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ABSTRACT: A novel catalyst, EcoMnOx, was prepared from waste biomass of Mn-hyperaccumulating plants. The valorization of this Mn-rich biomass is an alternative to its costly usual disposing and provides a new source of Mn. Extracted metal ions, including Mn^{2+}, were oxidized in mild conditions by H_2O_2/NaOH to afford EcoMnOx, as a polymetallic oxide material containing from 8.9 to 14.1 wt % Mn. Spectroscopic studies of this material revealed the presence of Mn layered mixed oxides, rich in Mn^{IV} along with Mn^{III} and Mn^{II} species. EcoMnOx catalytic properties were assessed in the aerobic oxidative cleavage of 1,2-diols, under atmospheric pressure of O_2 or air. With only 10 mol % Mn, up to complete conversions were obtained on activated benzylic and allylic diols, with excellent selectivity toward aldehydes or ketones (98–99%). Moreover, because of its heterogeneous nature, the catalyst can be removed easily by filtration, and reapplied for a minimum of six successive runs without any loss of activity. Finally, E-factor analysis showed the EcoMnOx generates 4 to 17 times less waste compared to classical reagents such as $NaIO_4$ and $Pb(OAc)_4$, respectively, highlighting the sustainable assets of this new heterogeneous catalyst.

KEYWORDS: Heterogeneous catalysis, Manganese oxide, Glycol cleavage, Ecocatalysis, Phytoextraction, Metal recycling
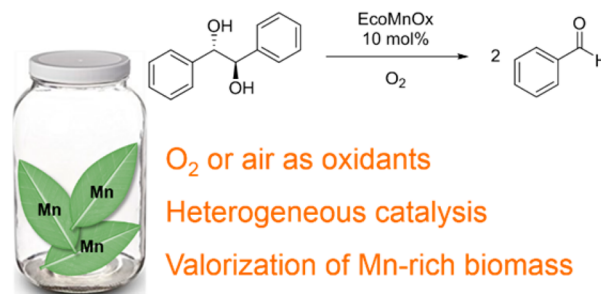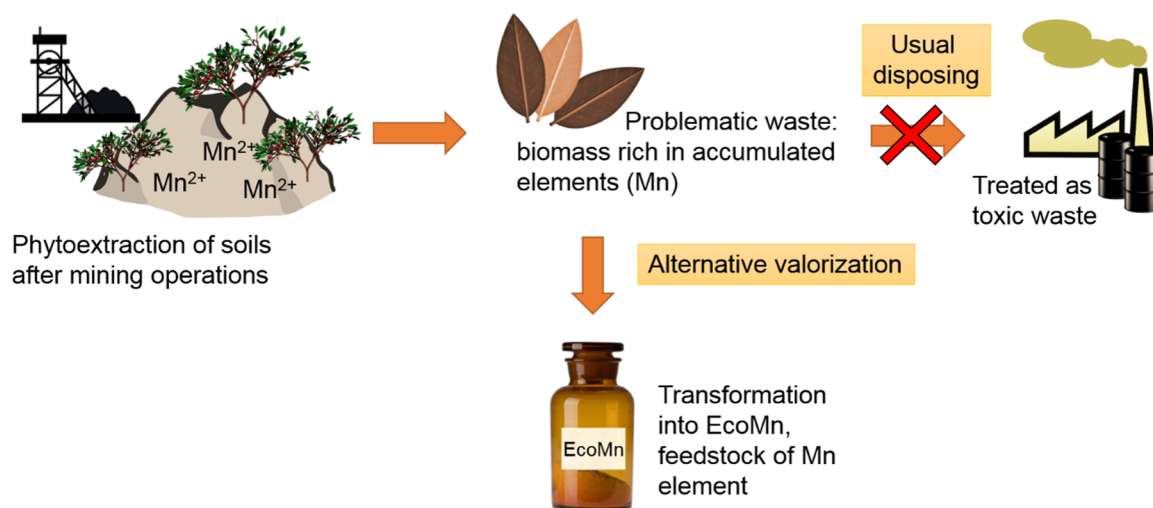
INTRODUCTION

Sustaining global population growth is one of the major upcoming challenges. According to the United Nations, the world population is expected to rise rapidly from the current 7.5 to 11.2 billion by the end of this century.[1] Population growth and the consequent increased urbanization inevitably trigger a rise in demand of natural resources, such as energy, water, and minerals. Even with a shift toward sustainable energy production modes, building the necessary infrastructures (such as wind turbines or solar panels) will require high quantities of metals, ranging from base metals to rare earth elements, which will be sequestered for decades. At the same time, global population growth will lead to an increased demand in consumer goods, such as personal electronic devices, likely to exacerbate this forthcoming metals scarcity. As a result, base metals demand is currently increasing by 5% annually, such that metal production for the next 15 years will need to match that from the start of humanity up to the current time.[2] This growing need for metals is also often decoupled from local production, stressing the risks of geopolitical tensions. For example, it has been stated that European industries consume more than 20% of the global production of metals, whereas European mines produce only 1.5% of iron and aluminum.[2,3]

Addressing future metal scarcity will suppose a necessary evolution of production and consumption habits, as well as a crucial improvement of current metals recycling rate. This can be dealt with the optimization of existing recycling processes, but also with the valorization of metal-rich wastes, unexploited until now.

Among these underestimated metal-rich wastes,[4−6] biomass from phytoextraction crops is very promising. Phytoextraction is an emerging biotechnology using plants to remove contaminants, including metal pollutants from soils.[7−10] Specific plants, named "hyperaccumulators" can uptake and store unusually high amounts of metal ions from the soil, achieving progressive decontamination of metal-polluted sites, like former mining areas. After accumulation, biomass from hyperaccumulators is harvested to avoid a new release of metal pollutants after plant death. However, the resulting metal enriched biomass is usually treated as a toxic waste, which induces a supplementary cost upon its disposal—a practice that is detrimental to the implementation of this ecofriendly

Figure 1. EcoMn production as alternative valorization of Mn-rich biomass from phytoextraction crops.

biotechnology. More importantly, disposing these valuable metals is even more regrettable, especially in view of the aforementioned metal shortages.[11,12] In order to overcome this situation, attempts of valorization of this metal-rich biomass have recently emerged.[13]

Ecocatalysis is a new strategy to valorize metal-rich biomass as a source of metal species for chemical catalysis.[14−17] As catalysis requires low amounts of metal (usually about a few mole percent) while promoting the synthesis of highly valuable compounds, the concept is potentially cost-effective enough to ensure its development on a large scale. Previous works have revealed the possibility of producing a manganese-rich material, starting from biomass of Mn-hyperaccumulating plants. The resulting material, named EcoMn, was used in organic synthesis directly as catalyst, or as source of Mn for producing more elaborate catalysts (Figure 1).[18,19] Manganese displays appealing properties for catalysis, thanks to its multiple stable oxidation states and its low toxicity.[20] Consequently, the use of manganese in industrial catalytic processes is expected to increase, as a substitute for precious metals or toxic elements.[21−23]

Herein, we describe the synthesis of EcoMnOx, a new material rich in Mn oxides, which is made from EcoMn starting with Mn-hyperaccumulating plants. Study of the oxidizing properties of this material revealed excellent catalytic performances for aerobic oxidative cleavage of activated 1,2-diols. This reaction is usually performed with stoichiometric reagents, such as sodium periodate or lead tetraacetate, producing large amounts of toxic byproducts. Classical reaction conditions for oxidative cleavage of 1,2-diols are thus challenged by current standards of green chemistry.[24,25] Although catalytic alternatives have been proposed recently, they suffer from several drawbacks, as these catalysts are either based on precious metals or are homogeneous and not reusable.[26,27] The heterogeneous nature of the EcoMnOx catalyst and its reuse are thus key advantages, combined to the use of O_2 or air as benign oxidant. This Mn catalyst prepared by valorization of waste biomass provides thus an efficient and sustainable alternative to previous methods of 1,2-diols oxidative cleavage.

EXPERIMENTAL SECTION

Materials and Methods. All commercially available chemicals were used as received. Solvents were purchased from Fisher Scientific and were of analytical grade; *meso*-hydrobenzoin (99%), (*R,R*)-hydrobenzoin (99%), *cis*-1,2-cyclohexanediol (99%), 2,3-diphenyl-2,3-butanediol (>90%), and benzopinacol (99%) were supplied by Sigma-Aldrich. Noncommercially available 1,2-diols were prepared by reduction of corresponding commercial diketones (purchased from Fisher Scientific), according to a known procedure.[28]

Characterization. ICP-AES measurements were performed using the PerkinElmer Optima 3000. Samples of 10 mg were digested and dissolved in 2% HNO_3 acid and were quantified against external standards. SEM analyses were performed using the Hitachi SU-70 field emission microscope. Samples were predried in vacuum overnight and were examined with a 10 kV bean power under ultrahigh vacuum without surface treatment. Energy-dispersive X-ray spectroscopy analysis (EDX) was performed using a Zeiss EVO HD15 microscope coupled with an Oxford X-MaxN EDX detector. XRPD measurements were performed on a Rigaku SmartLab X-ray diffractometer equipped with a Cu line-focus sealed tube and a NaI SC70 scintillation detector. Measurements were made with a 40 kV, 44 mA beam, with an incident slit of 2/3° and a length limiting slit of 5.00 mm, in the range 2θ from 10° to 90° locked couple scan type, a step size of 0.05°, and a scan speed of 10.33°/min. XPS analysis was performed using a ThermoScientific ESCALAB 250 instrument. Spectra were collected using a monochromatic Al X-ray source. A low energy electron flood and top-side contact were used for charge neutralization. Survey spectra were collected using a pass energy of 150 eV. Multiplex composition scans were acquired with 20 eV pass energy. FTIR spectra were recorded on a FTIR/Raman Thermo Nicolet 6700 spectrometer, in ATR mode. All dynamic light scattering (DLS) samples were suspended in methanol (1 mg/3 mL) and were sonicated for 5 min prior analysis. DLS was performed at an angle of 90° (ALV-5000, ALV-GmbH) using an incident laser of wavelength 532 nm (coherent). Thirty runs were recorded per sample, with a duration of 30 s per run. All DLS measurements were carried out at room temperature. Reaction products were characterized by $^1H/^{13}C$ NMR spectroscopy and by GC, by comparison of their retention times with those of pure standards, and analytical data were in accordance with those previously published. NMR characterization was performed with an Agilent DD2 400 MHz NMR spectrometer. GC were recorded on a Shimadzu GC-2010 Plus, equipped with an Agilent J&W GC column, DB-5, 60 m × 0.25 mm × 0.25 μm, using He as carrier gas, with a flame ionization detector (FID). All analyses were performed including dodecane as internal standard.

Preparation of EcoMn. EcoMn was prepared from biomass of the Mn-hyperaccumulating plant *Grevillea exul* subsp. *rubiginosa* (Proteaceae), by calcination, acidic extraction then concentration. *Grevillea exul* subsp. *rubiginosa* is a native plant from New Caledonia, grown on mining sites of this subtropical Pacific island, for phytoextraction

Table 1. ICP-AES Analysis of EcoMnOx Compared to Starting EcoMn

element wt % (±sd)	Fe	Mn	Ni	Ca	Mg	Al	Na	K
EcoMn	0.9 (±0.008)	6.7 (±0.04)	0.04 (±0.0004)	10.4 (±0.2)	5.3 (±0.09)	0.2 (±0.02)	2.0 (±0.1)	4.3 (±0.008)
EcoMnOx	0.3 (±0.006)	14.1 (±0.4)	nd[a]	28.2 (±0.2)	28.7 (±0.3)	nd[a]	0.5 (±0.09)	nd[a]

[a]Not detected.

purposes. Details of the procedure and EcoMn characterization were reported in previous publications.[18,19]

Preparation of EcoMnOx. A solution of EcoMn (0.9 mmol Mn) was prepared by dissolution in 10 mL of deionized water. Under stirring at 400 rpm, 0.28 mL (2.7 mmol) of a 30% aqueous solution of H_2O_2 were added in one portion. The resulting colorless solution was stirred for 5 min, then 2 mL of 19 M NaOH (38 mmol) solution were added in one portion, and a black precipitate appeared immediately. After rinsing the sides of the flask with 10 mL of deionized water, the black catalyst suspension was stirred at 800 rpm for 90 min. The resulting suspension was filtered through a glass microfiber filter (Whatman, 1.6 μm) before washing it with 3 portions of 100 mL deionized water, followed by one portion of 50 mL ethanol. The black resulting solid should not be fully left dry before the end of all rinses to preserve its activity. The black solid, labeled as EcoMnOx hereafter, was then collected and dried in air, in an oven at 105 °C, for 18 h.

Representative Procedure for Oxidative Cleavage of 1,2-Diols. In a typical reaction, a mixture of *meso*-hydrobenzoin (0.2 mmol), EcoMnOx (10 mol % Mn), and 1-butanol (1 mL) was added in a 7 mL flask, under a balloon filled with O_2. The mixture was heated to 100 °C under stirring (400 rpm) for 1 h. After reaction, the mixture was cooled to room temperature, and the catalyst removed by filtration through PTFE membrane syringe filter (Millipore, 0.2 μm). Conversion and selectivity were determined by GC-FID, using dodecane as internal standard. Most reactions were repeated twice, and average values were given.

RESULTS AND DISCUSSION

Catalyst Preparation and Characterization. Synthesis of EcoMnOx was adapted from literature for preparing birnessite-type Mn oxides using Mn^{II} salts.[29,30] In our case, the source of Mn^{II} ions was EcoMn prepared from Mn-hyperaccumulating plants and described in our previous works.[18,19] These precedent studies showed that EcoMn was mainly constituted of polymetallic chlorides. EcoMnOx was prepared by rapid oxidation of a solution of EcoMn in aqueous H_2O_2/NaOH, affording the new material as a precipitate, collected by filtration. Analysis of EcoMnOx by inductively coupled plasma atomic emission spectroscopy (ICP-AES) revealed that EcoMnOx was enriched in Mn (14.1 wt %) compared to starting EcoMn (6.7 wt %) (Table 1). This was due to EcoMnOx process of preparation, ensuring selective precipitation of insoluble oxides and hydroxides of Mn, Fe, Ca and Mg. Metal enrichment also resulted from substitution of Cl (in starting EcoMn) by O (in resulting EcoMnOx), of lower molar mass and double valence. Comparison of several batches of EcoMn and their corresponding EcoMnOx, prepared from *Grevillea exul* subsp. *rubiginosa* harvested in different locations, showed some variation in elemental content (e.g., Mn: 8.9–14.1 wt %), due to the natural origin of the biomass feedstock (Table S1). Unless specified, all the following analyses and reactions were performed with the batch of EcoMnOx described in Table 1.

X-ray photoelectron spectroscopy (XPS) confirmed the oxide nature of EcoMnOx (Figure S1). An indication of Mn oxidation state was given by Mn $2p_{3/2}$ binding energy (642.8 eV, Figure 2), characteristic of Mn^{IV}.[31] Mn 3s multiplet splitting supported this conclusion, while being less informative because
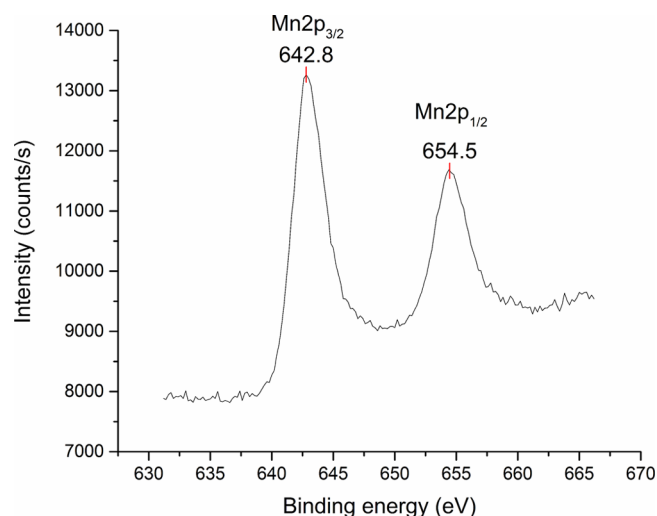
Figure 2. XPS Mn 2p peaks of EcoMnOx.

of obscuration of the peak by the interfering Mg peak (Figure S2). X-ray powder diffraction (XRPD) was performed to get complementary insights on EcoMnOx composition, as shown in Figure 3. Among detected crystalline species, the presence of
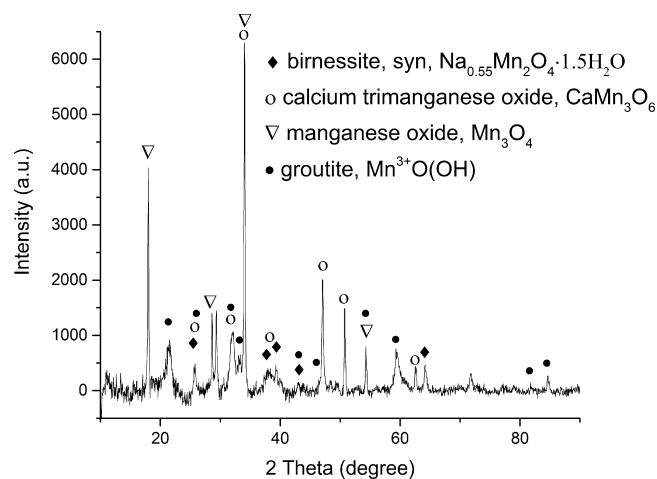
Figure 3. XRPD pattern of crystalline species detected in EcoMnOx.

birnessite was confirmed. Birnessite is a Mn layered mixed oxide, mainly composed of Mn^{IV} oxide, including also Mn^{III} and Mn^{II} species.[32] As birnessite is often of low crystallinity, its weak signal does not typically reflect its actual proportion in the EcoMnOx catalyst.[33] Interestingly, other Mn oxides with different oxidation states such as $CaMn_3O_6$ (Mn^{IV} and Mn^{III}),[34] groutite MnO(OH) (Mn^{III}), and Mn_3O_4 (Mn^{III} and Mn^{II}), were also detected. While the complex polymetallic nature of EcoMnOx did not allow quantification of each Mn oxidation state because of interferences with other ions like Fe^{3+}, these previous analyses demonstrated that Mn^{IV} was preponderant based on XPS analysis, along with some Mn^{III}

and Mn[II] species present. These observations are in accordance with the characteristics of layered Mn oxides such as birnessite, whose Mn average oxidation degree is typically between +3.4 and +3.99.[35] Fourier transform infrared (FTIR, Figure 4) spectroscopy confirmed the attribution of this layered oxide structure for EcoMnOx, with a characteristic absorption at 400 cm^{-1}.[36]
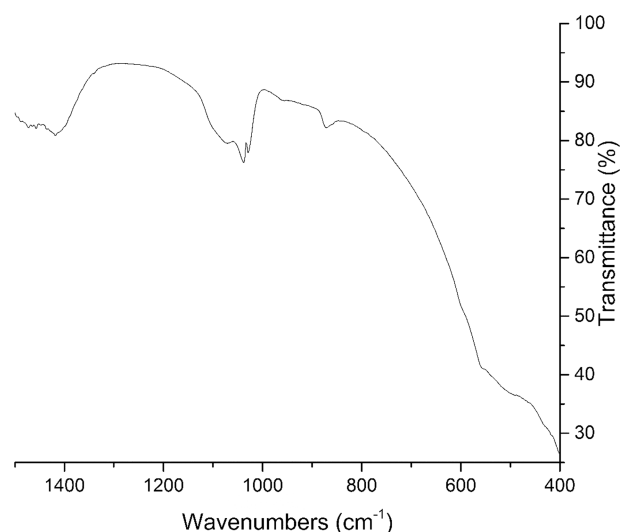

Figure 4. FTIR spectrum of EcoMnOx.

Morphological analysis by scanning electron microscopy (SEM) of EcoMnOx revealed the presence of structures of various sizes, within the range of 10−100 μm (Figure 5a). These structures proved to be aggregates of smaller particles, as shown on Figure 5b. Dynamic light scattering (DLS) measurements were thus conducted after sonication of EcoMnOx, in order to fragment the aggregates, and revealed that average particle size was 103 ± 91 nm.

Catalyst Performance Evaluation. EcoMnOx was then tested as catalyst for oxidative cleavage of meso-hydrobenzoin as model substrate, under atmospheric pressure of O$_2$. Solvent screening revealed that alcohols are the best solvents for the reaction (Table 2, entries 6−7). Previous works with manganese oxide reagents for 1,2-diols oxidative cleavage were only conducted with dichloromethane, in addition to requiring 40 equiv of Mn reagent toward substrate.[37] As

Table 2. Solvent Screening for EcoMnOx-Catalyzed Oxidative Cleavage of meso-Hydrobenzoin[a]

entry	solvent	T [°C]	conversion 1a [%][b]	selectivity 2a [%][b,c]
1	acetonitrile	78	43	>99
2	ethyl acetate	78	35	>99
3	toluene	78	55	>99
4	water	78	53	>99
5	acetic acid	78	47	>99
6	ethanol	78	61	>99
7	1-butanol	100	98	>99

[a]Reaction conditions: meso-hydrobenzoin 1a (42.9 mg, 0.2 mmol), EcoMnOx (10 mol % Mn), 1 mL of solvent, O$_2$ balloon, 1 h. [b]Conversion and selectivity were determined by GC using dodecane as internal standard. [c]Ratio of yield of aldehyde to conversion as a percentage.

alcohols are among the greener solvents for organic synthesis,[38,39] their use in this reaction is thus a valuable asset. With 10 mol % EcoMnOx (based on Mn content), almost complete conversion (98%) was obtained in 1 h, in 1-butanol allowing heating to 100 °C (Table 2, entry 7). A complete selectivity toward benzaldehyde was observed, with no traces of benzoic acid or other oxidation byproducts. No aldehyde disproportionation was noticed, even after prolonged reaction times.

Different atmospheres were also surveyed to assess the role of O$_2$. Even if O$_2$ lead to shorter reaction times, oxidative cleavage of meso-hydrobenzoin was also possible under air, with the same conversion in 3 h (Table 3, entries 1−2). The absence of conversion under N$_2$ confirmed that O$_2$ acted as terminal oxidant in the reaction (Table 3, entry 3). H$_2$O$_2$ was also tried as an alternative to O$_2$ for oxidative cleavage of 1,2-diols. Indeed, in a previous paper on alkene epoxidation with NaHCO$_3$/H$_2$O$_2$ catalyzed by EcoMn, some cleavage of the substrates was described, probably resulting of the hydrolysis of the epoxide, then oxidation of the resulting 1,2-diol.[19] However, when H$_2$O$_2$ was used in the present methodology, a complete decomposition of H$_2$O$_2$ was observed upon addition of the EcoMnOx catalyst, resulting in absence of conversion of meso-hydrobenzoin (Table 3, entry 4). This decomposition can be attributed to the Mn oxides in EcoMnOx, known to decompose H$_2$O$_2$ into H$_2$O and O$_2$.[40] This result showed that the active species in EcoMnOx were different from those involved in the epoxidation/cleavage of alkenes catalyzed by EcoMn, which in
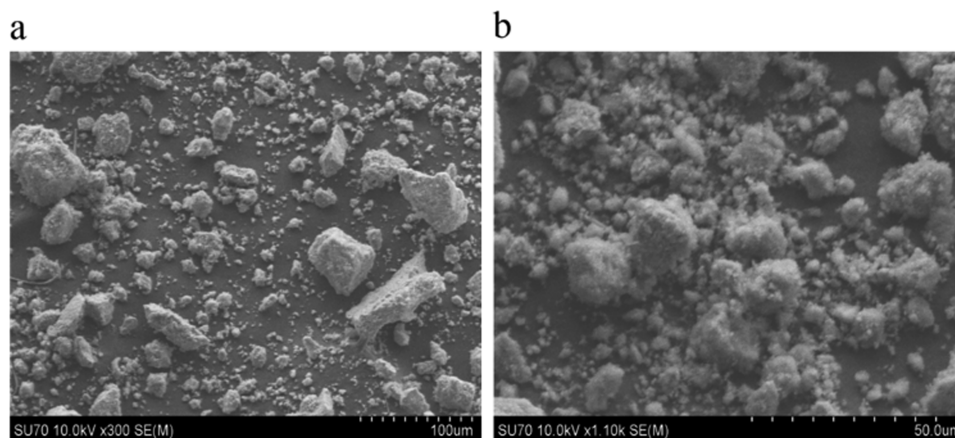

Figure 5. SEM images of EcoMnOx.

Table 3. *meso*-Hydrobenzoin Oxidative Cleavage with Different Mn Oxide Catalysts and Atmospheres[a]

entry	catalyst	atmosphere	t [h]	conversion 1a [%][b]	selectivity 2a [%][b,c]
1	EcoMnOx	O_2	1	98	>99
2	EcoMnOx	air	3	98	>99
3	EcoMnOx	N_2	1	2	
4[d]	EcoMnOx	N_2	1	0	
5	«synthetic» EcoMnOx[e]	O_2	1	99	>99
6	none	O_2	1	0	
7	commercial MnO_2	O_2	1	5	>99
8	commercial activated MnO_2	O_2	1	5	>99

[a]Reaction conditions: *meso*-hydrobenzoin **1a** (42.9 mg, 0.2 mmol), catalyst (10 mol % Mn), 1-butanol (1 mL), gas balloon, 100 °C. [b]Conversion and selectivity were determined by GC using dodecane as an internal standard. [c]Ratio of yield of aldehyde to conversion as a percentage. [d]Reaction performed in the presence of H_2O_2 (30 wt % aqueous solution, 3.0 mmol). [e]Catalyst prepared according the same protocol than EcoMnOx, but with commercial $MnCl_2 \cdot 4H_2O$.

the latter case were mainly Mn^{2+} ions with probably only transient formation of higher oxidation states.

In another control experiment, a "synthetic EcoMnOx", prepared in the same conditions than the biosourced catalyst, but starting from only pure $MnCl_2 \cdot 4H_2O$, gave an almost complete conversion (99%) with complete selectivity toward benzaldehyde (Table 3, entry 5). This result, combined to the absence of conversion without catalyst (Table 3, entry 6), confirmed that Mn oxides present in EcoMnOx were indeed the active species, and that other metal elements detected in EcoMnOx were only spectator elements. For this reason, even if some variation in elemental content was noted between several batches of EcoMnOx prepared from *Grevillea exul* subsp. *rubiginosa* harvested in different locations (Table S1), all the batches of EcoMnOx showed the same catalytic performances when used in 10 mol % Mn for oxidative cleavage of *meso*-hydrobenzoin.

As XPS and XRPD analyses have showed that Mn was mainly present under the oxidation state Mn^{IV} in EcoMnOx, we tested MnO_2 and activated MnO_2, both commercial, as catalysts in the reaction. While in both cases a complete selectivity toward benzaldehyde **2a** was observed, the conversion was only 5% (Table 3, entries 7−8). While EcoMnOx, MnO_2 and activated MnO_2 have a common content in Mn^{IV} oxide, previous studies have extensively showed that Mn^{IV} oxides can exist under a wide variety of forms, with completely different catalytic activities.[32] This could explain why EcoMnOx (and "synthetic EcoMnOx") was much more active than commercial MnO_2, due to its unique structure, resulting of its particular preparation.

Upon optimizing reaction condition, we extended the substrate scope to explore the versatility of EcoMnOx as shown in Table 4. Like *anti*-1,2-diol **1a**, the *syn*-1,2-diol **1b** also cleaved efficiently with high selectivity (Table 4, entry 1), but in a slightly longer reaction time. Benzylic 1,2-diol **1c** activated by electron-donating aromatic substituents was slightly more

reactive than those substituted by electron-withdrawing groups such as **1d** and **1e** (Table 4, entries 2−4). However, cleavage of the latter ones was still performed with high conversion and in short reaction times. Among the diols surveyed, selectivity toward the corresponding aldehyde or ketone was always high (≥98%), and overoxidized products such as carboxylic acids were not detected. Interestingly, 1,2-diols with secondary hydroxyl groups showed a higher reactivity than the tertiary ones (Table 4, entry 5), probably because of steric effects in the last case, affecting interaction with the catalyst. However, tertiary diols bearing highly activating substituents, like benzopinacol **1g**, were still cleaved with a complete conversion (Table 4, entry 6). Reaction with a less activated, mixed benzylic-aliphatic 1,2-diol **1h** yielded relatively little products even at prolonged reaction time, which indicated the method was highly selective toward dibenzylic diols (Table 4, entry 7). This particular selectivity was confirmed by the absence of conversion of *cis*-1,2-cyclohexanediol **1i** (Table 4, entry 8). High conversions (≥95%) were obtained with diverse activated 1,2-diols, like heterocyclic diol **1j** (Table 4, entry 9) and allylic diol **1k** (Table 4, entry 10), thereby extending the potential of the method. Since a difference in reaction times was observed between anti and syn diastereomers **1a** and **1b** respectively, a similar variation in reactivity should be probably noted for the pure diastereomers of the other substrates, used here as mixtures of variable syn/anti ratios.
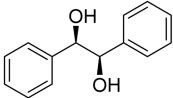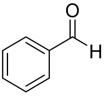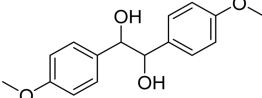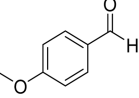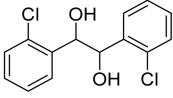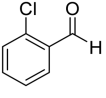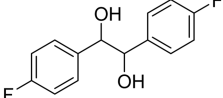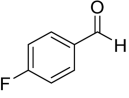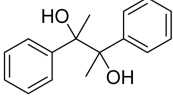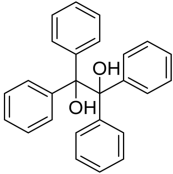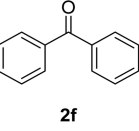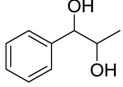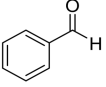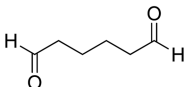
In order to investigate the kinetic aspects of the reaction, time-dependent studies were conducted. A EcoMnOx-catalyzed kinetic experiment with *meso*-hydrobenzoin revealed a first order rate equation toward substrate, with a rate constant of 5.48 h^{-1} (Figure 6). When the catalyst was removed by filtration shortly after the beginning of the kinetic experiment and then the reaction continued with the filtrate, no further conversion was observed, confirming the heterogeneous nature of the catalytic species (Figure 7).
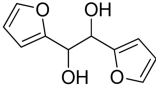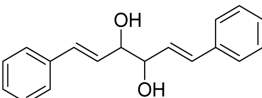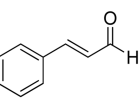
The heterogeneous nature of EcoMnOx enables catalyst recycling for multiple runs: for example, after oxidative cleavage of benzopinacol **1g**, EcoMnOx was separated by centrifugation, washed with ethanol and then dried. The recovered catalyst was reapplied for an identical experiment. The procedure was repeated six successive times, and the catalyst showed no apparent loss of activity (Figure 8).

The characterization of another batch of EcoMnOx was performed after reaction, in order to assess the stability of the catalyst. The content in metal elements remained virtually unmodified before and after oxidative cleavage of *meso*-hydrobenzoin (Table S2). Morphological analysis by SEM showed a constant size of aggregates before and after reaction (Figure S3). According to energy-dispersive X-ray (EDX) analysis, the oxygen content of EcoMnOx stayed the same (see Figure S4), which revealed that the oxide character of the material remained unmodified after reaction.

Finally, comparison with traditional reagents $NaIO_4$ and $Pb(OAc)_4$ highlighted the sustainability assets of this new method, especially for cleavage of activated 1,2-diols (Table 5). Not only the EcoMnOx-catalyzed version was performed in nontoxic 1-butanol, compared to classical dichloromethane and benzene, but the only byproduct formed with this method was water, whereas traditional reagents produce stoichiometric quantities of toxic wastes. In addition, the heterogeneous catalytic nature of EcoMnOx allowed its reuse in at least six successive runs without loss of activity. Finally, the combination of these characteristics was summarized in the E-factor value,

Table 4. Scope of the EcoMnOx-Catalyzed Aerobic Oxidative Cleavage of 1,2-Diols[a]

| entry	substrate 1[b]	product 2	t [h]	conversion 1 [%][c]	selectivity 2 [%][c,d]
1	1b	2a	3	97	99
2[e]	1c	2b	1	99	99
3[f]	1d	2c	1	91	98
4[g]	1e	2d	1	86	99
5[h]	1f	2e	24	54	99
6	1g	2f	1	100	99
7[i]	1h	2a	24	57	99
8	1i	2g	24	0	-
9[j]	1j	2h	24	98	99
10[k]	1k	2i	3	95	98

[a]Reaction conditions: substrate (0.2 mmol), EcoMnOx (10 mol % Mn), 1-butanol (1 mL), O_2 balloon, 100 °C. [b]Unless specified, the starting diols bearing two stereogenic centers were used as variable mixtures of diastereomers, with syn/anti ratio determined by ^{1}H NMR. [c]Determined by GC using dodecane as an internal standard. [d]Ratio of yield of aldehyde or ketone to conversion as a percentage. [e]Diol used in diastereomeric ratio syn/anti 15:85.[41] [f]Diol used in diastereomeric ratio syn/anti 26:74.[42] [g]Diol used in diastereomeric ratio syn/anti 29:71.[41] [h]Diol used in diastereomeric ratio syn/anti 54:46.[41] [i]Diol used in diastereomeric ratio syn/anti 30:70.[43,44] [j]Diol used in diastereomeric ratio syn/anti 42:58.[42] [k]Diol used in diastereomeric ratio syn/anti 52:48.[42]

assessing the ratio of amounts of waste formed by unit of product.[45] With a E-factor of 0.8 for *meso*-hydrobenzoin oxidative cleavage, the EcoMnOx-catalyzed method produced 4−17 times less waste than Pb(OAc)$_4$ and NaIO$_4$, respectively.
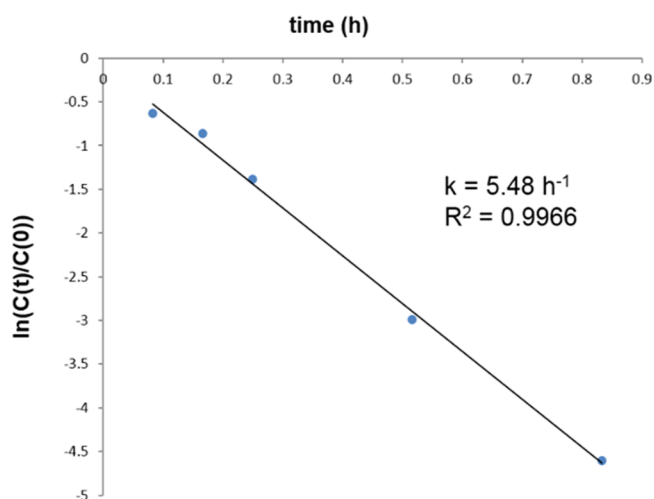
Figure 6. Kinetic study of the aerobic oxidative cleavage of *meso*-hydrobenzoin, catalyzed by EcoMnOx. Reaction conditions: *meso*-hydrobenzoin (0.2 mmol), EcoMnOx (10 mol % Mn), 1-butanol (1 mL), O_2 balloon, 100 °C. $C(0)$ original concentration of substrate; $C(t)$ concentration of substrate at time t.
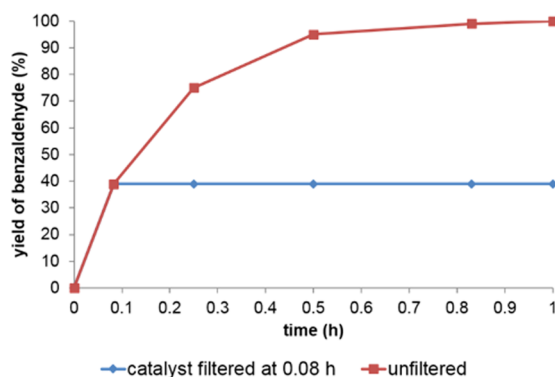
Figure 7. Effect of catalyst filtration on the aerobic oxidative cleavage of *meso*-hydrobenzoin. Reaction conditions: *meso*-hydrobenzoin (0.2 mmol), EcoMnOx (10 mol % Mn), 1-butanol (1 mL), O_2 balloon, 100 °C. After 0.08 h, EcoMnOx was removed by filtration then the reaction was continued with the filtrate. Yield of benzaldehyde was determined by GC using dodecane as an internal standard.
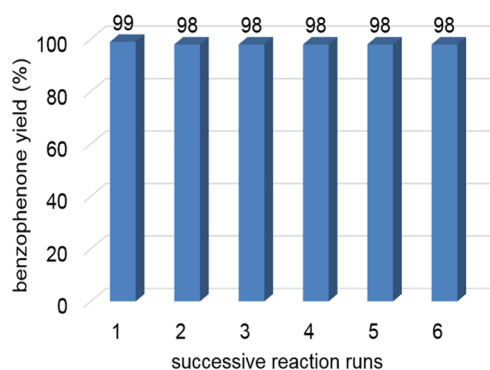
Figure 8. Reuse of EcoMnOx catalyst in successive reaction runs. Reaction conditions: benzopinacol (0.2 mmol), EcoMnOx (10 mol % Mn), 1-butanol (1 mL), O_2 balloon, 100 °C, 1 h. After reaction, the catalyst was recovered by centrifugation, rinsed with 2 × 4 mL of ethanol and then dried in oven under air at 105 °C for 2 h. Yields were determined by GC using dodecane as an internal standard.

Table 5. Comparison of the EcoMnOx-Catalyzed Method with $NaIO_4$ and $Pb(OAc)_4$, on the Basis of Sustainability Characteristics

	EcoMnOx/ O_2[a]	$NaIO_4$[b]	$Pb(OAc)_4$[b]
solvent typically used	1-butanol	dichloromethane	benzene
wastes formed	water	$NaIO_3$	$Pb(OAc)_2$
successive runs without loss of activity	≥6 (6 runs tested)	1	1
E-factor (E)[c]	0.8	13.9	3.2

[a]See the SI for details of reaction conditions and calculations. [b]Calculated for 90% yield in typical reaction conditions from ref 46. [c]*meso*-Hydrobenzoin oxidative cleavage was used as model reaction for E-factor calculations with the different methods.

CONCLUSION

In the face of metal shortages due to population growth and rapid urbanization, the EcoMn feedstock made from phytoextraction biomass serves as a novel, effective strategy to clean up and recycle Mn from mining waste. Through a simple process using readily available reagents, we turned this biosourced Mn feedstock into a new catalyst, EcoMnOx, that rivals the existing methodology for 1,2-diols oxidative cleavage. In mild reaction conditions, EcoMnOx catalyzed the aerobic oxidative cleavage of a range of activated 1,2-diols, with high conversion and selectivity. These promising results will motivate further mechanistic studies in order to determine the role of each Mn oxide species present in EcoMnOx, depending on their oxidation state and their possible cooperative catalytic effect. Considering the serious environmental concerns associated with some of the traditional reagents used for 1,2-diols oxidative cleavage, the heterogeneous nature of EcoMnOx catalyst, its possible reuse, and the formation of water as the sole byproduct while using O_2 or air as benign oxidants in a green solvent confer strong sustainable advantages to this new method.

ASSOCIATED CONTENT

Experimental details, XPS spectra, ICP-AES analyses, SEM images, EDX spectra, GC chromatograms, and E-factor calculations (PDF)

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The authors declare no competing financial interest.

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