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A green approach for the reduction of representative aryl functional groups using palladium ecocatalysts

Claude Grison a, Pauline Adler a, Pierre-Alexandre Deyris a, Sebastien Diliberto b and Clotilde Boulanger b

a Laboratory of Bio-inspired Chemistry and Ecological Innovations UMR 5021 CNRS, University of Montpellier, Grabels, France; b Institut Jean Lamour, UMR 7198, Centre National de la Recherche Scientifique, Université de Lorraine, Metz, France

ABSTRACT

The reduction of functional groups has been thoroughly explored in organic synthesis. Nevertheless, most of the existing methodologies are based on conditions far from being environmentally friendly, which limits their usefulness. Here we report a green approach for the reduction of representative aryl functional groups using Eco-Pd catalysts. The Eco-Pd catalysts were prepared from palladium enriched vegetal filters that biosorbed palladium from an aquatic environment. The Eco-Pd catalysts were characterized by MP-AES XRPD and XPS, and used in the reductions of aryl halides, aryl aldehydes and nitroarenes in green conditions. A mixture of glycerol and n-butanol was used, as the solvent system and as the reducing reagent, in the presence of non-hazardous inorganic bases and without any ligands. Although Eco-Pd catalysis within this solvent system was homogeneous, we were able to recover and reuse the ecocatalyst to efficiently catalyze new reduction reactions.

1. Introduction

The reduction of functional groups is a ubiquitous transformation in organic synthesis. A great variety of reducing systems has been described. The choice of a reducing agent depends on the desired chemo-, regio- and stereoselectivity. Many systems have been investigated to find the required reactivity. One of the most used systems of reducing agents is based on the addition or substitution of a nucleophile hydride ion or a radical. The reducing reagent can derive from alkali, alkaline earth or other metal hydrides (silicon, tin, transition metals) or Lewis acids such as alanes or boranes. However, metal hydrides require aprotic and anhydrous solvents, which can be hazardous, as THF, Et₂O, Me₂SO, DMF, HMPA, PhCH₃ (1). Most common alanes and aluminohydrides are inflammable, boranes, borohydrides and tin hydrides generate problematic wastes, which are regulated by REACH (2). Moreover the metal hydrides and sources of hydride equivalents are used in stoichiometric conditions and cannot be recycled, thus lead to higher E-factors (3). Reductions by dissolved metals and related methods raise similar issues.

Another system involves the use of dihydrogen in hydrogenation or hydrogenolysis reactions. Various catalysts (Ni, Fe, Pd, Pt, Ru, Rh, Os, Ir) are employed in micro and macro scale under heterogeneous or homogeneous conditions. Several factors such as the catalyst, the support, the solvent, the temperature and the pressure of dihydrogen affect the efficiency of the reduction. For example, it is well known that catalytic hydrogenation is very sensitive to steric hindrance and can require high temperature and pressure. These conditions constitute an industrial risk. The price of PGMs (platinum group metals) recently reached high records due to their geo-economic context. The phenomenon...
was reinforced by an increasing demand on world markets for PGMs such as Pd.

For the aforementioned reasons, the chemical industry is facing the imperative need to innovate for the development of available, eco-friendly, sustainable and recyclable reducing catalytic systems. In this context, we studied the synthetic potential of a green and versatile reducing tool, called Eco-Pd. Eco-Pd has been developed during pioneering works of our research group on the ecological recycling of palladium from specific plants.

While investigating the remarkable sorption mechanism realized by aquatic plant roots, it appeared that this phenomenon was unexpectedly chemical and not physiological due to the presence of carboxylate and phenolic groups that can chelate metallic elements without active internalization process. Our group could thus develop new vegetal filters using dead aquatic plant roots instead of living plants. The biosorption of transition metals was studied using these vegetal filters and showed a high efficiency. Pd-rich biomasses were thermally and chemically treated for the preparation of Eco-Pd catalysts (4–9). The use of Eco-Pd led to high yields in cross-coupling reactions such as Sonogashira coupling.

In this work, we have extended Eco-Pd catalytic activities in representative reduction reactions: microwave assisted reduction of aryl-bromides, -iodides and -aldehydes, and thermal reduction of nitroarenes.

2. Materials and methods

2.1. Reagents and instruments

All reagents and solvents used in this work were purchased from commercial sources. Analyzes by MP–AES: The samples were digested in 10 mL of reversed aqua regia (1:2 hydrochloric acid (37%); nitric acid (65%)) under a microwave-assisted digestion (Multiwave-Go Anton Paar) with the following program: 20–165°C in 20 min and then 10 min isothermal at 165°C. Samples were filtered and then diluted to 0.4 mg.L⁻¹ in 1% aqueous nitric acid. Mineral compositions were determined by using a microwave plasma-atomic emission spectroscopy (MP-AES) 4200 (Agilent Technologies) equipped with a concentric nebulizer and a double-pass cyclonic spray chamber. The pump speed during analysis was kept at 10 rpm and the sample introduction tube diameter was 0.89 mm. The analytical cycle consisted of 30 s rinsing withaq. 1% nitric acid followed by 25 s of sample uptake (pump speed 40 rpm) and then 20 s of equilibration before the reading at preselected integration times (pump speed 10 rpm). The integration time was set to 3 s for all elements. Unless otherwise stated, the automatic background correction mode available in the software was used. An Agilent SPS3 autosampler was used throughout the study.

X-ray diffraction (XRD) data measurements on the samples dried at 110°C for 2 h were performed by using a BRUKER diffractometer (D8 advance, with a Cu Ka radiation λ = 1.54086 Å) equipped with a Lynxeyes detector.

The XPS analyzes are carried out with the ESCALAB 250 device from Thermo Electron. The source of excitation is the monochromatic source, Al Ka line (1486.6 eV). The analyzed surface has a diameter of 500 µm. Photoelectron spectra are calibrated as binding energy relative to the energy of the C–C component of C1s carbon at 284.8 eV. The charge is compensated by an electron beam (−2 eV).

Gas chromatography analyzes were performed using a Thermo Scientific Trace 1300 device equipped with an El ionization source and an ISQ-QD detector. The reactions were monitored by using para-cymene as internal standard and FID methods for the calibration.

¹H NMR and ¹³C NMR spectra were recorded on a Bruker 400 AVANCE fitted with a dual ¹H/¹³C-gradient Z probe at 400 and 100 MHz respectively and using solvent as internal standard (7.26 ppm for ¹H and 77.16 ppm for ¹³C for CDCl₃).

Some reactions were carried out using a microwave-assisted digestion method (Multiwave-Go Anton Paar) with the following program: 20–120°C in 1 min and then 1 min isothermal at 120°C followed with 120–150°C in 1 min and 10 min (aryl iodides), 15 (aryl bromides), or 15–30 (aldehydes) min isothermal at 150°C.

2.2. Biomaterial collection and preparation for biosorption

- Eichhormia crassipes were purchased from a specialized grower (Nympha company, France). The plants were placed in an outdoor tank under greenhouse filled with water to which guano was added as fertilizer.
- Mentha aquatica was purchased from a specialized grower (Nympha company, France) that used hydroponics in order to maximize the roots of the plants.
- Pistia stratiotes was either purchased from a specialized grower (Nympha company, France) or directly collected by CNR (Compagnie Nationale du Rhône) from the Rhône river and Gardon river near the city of Comps (Gard, France).
- Ludwigia peploides was collected by CNR (Compagnie Nationale du Rhône) from the Sèze river and Rhône river near the city of Bagnols-sur-Cèze (Gard, France).
• *Reynoutria japonica* was collected by ETPB Gardons either from the Gardon d’Alès river near the city of La Grand-Combe (Gard, France), or by the Mixt Union Ganges le Vigan from the Hérault river near the city of Le Vigan (Gard, France).
• Bark pine and pinecone were collected in the region of Montpellier (Hérault, France) in fall 2018 and are from the species of black pine (*Pinus nigra*).
• Coffee grounds were obtained directly from our laboratory.

*Eichhornia crassipes, Mentha aquatica, Pistia stratiotes, Ludwigia peploides, Reynoutria japonica, bark pine and pine cone were dried in an oven at 80°C until constant weight. Then they were grounded, sifted through a 1.25 mesh sieves, and washed with water. Then they were dried 18 h at 80°C before biosorption. Coffee grounds were washed several times with hot water until the filtrate became colorless and then were dried 18 h at 80°C before biosorption.

### 2.3. Biosorption of palladium

5 g of biomaterial was loaded in a dry-loading cartridge InterChim PuriFlash 430. Then a 5-L aqueous solution of tetraaminepalladium(II) nitrate (Pd(NO₃)₂.4NH₃, concentration in Pd around 15 ppm) was flushed through the column (1.25 L h⁻¹). The solid was then removed from the cartridge and dried at 85°C for 24 h. The exact concentrations of both palladium solutions before and after biosorption were determined with MP-AES analyzes.

### 2.4. Preparation and characterization of the ecocatalysts

The dried palladium-loaded biomaterials were heated at 550°C under air for 4 h. The resulting powder was heated in vegetable hydrochloric acid (10) (1 mL per 100 mg of thermal residue) under reflux for 2 h. The resulting solution was cooled to room temperature, then filtrated through a pad of dicalite powder, that was beforehand washed with HCl 37%. The resulting solution was then concentrated under reduced pressure, affording Eco-Pd as a brown solid. Ecocatalysts were characterized by MP-AES analyzes.

Eco-CaCO₃ was obtained by thermal treatment of *Ostreidae* from Oléron. The Eco-Ca loading of Ca was 59%wt. Eco-CaO were prepared by thermal treatment from *Crepidula* (11). Both *Ostreidae* and *Crepidula* were collected from a local producer in Bouzigues (Hérault, France).

### 2.5. Procedure for the reduction reaction

**Microwave procedures:** Under argon, a Teflon microwave reactor was loaded with the substrate (1.0 mmol, 1 eq.), Eco-Pd (0.0035 mmol, 0.35 mol%) and K₂CO₃ (2 mmol, 2 eq.). A mixture of degassed n-butanol and glycerol (6 mL, v:v = 1:1) was added and the reactor was put in the microwave apparatus following the heating method specific to the substrate.

**Batch procedures:** Under argon, to a flask filled with the substrate (1.0 mmol, 1 eq.), Eco-Pd (1 or 2 mol%) and the base (2 mmol, 2 eq.) was added a mixture of degassed n-butanol and glycerol (1 or 2 mL, v:v = 1:4). The reaction mixture was stirred at 120°C for 18 h.

**Work-up:** The reaction mixture was diluted by addition of water (5 mL) and ethyl acetate (10 mL). After separation of the phases, the aqueous phase was extracted three times with 10 mL of ethyl acetate. The combined organic layers were dried on anhydrous magnesium sulfate and filtrated in a 100 mL volumetric flask. For GC yields, 0.2 eq. of *para*-cymene was added to the reaction mixture as an internal standard. Because of the volatility of the prepared product, all written yields are determined by GC-MS analyzes, using FID detector, for the reduction of aryl halides into the corresponding arenes.

### 2.6. Procedure for the recycling of the Eco-Pd catalyst

Reduction of 2-bromonaphthalene 1a was performed according to the general procedure. After completion of the reaction, grounded and dehydrated roots of *Eichornia crassipes* (1 g per 15 mg of palladium) were added to the reaction mixture, diluted in cyclohexane and water. After 2 h stirring at room temperature, the reaction media was centrifuged at 4000 rpm for 25 min. The post-solution was diluted with EtOAc to extract the product of the coupling reaction. The precipitate of Pd-loaded roots of *E. crassipes* and black Pd were subjected to the sequence thermal treatment/activation and a new Eco-Pd was reused for a new reduction reaction.

### 3. Results and discussion

#### 3.1. Characterization of the Eco-Pd catalysts

Eight plant roots were dried, grounded, washed and dried again to prepare a vegetal filter that was used to biosorb an aqueous solution of tetraaminepalladium(II) nitrate. The resulting Pd enriched vegetal filters were then transformed into eight Eco-Pd₁⁻₈ catalysts.
Table 1. Mineral compositions of the Eco-Pd catalysts.

<table>
<thead>
<tr>
<th>Eco-Pd</th>
<th>Biomass</th>
<th>Mineral composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>Eco-Pd_{1}</td>
<td>(Eichhornia crassipes)</td>
<td>± 0.001</td>
</tr>
<tr>
<td>Eco-Pd_{2}</td>
<td>(Mentha aquatica)</td>
<td>± 0.004</td>
</tr>
<tr>
<td>Eco-Pd_{3}</td>
<td>(Pistia stratiotes)</td>
<td>± 0.005</td>
</tr>
<tr>
<td>Eco-Pd_{4}</td>
<td>(Ludwigia peploids)</td>
<td>± 0.001</td>
</tr>
<tr>
<td>Eco-Pd_{5}</td>
<td>(Fallopia japonica)</td>
<td>0.39</td>
</tr>
<tr>
<td>Eco-Pd_{6}</td>
<td>(Pinecone)</td>
<td>± 0.005</td>
</tr>
<tr>
<td>Eco-Pd_{7}</td>
<td>(Bark pine)</td>
<td>0.6</td>
</tr>
<tr>
<td>Eco-Pd_{8}</td>
<td>(Coffee grounds)</td>
<td>± 0.003</td>
</tr>
</tbody>
</table>

n.d.: not detected.

The mineral composition of the Eco-Pd_{1–8} catalysts was analyzed by MP-AES (Table 1). The main mineral elements are Ca and Pd. They exhibit an inverse correlation according to the environmental habitat of the plants. Eco-Pd_{1–4} derived from aquatic plants present a high percentage of Ca at the expense of Pd. On the contrary, Eco-Pd_{5–8} derived from non-aquatic plants showed a high percentage of Pd at the expense of Ca. Eco-Pd_{4} derived from *Pistia stratiotes* was growing in an effluent rich in Mn explaining the naturally high percentage of Mn.

In every Eco-Pd_{1–8}, the palladium amount varies greatly from 3.7%wt. with *Pistia stratiotes* to 46.30%wt. with pinecone. The dispersion of palladium is an important aspect of Pd catalysis, which can be studied using these eight Eco-Pd catalysts within the reduction of aryl functional groups.

Eco-Pd_{1} was further analyzed by XRPD to identify palladium species under crystalline form. After thermal treatment, two Pd crystalline structures have been identified, PdO et K_{2}PdO_{2} (Figure 1).

After HCl treatment of the thermal residue, the diffractogram revealed the presence of K_{2}PdCl_{6} which corresponds to a high and rare oxidation state of Pd(IV) (Figure 2).

X-ray photoelectron spectroscopy (XPS) with Eco-Pd_{1} was performed in order to confirm the oxidation state of palladium (Figure 3).

The position in binding energy of the Pd3d5/2 photoelectron peak at 337.9 eV, confirms the presence of Pd (IV) in Eco-Pd_{1}.

![Figure 1. XRPD analysis of mineral residue.](image)
3.2. Reduction of aryl halides

An alternative green approach was developed for the reductions of aryl halide derivatives. Our strategy was based on using biosourced palladium-catalysts, Eco-Pd, non-hazardous and inorganic bases, in a green solvent and without any ligands.

Glycerol was chosen as the green solvent since it is a largely available, inexpensive, non-toxic and renewable compound (12). Here glycerol also plays the role of hydrogen donating reagent within Pd-catalyzed reductions, preventing the use of dihydrogen.

Due to the high viscosity of glycerol, glycerol was mixed with a green co-solvent, nBuOH.

An optimization of the aryl halide reduction conditions was first conducted using 2-bromonaphtalene 1a (Table 2) as a model substrate. Facing poor conversions under a classical thermal heating in batch (entry 1), a microwave-assisted activation was conducted to increase conversions while decreasing reaction time (entries 2–7). The microwave-assisted activation was also motivated by the use of glycerol as co-solvent, which has a low vapor pressure, a high microwave absorption and a rapid heating (13). Inorganic bases, as sodium, calcium or potassium carbonate, were tested (entries 2–5). Potassium carbonate gave the best conversion and yield by preventing the Ullmann homocoupling.

The influence of the ecocatalysts elemental composition was then tested using eight Eco-Pd1-8 catalysts (entries 7 and 8). Almost no difference was observed between the starting biomass, although presenting a Pd composition that varies from 3.7 to 40.08%wt., suggesting that Pd dispersion has a poor influence on the reactivity of the catalyst. Moreover, no difference was noted for Eco-Pd4, which has a high Mn%wt., suggesting that Mn does not play a role in the reduction reaction mechanism.

With the optimal conditions in hand, a substrate scope for the reduction of aryl halides was explored (Figure 3).

In general, reduction yielded, as expected, to better conversions for aryl iodide than for bromide. The presence of electron withdrawing groups – acetyl, nitro, cyano and chloro groups – did not affect the reduction of carbon-iodide bond forming the corresponding arenes 2b–2e in good yields (60%–79%). Two limitations were found when using trifluoromethyl group 2f, and
using methyl ester 2j, transesterification occurred with the solvent system instead of the reduction. It is noteworthy that Eco-Pd selectively catalyzed the reduction of carbon-iodide bond in presence of a chlorine atom and gave chlorobenzene 2e with 78% yield. Reduction of carbon-bromide bond gave similar high conversions but lower yields than reduction of carbon-iodide bond, due to a competitive reduction of the electron donating groups for 2b and 2c.

Interestingly the presence of electron-donating groups – methoxy and amino groups – was well tolerated; 2g and 2h could be prepared in good yields.

However, no reduction was observed with heteroaryl halides 1k–m. Thiophene derivatives mainly gave the homocoupling products.

We compared our methodology to literature regarding the reduction of the model substrate, 2-bromonaphthalene (Table 3). Although the reported methods gave similar yields to our methodology, they gave much lower TON and TOF, and are far from being respectful to the environment. Indeed, all reported conditions required using a high catalytic loading (1–16 mol%) of metal, cobalt (entry 1) or palladium (entries 2–5). The sources of hydrogen can be dihydrogen under a very high pressure (entry 1). And if the source of hydrogen is not hazardous, the methods require the use of ligands to promote the reaction (entries 2–5).

Regarding the reaction conditions, the solvent system, the reaction time and the yield, our methodology represents a great improvement of the existing methods towards the field of green chemistry.

### 3.3. Reduction of aryl aldehydes

The versatility of the reduction methodology was investigated by studying the reduction of aryl aldehydes (Figure 4). Based on the reduction of aryl halides, similar green conditions were used with an extended time of reaction to optimize the conversion.
In general, aryl aldehydes bearing an electron-withdrawing group, as cyano 5a and chloro 5b, gave the expected alcohol in good yields. The conditions were compatible with nitro 5c substituent but partially gave the reduced p-aminobenzylalcohol. Interestingly aryl aldehydes bearing an electron-donating group, such as methyl 5d, methoxy 5e or hydroxy 5f, gave excellent conversions but lower yields, which are due to loss of the hydrophilic products during extraction. Similarly non-substituted benzaldehyde and furfural led to benzyl alcohol 5g and compound 5h in quantitative conversions and moderate to good yields.
The major limitation of the method was the reduction of the dimethylamine substituted benzaldehyde 5i.

In the literature, several conditions could be found for the reduction of the 4-cyanobenzaldehyde 4a (Table 4). Once again, although the reported methods gave similar yields to our methodology, they gave much lower TON and TOF, and are far from being respectful to the environment. Indeed, numerous methods based on the use of silane and transition metal catalyst, as iron (19) or zinc (20), or the use of sodium borohydride are efficient but generate considerable amounts of waste (entry 1) or hazardous borylated wastes under REACH regulation (entry 3). Nickel is an excellent promoter of such reduction (21, 22). Amongst numerous methods, our group reported a Meerwein-Pondorf-Verley type reduction, which is based on using a nickel ecocatalyst in green conditions but that requires a long reaction time (entry 4) (23). Compared to other methods, our new procedure based on using Eco-Pd has similar yields but represents a short and more sustainable approach of such reduction.

### 3.4. Reductions of nitroarenes

As mentioned above, Eco-Pd could catalyze the reduction of p-nitrobenzaldehyde 4c to p-nitrobenzylalcohol 5c and also conducted to the formation of the by-product p-aminobenzylalcohol. Therefore the reduction of nitroarenes was investigated using Eco-Pd in a mixture of glycerol and n-butanol (Figure 5).

Based on the reduction of aryl halides and aryl aldehydes, similar green conditions were tested but the microwave activation was disappointing. Instead the reductions of nitroarenes were performed in batch at

![Table 4. Comparison with the literature of the reduction of 4-cyanobenzaldehyde 4a](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Conditions</th>
<th>Yield</th>
<th>Conv.</th>
<th>TON</th>
<th>TOF (h⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Zn] (0.5 mol%) MeOH (0.25 eq.), HSi(OEt)₃ (2 eq.) Toluene, 60°C, 1 h</td>
<td>91% ⁹</td>
<td>98%</td>
<td>200</td>
<td>200</td>
<td>(20)</td>
</tr>
<tr>
<td>2</td>
<td>Pd@N-C nanocatalyst H₂ (5 bar), MeOH, 30°C, 9.5 h</td>
<td>100%</td>
<td>100%</td>
<td>–</td>
<td>–</td>
<td>(24)</td>
</tr>
<tr>
<td>3</td>
<td>TRGO⁺NaBH₄ (0.5 eq.) H₂O, r.t., 10 min</td>
<td>92%</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>(25)</td>
</tr>
<tr>
<td>4</td>
<td>Eco-Ni (1 mol%) Al₂O₃, i-PrOH, 80°C, 18 h</td>
<td>83% ⁶</td>
<td>–</td>
<td>100</td>
<td>5.6</td>
<td>(23)</td>
</tr>
<tr>
<td>5</td>
<td>Eco-Pd₅ (0.35 mol%) K₂CO₃ (2 eq.), glycerol/n-BuOH MW, 150°C, 10 min</td>
<td>91% ⁹</td>
<td>&gt;99%</td>
<td>286</td>
<td>1683</td>
<td>This work</td>
</tr>
</tbody>
</table>

⁹GC yields; ⁶Isolated yield; ⁷Pd catalyst prepared by carbonization from Na₂PdCl₄ and chitosan; ⁸TRGO: Tulsi leaf extract reduced graphene oxide.

Figure 5. Scope and limitations of the method for the reduction of aldehydes.
120°C for 18 h and using 2 mol% of Eco-Pd1. Moreover, the base was changed to Eco-CaO (11). In general, nitroarenes were transformed into the desired aminoarenes but systematically azoarenes and azoxyarenes were observed as well. Reduction of nitrobenzene gave aniline 7a in a good yield of 65%. The presence of an electro-withdrawing group did not clearly affect the reduction, while the presence of an electro-donating group decreased the yield, due to hydrophilicity of the products 7d and 7e.

We compared our methodology to the literature regarding the reduction of nitrobenzene 6a (Table 5). The reported methods gave better yields than our methodology but required the use of a large excess of

<table>
<thead>
<tr>
<th>Entry</th>
<th>Conditions</th>
<th>Yield</th>
<th>Conv.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N₂H₂H₂O₂ (2 eq.) Pd/SBA-COOHb (10 mg/mmol) Water, r.t., 5 min</td>
<td>&lt;c</td>
<td>100%</td>
<td>(26)</td>
</tr>
<tr>
<td>2</td>
<td>CNT/PdFe/CN² (30 mg/mmol) NaBH₄ (100 eq.), H₂O/EtOH (1/9), 8 h</td>
<td>99.9%</td>
<td>–</td>
<td>(27)</td>
</tr>
<tr>
<td>3</td>
<td>N₂H₂H₂O₂ (3 eq.) [Sb₃MoIV-MoVI] (1 mol%) EtOH, 60°C, 30 min</td>
<td>100%</td>
<td>–</td>
<td>(28)</td>
</tr>
<tr>
<td>4</td>
<td>Rh@S-1-H² (1.1 mol%) NH₂BH₃ (10 eq.), MeOH/H₂O, 25°C, 1.5 min</td>
<td>&gt;99%</td>
<td>100%</td>
<td>(29)</td>
</tr>
<tr>
<td>5</td>
<td>Eco-Pd (2 mol%) Eco-CaO (2 eq.), glycerol/n-BuOH (4/1) 120°C, 18 h</td>
<td>65%&lt;sup&gt;a&lt;/sup&gt;</td>
<td>&gt;99%</td>
<td>This work</td>
</tr>
</tbody>
</table>

<sup>a</sup>GC yields; <sup>b</sup> Mesoporous silica; <sup;c</sup> no yield was reported in the communication; <sup>d</sup> double-layered carbon nanotubes/nitrogen-doped carbon loaded with Pd and Fe; <sup>e</sup> single-atom Rh catalysts embedded in zeolites under hydrothermal conditions and subsequent ligand-protected direct H₂ reduction.

<table>
<thead>
<tr>
<th>Run</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield (conv.)</td>
<td>91% (99%)</td>
<td>69% (95%)</td>
<td>61% (95%)</td>
<td>67% (97%)</td>
</tr>
</tbody>
</table>

120°C for 18 h and using 2 mol% of Eco-Pd1. Moreover, the base was changed to Eco-CaO (11). In general, nitroarenes were transformed into the desired aminoarenes but systematically azoarenes and azoxyarenes were observed as well. Reduction of nitrobenzene gave aniline 7a in a good yield of 65%. The presence of an electro-withdrawing group did not clearly affect the reduction, while the presence of an electro-donating group decreased the yield, due to hydrophilicity of the products 7d and 7e.

We compared our methodology to the literature regarding the reduction of nitrobenzene 6a (Table 5). The reported methods gave better yields than our methodology but required the use of a large excess of

**Table 5. Comparison with the literature regarding the reduction of nitrobenzene**

**Table 6. Recyclability of the Eco-Pd catalyst**

**Figure 6. Reduction of nitrobenzene.**
reducing reagent (entries 2 & 4), which can be hazardous (entries 1 & 3) and treatments that generate hazardous wastes (entries 2 & 4).

Regarding the reaction conditions, the catalytic concentrations and the solvent system, our methodology represents a great improvement of such reduction towards the field of green chemistry.

3.5. Recycling of the catalyst

The high polarity of the solvent system, glycerol/nBuOH, facilitated the solubility of Pd salts, making this reaction a homogeneous catalysis. A major drawback of homogeneous catalysis is the difficulty to recover and reuse the catalyst, but it is a key principle of green chemistry.

After completion of the reduction, a fraction of Eco-Pd was reduced into black Pd(0) by glycerol while the rest remained soluble in the reaction solvent system. The soluble part of Eco-Pd was biosorbed by root powder of *E. crassipes* directly from the organic media. After centrifugation of the reaction mixture, the biosorbed Eco-Pd and black Pd(0) were subjected to the thermal treatment/activation generating a new Eco-Pd, which could be reused for a new reduction.

Recycling of Eco-Pd was studied through the reduction of 2-bromonaphthalene 1a. Up to four successive runs were tested after recycling of the same Eco-Pd1 (Table 6). After the first run, conversions remained quantitative and yields slightly decreased and remained similar for the second, third and fourth run (Figure 6).

The mineral composition of Eco-Pd1 was analyzed by MP-AES after each run and does not change much since between 75% and 90% of Pd was recovered by recycling. The mass percentage of Pd slightly decreased while the mass percentage of K increased, which might be due to the biosorption of K, which derived from K2CO3. However, the efficiency of Eco-Pd1 was not altered after recycling.

4. Conclusion

In conclusion, we demonstrated the recycling of palladium from aquatic environment and its reuse in green metal-catalyzed syntheses. Palladium was efficiently recycled from water through biosorption using a vegetal filter based on aquatic plants or coffee grounds. The palladium enriched vegetal filters were transformed into Eco-Pd catalysts that were used in the reduction of aryl functional groups. Green conditions, based on using the Eco-Pd catalysts in a mixture of glycerol and n-butanol, were compatible for the reductions of aryl halides, aryl aldehydes and nitroar- enes. Moreover, the Eco-Pd catalysts were easily recycled from the reaction mixtures and reused to efficiently catalyze new reduction reactions.

Compared to common metal hydrogenation or hydride-based methodologies, our technology uses catalytic concentrations of reducing reagents, a green solvent system and does not generate hazardous waste, representing a great alternative of key reductions towards the field of green chemistry.

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Notes on contributors

**Claude Grison** is CNRS Research Director. She is leading the Laboratory of Bio-inspired Chemistry and Ecological Innovations (Montpellier, France), which is dedicated to the implementation of new ecological solutions and innovative chemical tools for the ambitions of tomorrow’s chemistry. C. Grison is the pioneer of the ecocatalysis concept, which represents a major break-through at the interface between ecology and chemistry.

**Pauline Adler** is Assistant-Professor at the University of Montpellier. She worked in Montpellier at the Laboratory of Bio Inspired Chemistry and Ecological Innovations under the supervision of Pr. Claude Grison. Her research interests are focused on the Pd-based ecocatalysts in organic chemistry.

**Pierre-Alexandre Deyris** is Researcher at the University of Montpellier. He worked in Montpellier at the Laboratory of Bio Inspired Chemistry and Ecological Innovations under the supervision of Pr. Claude Grison. His research interests are focused on the Pd recycling and the preparation and the use of Pd-based ecocatalysts in sustainable chemistry.

**Clotilde Boulanger** is Full Professor at the University of Lorraine. She is Deputy Director of the Jean Lamour Institute, which is dedicated to fundamental and applied research in materials science and process. C. Boulanger has created the Chemistry and electrochemistry of materials” research group at Metz.

