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Ecological Recycling of a Bio-Based Catalyst for Cu Click Reaction: a New Strategy for a Greener Sustainable Catalysis

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Ecological Recycling of a Bio-Based Catalyst for Cu Click Reaction: a New Strategy for a Greener Sustainable Catalysis

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We report the elaboration of novel bio-sourced ecocatalysts for the Cu catalyzed azide-alkyne cycloaddition reaction (CuAAC). Ecocatalysis is based on the recycling of metals issued from rhizofiltration of metal rich effluents, and an innovative chemical valorization of the subsequent biomass in the field of catalysis. Taking advantage of the remarkable ability of *Eichhornia crassipes* to accumulate Cu(II) into its roots, these can be directly used for the preparation of copper containing ecocatalysts, called EcoCu, which appear as highly active catalysts in the CuAAC reaction. Furthermore, the recycling of Cu from the reaction mixture *via E. crassipes* is carried out ecologically. The resulting EcoCu$_2$ material displays reusability for the CuAAC reaction under identical experimental conditions without a loss of its catalytic activity.

1. Introduction

Some intensive mining activities, quarrying and industrial metallurgic activities are responsible for the pollution of soils and aquatic systems in the form of metal trace elements (TEs).[1] This is incredibly worrying, since the soil plays an essential role largely determining food production and water quality. Moreover, TEs are some of the most harmful compounds. They are not biodegradable and persist in contaminated organisms and ecosystems. Today, preserving the quality of soils and water has become a priority. There is a real need to develop innovative and efficient technologies to restore polluted sites and ecosystems. Phytoremediation is used to solve environmental problems caused by TEs. The most heavily researched phyotechnologies are phytoextraction and rhizofiltration. In the case of phytoextraction, TEs are extracted by plants and stored in their leaves.[1a, 2] With the rhizofiltration, the process occurs in an aquatic medium and TEs are bioconcentrated into roots.[1b] However, their development is still restricted by the fact that contaminated biomass is not recovered; the aerial parts of metal hyperaccumulating plants or the roots of aquatic plants are considered as contaminated wastes. Our group has recently proposed the new concept of ecocatalysis as a unique use of phytoextraction.[3] Taking advantage of the remarkable adaptive capacity of some plants to hyperaccumulate TEs,[4] ecocatalysis is based on the novel use of metal species of plants origin as reactants and catalysts of fine organic chemical reactions. Showing for the first time that the above-ground parts of land plants that hyperaccumulate Zn, Ni and Mn could be transformed into ecocatalysts. The first results showed that these ecocatalysts could be used as new generation Lewis acid catalysts[1a, 5]. Multicomponent reactions, Diels-Alder[6] and domino reactions[7] are particularly efficient. Soft oxidation reactions like epoxidation[8] or the chaining *in situ* of the oxidation/epoxide opening/oxidative cleavage sequence[9] could be compared favourably with the current industrial processes to access platform molecules. The polymetal systems obtained from the biomass produced by phytoextraction are original (unusual oxidation levels, new associated chemical species, effects of synergy). They can be used as heterogeneous catalysts in synthetic transformations giving access to molecules with high added value for fine and industrial chemicals (perfumes and cosmetics,[5b] medicines and oligomers of biological interest,[10] highly functionalised aromatic heterocyclic compounds,[11] key intermediaries of varied industrial chemical processes and biopesticides).[12]

We have recently reported bio-based and bio-sourced EcoPd catalysts, which enable innovative recovery of metal charged biomass from plants used in rhizofiltration to extract palladium from synthetic solutions.[1b] We have shown that the obtained EcoPd catalysts exhibited high catalytic activity in Heck and Suzuki cross-coupling reactions and required considerably lower EcoPd quantity compared to conventional palladium catalysts. The developed synthetic protocols based on the use of bio-based catalysts present several advantages: low catalyst loading, high catalytic activity and selectivity, short re-

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Table 1. Copper concentration in roots and leaves of *E. crassipes* (wt% ± standard deviation), and BCF and TF calculation					
[Cu] in effluent (mg/L)	Roots (wt% ± SD)	BCF (in roots)	Leaves (wt% ± SD)	BCF (in leaves)	TF
11.5	0.27 ± 0.0013	234	0.0028 ± 0.015 (petiole)	2.4 (petiole)	0.010 (petiole)

action times, eco-friendly reaction conditions, and the possibility of catalyst recovery and reuse.
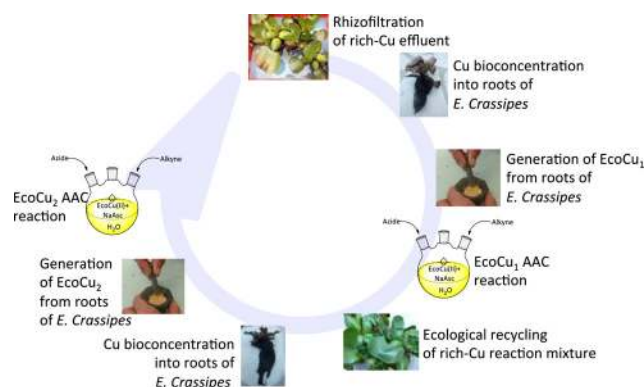
Scheme 1. Process of ecological recycling of EcoCu illustrated by the CuAAC click reaction.

Here, we report greener bio-based alternatives for catalysis taking into account new environmentally safe and sustainable catalytic processes. Our approach is based on three principles: *i)* a focus on homogeneous catalysis involving a non-endangered metal, through the example of the Cu(I)-catalyzed Azide-Alkyne Cycloaddition (CuAAC)[13] *ii)* the preparation of a bio-based catalyst obtained by rhizofiltration of contaminated aqueous media *iii)* an ecological catalyst recycling *via* a second rhizofiltration procedure of the primary reaction mixture (Scheme 1).

The main objective of this work is to demonstrate for the first time that homogeneous catalysts involving low cost metals can be easily recycled through an eco-friendly and efficient technology based on rhizofiltration. In other terms, we wish to show that ecological recycling can be considered as a "resource" of metal catalysts.

2. Results and Discussion

2.1. EcoCu$_1$ Catalyst preparation and characterization

2.1.1. Preparation of the EcoCu$_1$

Rhizofiltration of Cu(II) rich effluents

EcoCu$_1$ was obtained *via* rhizofiltration of Cu(II)-containing aqueous media. Previously, *Bacopa monnieri, Lolium multiflorum* and *Eichhornia crassipes* have been studied to test their ability to accumulate copper into their roots. It was found that *Bacopa monnieri* accumulates efficiently copper into its roots,[14] whereas *Lolium multiflorum* accumulates both copper and palladium.[15] Its main asset relies on its well-developed root biomass. Finally, *Eichhornia crassipes* was also known to accumulate copper, to multiply easily and to form an amazing quantity of root biomass. For these reasons, *E. crassipes* has all the assets to be used as bioaccumulator for Cu(II) and for the synthesis of Cu-based ecocatalysts[16].

Thus, the Cu-based ecocatalysts were synthesized via rhizofiltration using *E. Crassipes*, using an acidic aqueous copper(II) nitrate solution($c_{Cu(NO3)2}$ = 11.5 mg/L). After 6 days of rhizofiltration, the copper concentration in roots and leaves of *E. crassipes* was determined by ICP-MS analysis after drying. The results are shown in Table 1. We observed that the concentration of copper in the root biomass of *E. crassipes* and the bioconcentration factors (BCF: Cu concentration in roots divided by Cu concentration in water) are very high. Moreover, the translocation factors (TF: Cu concentration in shoot divided by Cu concentration in root) in the petiole and leaves of *E. crassipes* remain low, indicating that Cu principally remained on the roots.

Transformation of biomass into EcoCu$_1$.

EcoCu$_1$ derived from *Eichhornia crassipes* was prepared from harvested plants' roots following the described procedure (see experimental part, section 3.1.). The roots were calcined at 550 °C for 6 h in order to remove organic matter. The resulting ashes were treated with concentrated hydrochloric acid, transforming the metal oxides to the corresponding chlorides. After filtration, evaporation of the acid yielded the EcoCu$_1$ catalyst.

2.1.2. ICP-MS characterization of the EcoCu$_1$

Table 2 shows mineral composition of the EcoCu$_1$ catalyst. The analysis showed that Cu was the major transition metal in the ecocatalyst (4.3 wt%). Small amounts of Fe were also observed, together with Mg, Ca, Na and K. These elements are present as they are essential for plant growth. Because of the natural origin of the EcoCu$_1$ catalyst, some questions may arise regarding the reproducibility of the composition of the ecocatalyst. For this reason, the preparation of EcoCu$_1$ catalyst was replicated 10 times. Table 2 described the average of the obtained data.

2.1.3. Acidity characterization of the EcoCu$_1$ catalyst

In the CuAAC reaction, the electron density of the metal is essential to promote the stepwise cycloaddition process. There-

Na	Mg	Al	K	Ca	Fe	Zn	Cu
2.4 ± 0.021	1.3 ± 0.014	0.5 ± 0.025	2.3 ± 0.019	7.7 ± 0.017	0.5 ± 0.013	0.00 ± 0.016	**4.3** ± 0.026

fore, we studied the Lewis and Brønsted acid properties of the EcoCu$_1$catalyst. We compared this ecocatalyst with commercial copper(II) chlorides, i.e. anhydrous CuCl$_2$ and CuCl$_2$.2H$_2$O. Lewis acidity is usually defined by its strength and its hardness according to the HSAB principle, described by Pearson[17]. A conventional method was used: the pyridine adsorption/desorption on the catalysts, monitored via infrared spectroscopy. This method enables a comparison of the Lewis acid strength and Brønsted acidity between different catalysts by monitoring pyridine infrared absorption bands between 1400 and 1660 cm^{-1}. Infrared spectra of pyridine adsorbed on EcoCu$_1$, on commercial anhydrous CuCl$_2$, and on CuCl$_2$.2H$_2$O were recorded at 150 °C in order to distinguish physisorbed pyridine from pyridine coordinately bonded to Lewis acid sites. The absorption bands around 1450 cm^{-1} observed on the spectra are characteristic of strongly bonded pyridine to Lewis acid sites (Figure 1). Because the frequencies of these absorption bands were
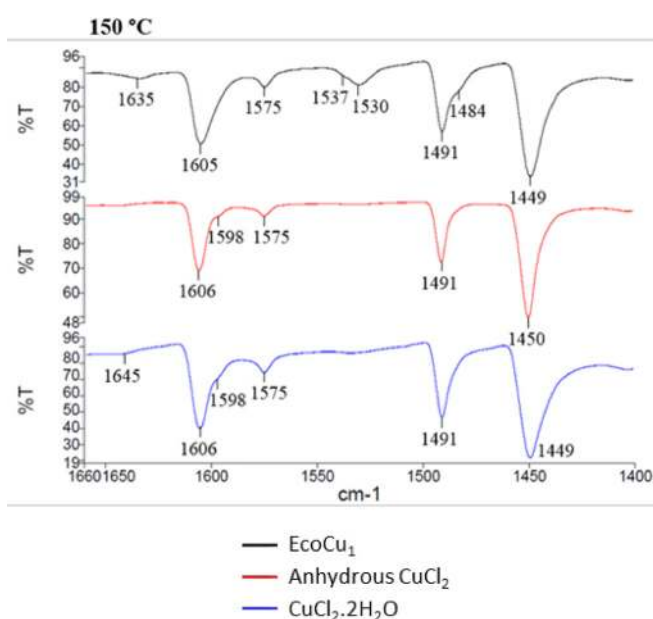

Figure 1. IR spectra of pyridine adsorbed on EcoCu1, on commercial anhydrous CuCl$_2$ and CuCl$_2$.2H$_2$O.

similar in the three catalysts, we can conclude that the strength of the Lewis acidity is not significantly different between EcoCu$_1$, anhydrous CuCl$_2$ and CuCl$_2$.2H$_2$O. Besides, the absorption band, characteristic of the pyridinium ion, was observed at 1530 cm^{-1} with EcoCu$_1$. The presence of pyridinium cations in the material treated at 150 °C indicates that EcoCu$_1$ displays no-

ticeable Brønsted acidity contrary to both commercial copper(II) chlorides.

2.1.4. XRD of the EcoCu$_1$ catalyst

XRD analyses were performed in order to determine the crystalline structure of the complexes in the EcoCu$_1$ catalyst (Figure 2). One polymetallic compound
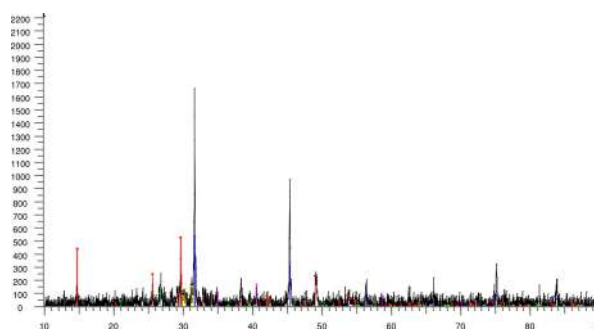

Figure 2. X-ray diffractogram of EcoCu$_1$.

was detected: K$_6$Fe$_2$O$_5$. This compound is an efficient catalyst for the industrial ethylbenzene dehydrogenation to styrene process[18]. Manganese was present in the manganosite form MnO, in the presence of sodium chloride and calcium sulfate hydrate. Copper was not present in a crystalline form.

2.1.5. Surface properties of the EcoCu$_1$ catalyst

Finally, the surface properties of the EcoCu$_1$ catalyst were determined via nitrogen sorption. We observed that the material displays rather low porosity with a specific surface area S$_{BET}$ of 12.0 m^2/g and a mesopore volume V$_{meso}$ of 0.07 cm^3/g. The nitrogen uptake appears in particular at high P/P$_0$ values indicating broad pore size distribution and an average pore size larger than 10 nm, which is due in particular to intergranular porosity.
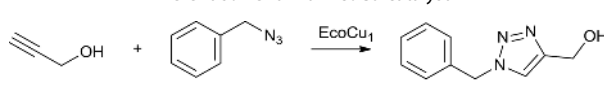
2.2. Eco-CuAAC Click Reaction

The copper(I) catalyzed 1,3-dipolar cycloaddition of azides with alkynes is an ideal model reaction for different reasons. This first example of "click-chemistry"[19] is based on "fusion" mechanisms between two molecules with perfect atom-economy. Moreover, the modern copper-catalysed reaction illustrates the interest of using non-endangered metal, Cu, to promote the selective formation of substituted 1,2,3-triazoles. Finally, the CuAAC has been widely used in synthesis[13a], medicinal chemistry[20], molecular biology[20b, 21], and materials science[22]due to the chemical ligation properties.[13a, 23] Numerous applications are continually reviewed and enriched by new results in many areas. For example, the reaction is very important for the labelling of bio-macromolecules[24] or functional tools to understand

complex biological systems[25] to elaborate valuable tools for biochemists. These results illustrate the interest to synthesize triazoles using aqueous systems. In the context of Green Chemistry, the development of ligand-free catalysts is an additional challenge. It is a double advantage in terms of cost (the high cost of the ligands limit the industrial interest of the process) and of purification (the delicate step of separation between ligand and product is avoided).

Here, we investigated the capacity of $EoCu_1$ to promote the CuAAC transformation in a model reaction between benzyl azide and propargyl alcohol (Table 3).

Table 3. CuAAC Click reaction of benzylazide with propragyl alcohol in different solvent with EcoCu catalyst

Entry	Solvent	Conversion (%)[a,b]
1[a]	H_2O	>99
2[a]	EtOH	>99
3[a]	iPrOH	>99
4	MeTHF	>99
5	DMF	>99
6[c]	H_2O	0

[a] Reaction conditions: 1 mmol **1a**, 1 mmol **2a**, 5 mmol NaAsc, 20 mmol TEA, 5 mol% Cu, 25°C, 16h.
[b] Conversions reported were determined by GC-MS after calibration with hexadecane as internal standard
[c] Blind experiment in which the ecocatalyst has been obtained by the same experimental methodology employed for EcoCu (calcination + acidic treatment) but with a plant that has not been in contact with the a $CuNO_3$ solution

Thermal treatment of plants' roots used to produce $EcoCu_1$ determines the oxidation state of copper present in $EcoCu_1$: under air flow, Cu(II) species are exclusively formed. It is generally accepted that Cu(II) salts are not efficient catalysts in the CuAAC reaction. Sodium ascorbate, a natural and aqueous soluble reducing agent, is the reagent of choice to generate an active Cu(I) catalyst in situ.[13b] The treatment of yellow $EcoCu_1$ (II) by sodium ascorbate yielded the gray-green $EcoCu_1$(I) in five minutes at room temperature. We further used a tertiary amine (triethylamine, TEA) as ligand and/or base. The expected role of this compound is the stabilisation of the Cu(I) species[26] and the neutralization of BrØnsted acidity in $EcoCu_1$ (see IR studies above), which can be a disadvantage in the catalytic cycle due to the formation of a copper(I) acetylide intermediate.
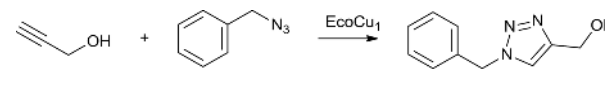
We observed that $EcoCu_1$ is an highly active catalyst for 1,3-dipolar cycloaddition reaction in various media (Table 3). Nearly total conversions were found for reactions carried out in water, ethanol, isopropanol, methyltetrahydrofuran and dimethylformamide. The polymetallic composition of $EcoCu_1$ did not seem to affect the interactions between the copper site and the substrate. The catalyst displays high selectivity; no formation of side products was observed, and the only formed product was the 1,4-subsituted triazole **3a**. In particular, no oxidative Glaser coupling was detected under aerobic conditions. This result illustrates the high regioselectivity of the $EcoCu_1$ catalyst in the CuAAC click reaction, in line with results obtained with the utilization of classical copper catalysts. A large difference was observed when TEA was replaced by K_2CO_3 under air. Under these conditions, the coupling reaction of alkyne and the formation of hexa-2,4-diyne-1,6-diol was the main reaction we observed.

These results were interesting; the most efficient conditions described in the literature employed $CuSO_4$ in aqueous conditions or CuI, CuBr, $Cu(OAc)_2$ or Cu in organic solvents. The efficiency of CuCl ou $CuCl_2$/NaAsc was rarely described[22b]. In order to unambiguously prove the catalytic activity of $EcoCu_1$ (I) derived from the system NaAsc - $EcoCu_1$(II), the reaction was performed without adding NaAsc to the reaction mixture. Under these conditions, we observed no significant product formation.

In order to optimize the reaction conditions with water, we closely studied different other parameters of the reaction such as the presence of TEA, the quantity of sodium ascorbate, the quantity of added $EcoCu_1$ and the influence of the reaction time (Table 4). It is interesting to note that $EcoCu_1$ is active at

Table 4. Influence of TEA and NaAsc on the EcoCuACC Click reaction

Entry	TEA (eq.)	NaAsc (eq.)	Mol% Cu	time	Yield[a,b] [%]
1[a]	20	5 eq.	5	16 h	>99
2[a]	20	5 eq.	1	5 days	58
3[a]	20	5 eq.	5	4 h	>99
4	20	5 eq.	5	1 h	50
5	**0**	**5 eq.**	**5**	**1 h**	**>99**
6	0	2 eq.	5	1 h	44
7	0	1.5 eq.	5	1 h	7
8	0	1 eq.	5	1 h	0

[a] Reaction conditions: 1 mmol **1a**, 1 mmol **2a**, H_2O, 25°C.
[b] Yields reported were determined by GC-MS after calibration with hexadecane as internal standard

room temperature. In an initial trial, we observed that the reaction went to completion after 4 h (entry 3). 5 mol% represented the ideal amount of Cu in EcoCu. An excess of sodium ascorbate was required and at least 5 eq. were necessary (entries 5–8). Surprisingly, TEA interfered negatively with the reaction. We observed higher catalytic activity in the absence of the amine (entry 5). The optimized reaction conditions are as follows: treatment of $EcoCu_1$ by sodium ascorbate and the addition of azide **2a** and alkyne **1a** in water led to the expected triazole **3a** quantitatively after only 1 h at room temperature.

In order to confirm the synthetic potential of $EcoCu_1$ in the CuAAC, we studied the general application of the reaction with various azides and alkynes. As shown in Table 5, the reaction proceeded with aliphatic, aromatic and functional substrates

Table 5. CuAAC Click reaction of different azides and alcohols by the EcoCu methodology					
Entry	Azide 1	Alkyne 2	Product 3	Yield (%) [a,b] (this work)	Yield[Ref]
1			3b	>99 (92)	>99[29]
2			3c	>99	-
3			3d	>99 (78)	>99[29]
4			3e	98	98[28]
5			3f	>99	61[28]
6			3 g	>99	85[28]
7			3 h	>99	93[28]
8			3i	>99	79[28]
9			3j	>99	>99[30]
10			3k	>99	-

[a] Reaction conditions: 2 eq. NaAsc, 25 °C, 1h, H_2O.
[b] Yields determined by GC-MS after calibration with an internal standard. Values between parentheses are isolated yields.

Table 6. ICP MS analysis of aqueous and organic layers after the reaction performed with $EcoCu_1$. (mg/L ± standard deviation).

Aqueous layer

Na	Mg	Al	K	Ca	Fe	Zn	Cu
128.9 ±0.020	22.5 ±0.030	8.01 ±0.028	47.2 ±0.017	59.8 ±0.060	17.6 ±0.022	2.55 ±0.023	78.7 ±0.018

Organic layer

Na	Mg	Al	K	Ca	Fe	Zn	Cu
48.6 ±0.008	1.33 ±0.002	0.20 ±0.054	1.77 ±0.032	45.3 ±0.017	0.45 ±0.015	0.72 ±0.010	4.57 ±0.013

such as propargyl ester, alkenyl, amino and alcohol moieties. No rate difference was observed between primary and secondary azides. The activity of $EcoCu_1$ catalyst was comparable to the homogeneous Cu catalysts[27] and recent Cu(I) Schiff base network polymer heterogeneous catalysts described by Taskin et al.[28]

Another interesting issue is the simplicity of the treatment. No chromatographic purification or other purification step was required. A simple addition of Me-THF or EtOAc allowed the isolation of the reaction products with a high degree of purity.

2.3. Ecological recycling and use of recycled $EcoCu_2$

2.3.1. CuAAC and rhizofiltration of reaction mixture

The concept of ecological recycling involves the reuse of metal containing waste via rhizofiltration. For this purpose, we studied a second rhizofiltration of the Cu containing reaction mixture of a CuAAC reaction with *E. crassipes.*

We studied the reaction between benzyl azide and phenylacetylene on a 371 mg scale under standard reaction conditions (2 eq. NaAsc, 25 °C, 1 h, H_2O). The reaction product **3d** was extracted with Me-THF. The metal content of the aqueous and organic layers were then analyzed by ICP MS. (Table 6).

The ICP-MS analysis indicates that 95 % of the copper remained in the aqueous layer. The result was similar with other elements. Surprisingly, significant amounts of sodium and calcium were present in the Me-THF phase. The presence of these cations could be explained by the contamination of glassware.

The straightforward rhizofiltration of the aqueous layer *via E. crassipes* led to the ecological recycling of Cu. The experimental conditions were similar above-mentioned (see chapter 2.1.1.). The roots of *E. crassipes* were directly transformed into the regenerated ecocatalyst labelled $EcoCu_2$.

2.3.2. Characterization of $EcoCu_2$

ICP-MS analyses of recycled $EcoCu_2$ were performed after dilution of the mineralized solid in an aqueous solution of 1% nitric acid (Table 7).

Table 7. ICP MS analysis of EcoCu$_2$.							
Na	Mg	Al	K	Ca	Fe	Zn	Cu
0.97 ± 0.018	1.20 ± 0.030	1.05 ± 0.034	1.10 $\pm 0.$	3.55 ± 0.036	1.35 ± 0.041	0.02 ± 0.033	2.29 ± 0.037

The analysis showed that Cu was still the major transition metal in the EcoCu$_2$. The ecocatalyst derived from ecological recycling was less concentrated in Cu (2.29 wt%) than EcoCu$_1$ derived from the first rhizofiltration (4.30 wt%), because the bioconcentration of *E. crassipes* was not quantitative in the adopted conditions. However, the copper level is still sufficient for ecocatalysis. A small amount of Fe was observed in both ecocatalysts EcoCu$_1$ and EcoCu$_2$. Iron was the second most abundant transition metal in the ecocatalysts, with contents of 0.50 wt% in EcoCu1 and 1.35 wt% in EcoCu$_2$. The quantities of Mg, Ca, Na and K were similar between the two materials.
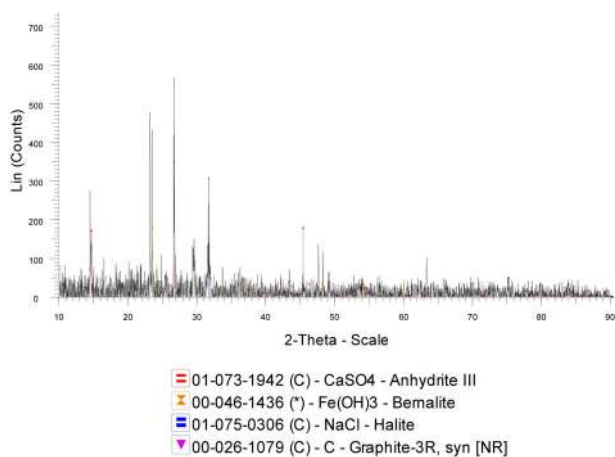

01-073-1942 (C) - CaSO4 - Anhydrite III
00-046-1436 (*) - Fe(OH)3 - Bernalite
01-075-0306 (C) - NaCl - Halite
00-026-1079 (C) - C - Graphite-3R, syn [NR]

Figure 3. X-ray diffractogram of EcoCu$_2$.

XRD analysis of EcoCu$_2$ (Figure 3) has been performed in order to compare the structure of the EcoCu$_1$ and EcoCu$_2$ catalysts.

XRD analysis of the EcoCu$_2$ material showed that iron was present in the bernalite form. Thus, contrary to EcoCu$_1$, iron was in the Fe(III) state. It is known that the synthesis of this mineral appears to be a challenge, because the synthesis of bernalite by crystallization from Fe(OH)$_3$ is difficult. Manganosite form MnO was not present, but graphite-3R was found. This could be the result of the incomplete combustion of lignine during the thermal treatment. Similar to EcoCu$_1$, copper was present only in amorphous form.

2.3.3. Use of recycled EcoCu$_1$ into EcoCu$_2$

In order to prove the catalytic activity of EcoCu after ecological recycling, the CuAAC reaction between benzylazide and phenylacetylene has been performed with EcoCu$_2$. Under the conditions of the model test reaction (2 eq. NaAsc, 25 °C, 1 h, H$_2$0, 5 mol% Cu), 3d was quantitatively obtained. EcoCu$_2$ contained about 2 times less copper than EcoCu$_1$, but its reactivity was maintained. This result demonstrates that the other metal species have no negative effect on the rate of the reaction. Also, this interesting result constitutes a proof of concept for ecological recycling in homogeneous catalysis.

3. Conclusions

We have shown for the first time that EcoCu catalysts enable the innovative recovery of metal charged biomass from plants used in rhizofiltration to decontaminate effluents rich in copper.

EcoCu produced from *E. crassipes* roots is a highly efficient homogeneous catalyst for the CuAAC reaction. The process is very simple, carried out in aqueous media, and does not require the presence of an amine. The products obtained with EcoCu catalysts do not require further purification.

Another special and innovative advantage is that EcoCu can be reused through ecological recycling of the reaction mixture via a second rhizofiltration cycle. The recycled EcoCu displays similar catalytic activity. This easy recovery of EcoCu is another valuable asset in terms of Green Chemistry.

[1] a) G. Losfeld, P. V. de La Blache, V. Escande, C. Grison, *Green Chem. Lett. Rev.* **2012**, *5*, 451–456; b) C. Garel, B.-L. Renard, V. Escande, A. Galtayries, P. Hesemann, C. Grison, *Appl. Catal., A* **2015**, *504*, 272–286; c) C. Grison, J. Escarré, M.-L. Berthommé, J. Couhet-Guichot, C. Grison, F. Hosy, *Actual. Chimique* **2010**, 27–32.

[2] C. M. Grison, B. L. Renard, C. Grison, *Bioorg. Chem.* **2014**, *52*, 50–55.

[3] a) C. Grison, *Environ. Sci. Pollut. Res. Int.* **2015**, *22*, 5589–5591; b) G. Losfeld, V. Escande, T. Jaffré, L. L'Huillier, C. Grison, *Chemosphere* **2012**, *89*, 907–910; c) G. Losfeld, V. Escande, T. Mathieu, C. Grison, *Tech. Ing.* **2011**, *IN 135*, 1–8.

[4] a) G. Losfeld, R. Mathieu, L. L'Huillier, B. Fogliani, T. Jaffré, C. Grison, *Environ. Sci. Pollut. Res.* **2015**, *22*, 5608–5619; b) B. Lange, O. Pourret, P. Meerts, P. Jitaru, B. Cances, C. Grison, M. P. Faucon, *Chemosphere* **2015**, *146*, 75–84.

[5] a) C. Grison, M. Mazel, A. Sellini, V. Escande, J. Biton, C. Grison, *Environ. Sci. Pollut. Res. Int.* **2015**, *22*, 5667–5676; bV. Escande, T. Olszewski, C. Grison, *Environ. Sci. Pollut. Res.* **2014**, 1–14; c) G. Losfeld, P. Vidal de la Blache, V. Escande, C. Grison, *WIT Trans. Ecol. Environ.* **2012**, *1*, 563–575;

d) G. Losfeld, V. Escande, P. Vidal de La Blache, L. L'Huillier, C. Grison, *Catal. Today* **2012**, *189*, 111–116.

[6] V. Escande, T. K. Olszewski, C. Grison, *C.R. Chim*. **2014**, *17*, 731–737.

[7] C. Grison, V. Escande, E. Petit, L. Garoux, C. Boulanger, C. Grison, *RSC Adv*. **2013**, *3*, 22340.

[8] V. Escande, B. L. Renard, C. Grison, *Environ. Sci. Pollut. Res. Int*. **2015**, *22*, 5633–5652.

[9] V. Escande, E. Petit, L. Garoux, C. Boulanger, C. Grison, *ACS Sustainable Chem. Eng*. **2015**, *3*, 2704–2715.

[10] a) V. Escande, A. Velati, C. Garel, B.-L. Renard, E. Petit, C. Grison, *Green Chem*. **2015**, *17*, 2188–2199; b) V. Escande, L. Garoux, C. Grison, Y. Thillier, F. Debart, J.-J. Vasseur, C. Boulanger, C. Grison, *Appl. Catal., B* **2014**, *146*, 279–288; c) Y. Thillier, G. Losfeld, V. Escande, C. Dupouy, J.-J. Vasseur, F. Debart, C. Grison, *RSC Adv*. **2013**, *3*, 5204.

[11] V. Escande, T. K. Olszewski, E. Petit, C. Grison *ChemSusChem* **2014**, *7*, 1915–1923.

[12] V. Escande, A. Velati, C. Grison, *Environ. Sci. Pollut. Res. Int*. **2014**, *22*, 5677–5685.

[13] a) M. Meldal, C. W. Tornøe, *Chem. Rev*. **2008**, *108*, 2952–3015; b) V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless, *Angew. Chem., Int. Ed*. **2002**, *41*, 2596.

[14] a) S. D. Ebbs, L. V. Kochian, *J. Environ. Qual*. **1997**, *26*, 776–781; b) Y. Ma, M. Rajkumar, H. Freitas, *J. Environ. Manage*. **2009**, *90*, 831–837; c) A. Rodríguez-Vila, E. F. Covelo, R. Forján, V. Asensio, *J. Environ. Manage*. **2015**, *147*, 73–80.

[15] a) B. A. Lesniewska, J. Messerschmidt, N. Jakubowski, A. Hulanicki, *Sci. Total. Environ*. **2004**, *322*, 95–108; b) K.-M. Jolanta, M. Alina, *Soil Sci. Ann*. **2013**, *64*, 19–23.

[16] a) S. Rezania, M. Ponraj, A. Talaiekhozani, S. E. Mohamad, M. F. Md Din, S. M. Taib, F. Sabbagh, F. M. Sairan, *J. Environ. Manage*. **2015**, *163*, 125–133; b) G. Swain, S. Adhikari, P. Mohanty, *J. Agr. Sci. Tech*. **2014**, *2*, 1; c) E. Melignani, L. de Cabo, A. Faggi, *Environ. Sci. Pollut. Res*. **2015**, *22*, 8307–8315.

[17] a) R. G. Pearson, *J. Am. Chem. Soc*. **1963**, *85*, 3533–3539; b) R. G. Pearson, *Inorg. Chim. Acta* **1995**, *240*, 93–98.

[18] S. C. Ndlela, B. H. Shanks, *Ind. Eng. Chem. Res*. **2006**, *45*, 7427–7434.

[19] H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem. Int. Ed*. **2001**, *40*, 2004–2021.

[20] a) S. G. Agalave, S. R. Maujan, V. S. Pore, *Chem. Asian J*. **2011**, *6*, 2696–2718; b) P. Thirumurugan, D. Matosiuk, K. Jozwiak, *Chem. Rev*. **2013**, *113*, 4905–4979.

[21] C. S. McKay, M. G. Finn, *Chemistry & Biology* **2014**, *21*, 1075–1101.

[22] a) G. Clavé, G. Delport, C. Roquelet, J.-S. Lauret, E. Deleporte, F. Vialla, B. Langlois, R. Parret, C. Voisin, P. Roussignol, B. Jousselme, A. Gloter, O. Stephan, A. Filoramo, V. Derycke, S. Campidelli, *Chem. Mater*. **2013**, *25*, 2700–2707; b) L. Liang, D. Astruc, *Coord. Chem. Rev*. **2011**, *255*, 2933–2945.

[23] G. Clavé, H. Boutal, A. Hoang, F. Perraut, H. Volland, P.-Y. Renard, A. Romieu, *Org. Biomol. Chem*. **2008**, *6*, 3065–3078.

[24] a) E. Lallana, F. Fernandez-Trillo, A. Sousa-Herves, R. Riguera, E. Fernandez-Megia, *Pharm. Res*. **2012**, *29*, 902–921; b) V. Aragão-Leoneti, V. L. Campo, A. S. Gomes, R. A. Field, I. Carvalho, *Tetrahedron* **2010**, *66*, 9475–9492; c) J. F. Lutz, Z. Zarafshani, *Adv. Drug. Deliv. Rev*. **2008**, *60*, 958–970.

[25] a) P. Kele, X. Li, M. Link, K. Nagy, A. Herner, K. Lorincz, S. Beni, O. S. Wolfbeis, *Org. Biomol. Chem*. **2009**, *7*, 3486–3490; b) M. Grammel, H. C. Hang, *Nat. Chem. Biol*. **2013**, *9*, 475–484.

[26] S. Díez-González, *Catal. Sci. Technol*. **2011**, *1*, 166.

[27] I. Luz, F. X. Llabrés i Xamena, A. Corma, *J. Catal*. **2010**, *276*, 134–140.

[28] O. S. Taskin, S. Dadashi-Silab, B. Kiskan, J. Weber, Y. Yagci, *Macromol. Chem. Phys*. **2015**, *216*, 1746–1753.

[29] S. Diez-Gonzalez, S. P. Nolan, *Angew. Chem. Int. Ed. Engl*. **2008**, *47*, 8881–8884.

[30] C. Vidal, J. Garcia-Alvarez, *Green Chem*. **2014**, *16*, 3515–3521.