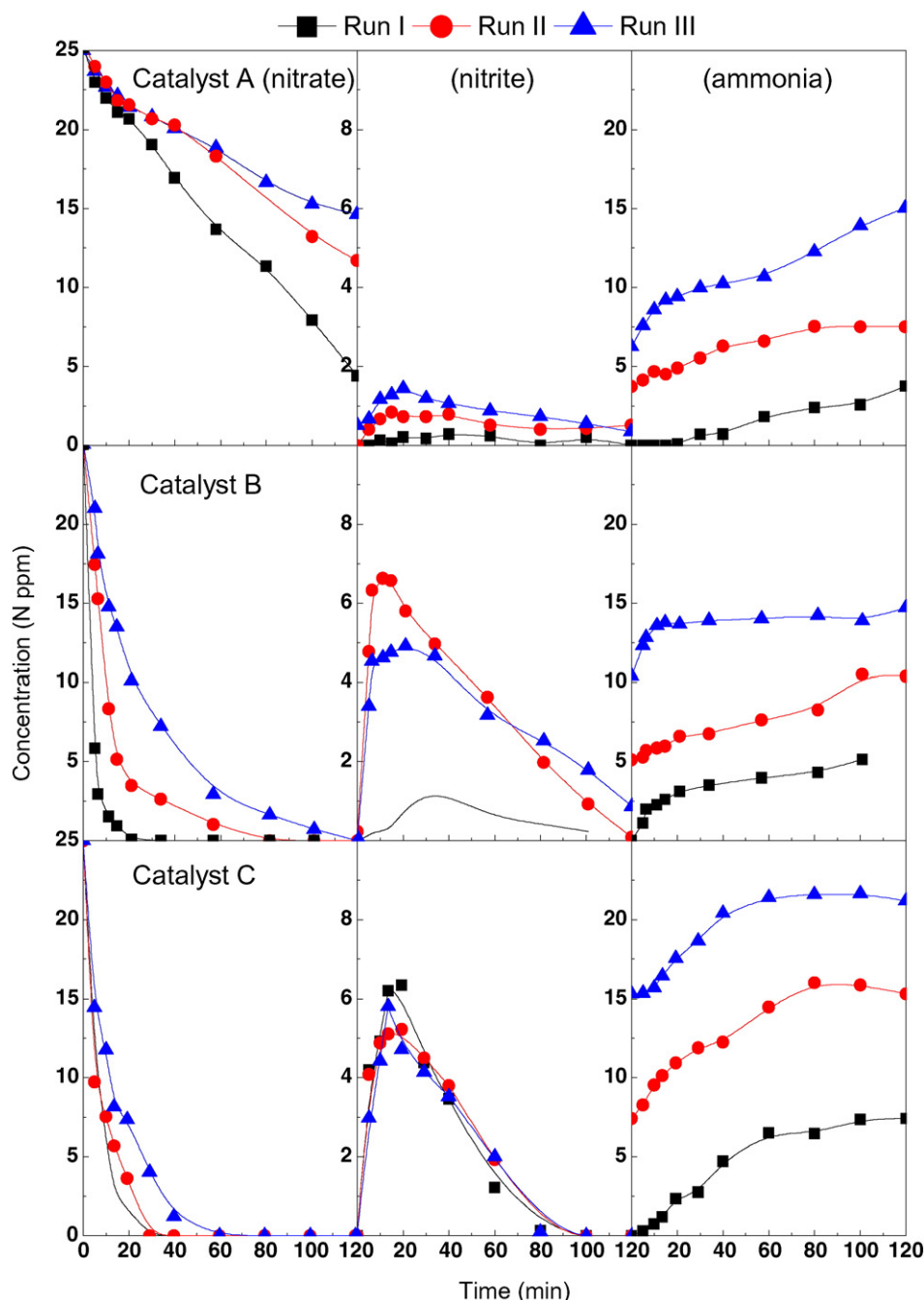

Fig. 1. Concentrations of nitrate, nitrite and ammonium after three consecutive pulses of 25 ppm of nitrate (Catalysts A, B and C), under hydrogen flow.

2.2.2. Scanning electron microscopy (SEM)

The images were obtained using a JEOL scanning electron microscope; model JSM-35C, equipped with an energy dispersive analytical system (EDS, EDAX™).

2.2.3. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) analyses were performed in a multi-technique system (SPECS) equipped with a dual Mg/Al X-ray source and a hemispherical PHOIBOS 150 analyzer operating in the fixed analyzer transmission (FAT) mode. The spectra were obtained with a pass energy of 30 eV and the Mg-KX-ray source was operated at 200 W. The XPS analyses were performed on the fresh and used catalysts pre-treated in the load-lock chamber in a flowing H_2/Ar mixture for 1 h. The spectral Pd3d, In3d, Sn3d, O1s and C1s were recorded. The C spectrum (284.6 eV) was used as a baseline for determining the position of the peaks in each spectrum.

2.2.4. Activity test

The catalytic reduction of nitrate was performed in a three-necked round bottom flask (volume 250 ml) equipped with a magnetic stirrer (800 rpm). Using hydrogen as reducing agent, a stirred batch reactor was loaded with 120.0 mL of distilled water and 300 mg of the catalyst. A pretreatment was carried out under a flow of N_2 (100 mL/min) for 15 min and of H_2 (100 mL/min) for 60 min at 25 °C. Subsequently, 1.8×10^{-3} M KNO_3 (25 N-ppm of nitrate) was loaded as initial concentration and a hydrogen flow of 400 mL/min was fed to the batch reactor through a tube into the solution. The OH^- formed during the reduction was neutralized by the addition of small amounts of HCl 0.1 M to maintain the pH of 5. Each reaction was performed in 3 consecutive runs. Every 2 h 25 N-ppm nitrate was added to the reactor.

Samples of 0.25 mL were taken from the vessel for the determination of nitrate, nitrite and ammonium using Visible spectroscopy (Cole Parmer1100 Spectrophotometer) combined with colorimetric reagents. For the nitrates determination the Cd column method and then the colorimetric Gries reaction were used [8]. This method is the same used for the determination of nitrites. Ammoniun was analyzed by the method of Berthelot [9].

Catalytic results are expressed as conversion X (%) and selectivity S (%) that are defined as:

$$X(\%) = [1 - (C/C_0)] \times 100 \qquad (1)$$

$$S(\%) = [C_A/(C_0 - C)] \times 100 \qquad (2)$$

where C_0 is N-ppm of nitrates at the beginning of the reduction process, C is N-ppm of nitrates at time t, and C_A is N-ppm of products (nitrites or ammonia) at time t. Nitrogen selectivity was calculated by difference $(100 - S_{NO2} - S_{NH4})$. Other species such as NO and N_2O are negligible due to the rapid reduction into N_2 when palladium catalysts are used [4].

3. Results and discussion

3.1. reaction studies

Fig. 1 shows the concentrations of nitrate, nitrite and ammonium after three consecutive pulses of 25 ppm of nitrate (reactions a, b and c), under hydrogen flow. The second and third pulses were injected after 2 hours of reaction. During the first 20 min of time-on-stream, the nitrate concentration dropped quickly when using the B and C catalysts. The final ammonium concentration was less than 8 N-ppm (in each run), and despite being higher than the admitted by regulations, it can be removed with a simple process of chlorination [10]. The nitrite concentration presents the behavior of an intermediate product. The maximum observed nitrite concentration was found at about 20 min when using catalysts B (run II) and C (run I). On the other hand, in

reaction A it was always very low (close to zero) during the whole reduction process, probably due to the low nitrate conversion of this catalyst.

For the B and C catalysts, the conversion of nitrate reached 100% in the 3 runs. In the first run, at the end of the reaction, the selectivity to N_2 reached a value of 77% for the B catalyst, while a selectivity of 70% was obtained for the C catalyst. For the catalyst A, after 120 min of reaction the conversion was 80% and the selectivity to N_2 was 84%.

Table 2 compares the selectivities for the three catalysts measured at the same nitrate conversions (25% and 80%). In this table, results with a $PdIn/Al_2O_3$ catalyst, previously obtained in our group [5] are shown for comparison (Catalyst D). Catalyst B and C have similar selectivities to N_2 when measured at 25% of conversion, being the conversion rate of catalyst C higher than of catalyst B. Nevertheless, one can observe on Fig. 1 that after 2 h of experiment the ammonium concentration is higher when catalyst C was used, meaning that catalyst B would be preferred. It can be seen that selectivities obtained with catalysts B and C are similar to those obtained with the alumina supported catalyst (Catalyst D). For all catalysts, the selectivity to N_2 fall through the use in consecutive runs. These results suggest that the catalysts show a slow transformation with time under practical conditions, which can be originated from the sintering of Pd crystals when exposed to aqueous reaction media.

Several catalytic formulations have been employed for nitrates reduction in water. Among them, those more studied are PdCu and PdIn bimetallic catalysts. Trawczynski et al. [11] using PdCu catalysts supported on active carbon reported 74.4% of nitrate conversion and 52.2% of selectivity to N_2 after 30 min of reaction. Gao et al. [12], using PdIn catalysts supported on mesoporous alumina, obtained the complete reduction of nitrate after 80 min of reaction, with maximum selectivity to N_2 of 72%. Our catalysts B and C presented complete nitrate conversion at lower times, and similar selectivities, but the for the used catalysts (run II and III) the selectivities were lower.

3.2. Catalysts characterization

3.2.1. XRD results

Fresh and used samples A, B and C showed several of the expected reflections of palladium face-centered cubic (fcc) structure. These reflections appear at 40.1°, 46.7°, 68.1°, 82.1° [13]. In Fig. 2, DRX patterns of the bare fibers and the fresh and used catalyst C are shown. The In reflection signals do not appear in none of the catalysts, however, these peaks cannot be clearly distinguished because the Pd peak of 46.7° is more intense than the In signal. This also may be due to the low In loadings and the high dispersion of the particles on the sample. The characteristic peaks of palladium oxide are not observed in any of the samples,

Table 2
Selectivity to nitrogen measured at 25% and 80% of nitrate conversion for the catalysts A, B, C y D.

Catalyst	Pulse	t (min)[a]	S_{N2} (%)[c]	S_{N2} (%)[d]
A	I	50.0	90	84
A	II	86.5	66	NR[e]
A	III	120.0	50	NR
B	I	1.6	98	80
B	II	5.1	84	60
B	III	10.3	53	60
C	I	2.4	99	71
C	II	2.4	86	59
C	III	3.4	63	64
D[b]	I	3.3	87	78
D	II	6.1	76	71
D	III	9.4	67	59

[a] time needed to reach 25% of nitrate conversion
[b] Pd,In/Al_2O_3 catalyst, from reference [5]
[c] selectivity to N_2 at 25% of nitrate conversion
[d] selectivity to N_2 at 80% of nitrate conversion
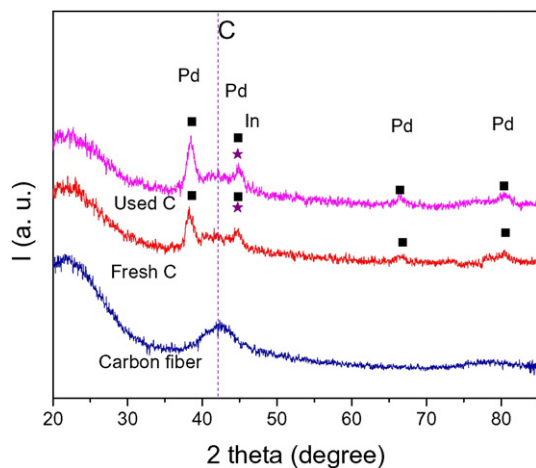[e] NR: 80% of nitrate conversion was not reached after 120 min.

Fig. 2. The XRD patterns of fresh and used catalyst C.

which suggests that Pd is in the reduced form despite the exposure to air.

3.2.2. SEM results

The SEM images show the morphologies of Pd and PdIn samples (Fig. 3). The picture of a sample with low Pd loading (0.14 wt.%) is also included for comparison (Fig. 3a). It can be observed, that the Pd concentration rise with increasing Pd loading, when Fig. 3a is compared to Fig. 3b. For the Pd sample with 1.8 wt.% of Pd (Fig. 3b), few individual particles were distinguished and the formation of a thin layer was detected. When the Pd load was equal to 0.14 wt.%, a high dispersion of Pd particles with a crystal size distribution between 65 and 150 nm was observed (Fig. 3a). Fig. 3c and d show micrographs of catalyst C, fresh, and used in three consecutive nitrate pulses (360 min of time-on-stream). It can be seen that the structure of the catalytic film changed after the contact with the reaction media. As a consequence of this change, an important drop in N_2 selectivity was observed.

The SEM pictures suggest that the large white particles that are deposited on top of the continuous layer of Pd (Fig. 3c) could be In particles.

3.2.3. XPS results

Table 3 shows that the binding energy for the Pd $3d_{5/2}$ feature did not present a significant shift with respect to that of metallic Pd (BE from 334.10 to 335.70 eV) [12], and only the catalyst C used showed energies slightly less than 335 eV. This value corresponds to metallic Pd, suggesting that Pd was not oxidized when the solids were exposed to ambient conditions. Taking into account that the palladium was obtained by electroless plating and deposited in its reduced form, this behavior was predictable.

The binding energy for the In $3d_{5/2}$ feature present a shift with respect to that of metallic In (BE from 443.15 to 444.6 eV) [12], 445.08 eV in the sample B; 443.61 in the sample C and 445.39 eV in the sample A. A higher BE indicates that the metal may be partially oxidized and that changes can be associated to the In oxidation to In_2O_3 due to the redox process of nitrate reduction.

It can be seen that the Pd:In surface ratio is about ten times lower than the bulk value for the catalysts B and C, which indicates that In is selectively deposited onto Pd particles during the sequential electroless plating procedure. After reaction, this ratio is even lower for the two more active samples.

4. Conclusions

The catalyst performance for nitrates reduction can be improved by using the sequential electroless plating method. With this procedure, homogeneous structures were obtained, with In particles deposited at the top of a tiny Pd film.

Among the catalysts studied in this work, the catalyst of PdIn/carbon fibers having the highest loading of indium (Catalyst C) is the most active one to eliminate nitrates in water using hydrogen as a reductant agent. However, Catalyst B showed the smaller ammonium concentration at end of the reaction.
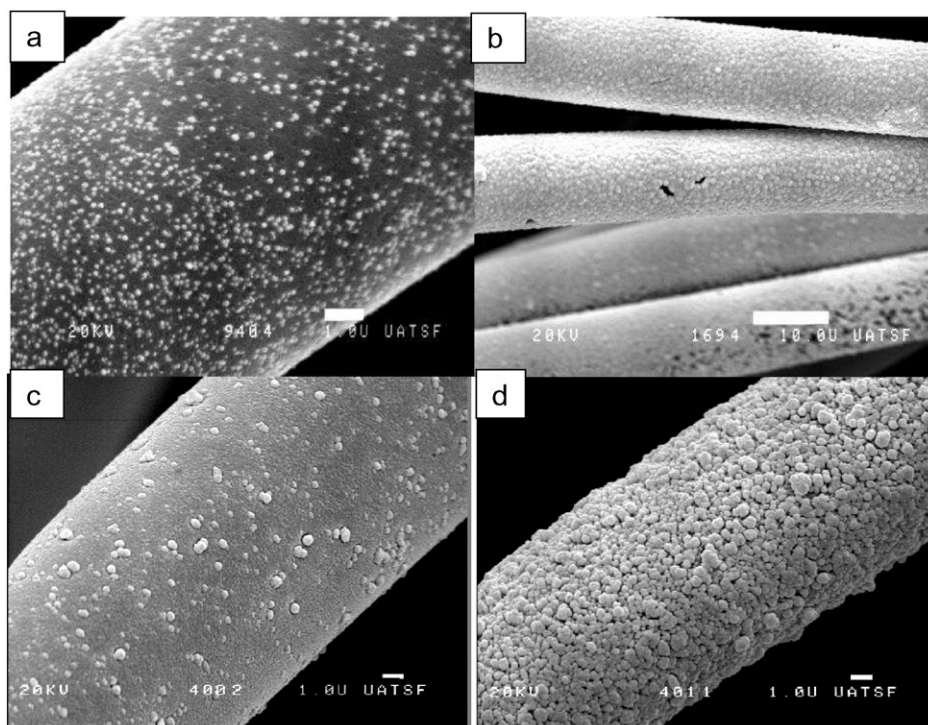

Fig. 3. SEM images of carbon fibers. a) carbon fiber with 0.14 wt% Pd loading; b) carbon fiber with 1.8 wt% Pd loading; c) fresh C catalyst; d) used C catalyst.

Table 3
Surface analysis of the fresh and used catalysts performed by XPS.

Pd, In catalysts	Binding energies (eV)		(Pd/In) surface	(Pd/In) bulk
	Pd $3d_{5/2}$	In $3d_{5/2}$		
A fresh	335.67 (63.2%) 337.56 (36.8%)	445.39	3.53	9.5
A used	336.00 (73.9%) 337.98 (26.1%)	446.51	4.37	9.5
B fresh	335.05 (68.5%) 337.17 (31.5%)	445.08	0.32	3.5
B used	335.00 (61.2%) 336.72 (38.8%)	445.35	0.12	3.5
C fresh	335.29 (72.8%) 337.24 (27.2%)	443.61	0.20	2.0
C used	334.75 (67.2%) 336.39 (32.8%)	445.16	0.13	2.0

The structure of the catalysts changed after reaction but, for the more active catalyst (C) only a small deactivation was observed, but an important drop in N_2 selectivity occurred.

Application of catalytic nitrate reduction is still limited due to generation of ammonia, which is relatively high for the catalysts studied in this work. Although selectivity should be improved, the PdIn/carbon fibers catalyst produced at this paper present high activity with the advantage of using a structured support, which encourages further studies to obtain more insight into the reaction mechanism and active sites.

Acknowledgments

References

[1] A. Pintar, J. Batista, Catalytic hydrogenation of aqueous nitrate solutions in fixed-bed reactors, Catal. Today 53 (1999) 35.
[2] U. Matatov-Meytal, M. Sheintuch, The relation between surface composition of Pd–Cu/ACC catalysts prepared by selective deposition and their denitrification behavior, Catal. Commun. 10 (2009) 1137–1141.
[3] P.P. Mardilovich, Y. She, Y.H. Ma, M. Rei, Defect-free palladium membranes on porous stainless-steel support, AICHE J 44 (1998) 310–322.
[4] M.L. Bosko, F.A. Marchesini, L.M. Cornaglia, E.E. Miró, Controlled Pd deposition on carbon fibers by electroless plating for the reduction of nitrite in water, Catal. Commun. 16 (2011) 189–193.6.
[5] F.A. Marchesini, S. Irusta, C. Querini, E.E. Miró, Spectroscopic and catalytic characterization of Pd–In and Pt–In supported on Al_2O_3 and SiO_2, active catalysts for nitrate hydrogenation, Appl. Catal., A 348 (2008) 60–70.
[6] U. Matatov-Meytal, M. Sheintuch, Activated carbon cloth-supported Pd–Cu catalyst: application for continuous water denitrification, Catal. Today 102–103 (2005) 121–127.
[7] S.R. de Miguel, J.I. Vilella, E.L. Jablonski, O.A. Scelza, C. Salinas-Martinez de Lecea, A. Linares-Solano, Preparation of Pt catalysts supported on activated carbon felts (ACF), Appl. Catal. A Gen. 232 (2002) 237–246.
[8] Standard Methods for the Examination of Water and Wastewater, 21 ed. APHA, Washington, 1992.
[9] P.L. Searle, The Berthelot or lndophenol reaction and its use in the analytical chemistry of nitrogen, Rev. Anal. 109 (1984).
[10] D. Beham, T. Graham, N. Bunce, Chemical methods for remediation of ammonia in poultry rearing facilities: a review, Biosyst. Eng. 115 (2013) 243–2320.
[11] J. Trawczynski, P. Gheeka, J. Okalb, M. Zawadzkib, M.J. Ilan Gomez, Reduction of nitrate on active carbon supported Pd-Cu catalysts, Appl. Catal. A Gen. 409-410 (2011) 39–47.
[12] Z. Gao, Y. Zhang, D. Li, C.J. Werth, Y. Zhang, X. Zhou, Highly active Pd–In/mesoporous alumina catalyst for nitrate reduction, J. Hazard. Mater. 286 (2015) 425–431.
[13] A.V. Naumkin, A. Kraut-Vass, S.W. Gaarenstroom, C.J. Powell, National Institute of Standards and Technology, 2014.