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Biochar from recovered cellulose as new admixture in constructed wetlands for micropollutant removal: A circular approach

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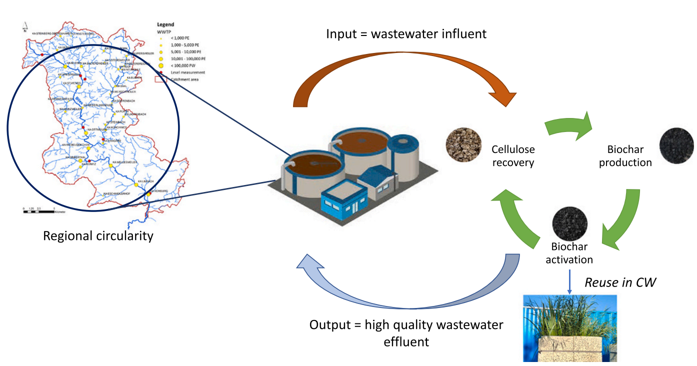
HIGHLIGHTS

- Wastewater cellulose can be recovered and valorized.
- Biochar produced from recovered cellulose is a suitable admixture in wetlands.
- The use of activated biochar from cellulose increases the wetland's efficiency.
- Persistent micropollutants (i.e. carbamazepine) are well eliminated (>90 %).
- A circular initiative is possible with biochar produced from large treatment plants.

GRAPHICAL ABSTRACT



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ABSTRACT

This study aimed to evaluate the suitability of biochar produced by pyrolysis from recovered wastewater cellulose and activated biologically as an admixture in Constructed Wetlands (CWs) when applied as a post-treatment step to remove micropollutants (MPs) from municipal wastewater effluent. Two planted vertical flow mesocosm CWs with cellulose-based admixtures of different origins (plant residue and recovered toilet paper) were fed with a municipal wastewater effluent representative for rural catchments. The results showed an average MPs elimination of 89.1 % for the activated biochar produced from recovered cellulose when 15 relevant compounds are considered and a reduction of the risk from compounds cocktail below the maximum acceptable level having diclofenac, carbamazepine, PFOS, ciprofloxacin and clarithromycin as main risk drivers (Risk Quotient > 1). The implementation of a circular approach to reduce MPs was finally conducted for the Blies catchment (Saarland region in Germany) characterized by low population density and small, sensitive water bodies. This approach demonstrates the feasibility of combining cellulose recovery with a fine sieve in large wastewater treatment plants (WWTPs) and providing biochar produced from recovered cellulose as an admixture to small WWTP where CW is an affordable solution for MP mitigation.

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1. Introduction

The concept of sustainability has gained great attention in the last decade due to rising environmental problems such as biodiversity loss, water, air, soil pollution and resources depletion (Schöggl et al., 2020). In addition to that, high unemployment rate and increased inequalities forced policymakers to enable the implementation of a new paradigm namely Circular Economy (CE) where ideally natural resources that provide inputs for production and consumption as well as output for waste, are better managed within a regenerative closed-loop system (EC, 2015; Geissdoerfer et al., 2017) in accordance with the goals of the 2030 Agenda for Sustainable Development (*UN*, 2015).

Wastewater treatment plants (WWTPs) are designed to reduce the impact of urban emissions on receiving surface water bodies. However, wastewater (as well as sewage sludge) contains valuable components that can be recovered and used as raw material for biobased products. Despite the most valuable component valorised has been traditionally phosphorous for the production of fertilizer as struvite and chemicals (Egle et al., 2016), more effort has been devoted recently to the recovery of carbon-based materials such as cellulose, lipids and volatile fatty acids to develop new value chains, i.e. biochar, biodiesel and PHA bioplastics respectively (Frkova et al., 2020; Khan et al., 2022; Muniz Sacco et al., 2023).

The production of activated biochar using cellulose recovered from WWTPs represents an opportunity to create a circular resource. An average person was reported to use around 85 rolls of toilet paper (mainly consisting of cellulose) every year which translates to 4 million tons for the 27 European Union countries ending up in the WWTPs (Li et al., 2020). At small WWTPs the separation of cellulose waste from the influent streams is conventionally foreseen within a screen and a sand trap and is usually disposed in the landfill or incinerated. However, cellulose fibers constituting up to 30 % of the influent chemical oxygen demand (COD) of 120 g PE^{-1} d^{-1} (Ruiken et al., 2013) are mainly biodegraded in the secondary treatment of a conventional WWTP with a consequent increase of energy needed to ensure aeration. As an alternative, cellulose fibers could be recovered from the wastewater influent before the secondary treatment by using a fine sieve (Ruiken et al., 2013) and further processed for several purposes, such as biochar production via slow pyrolysis (100–1000 °C with a residence time ranging from minutes to hours) (Zhang et al., 2021). To increase its applicability by improving its general properties (porosity, surface area and reactivity), the resulting biochar can be activated (Vilén et al., 2022) inducing, however, significant environmental impact (Bayer et al., 2005).

The biochar recovered from cellulose has been previously activated with a physical (by using steam) and a chemical activation (by heating the biochar with an acid) (M. N. Khan et al., 2022). However, results showed a lower performance for both activated products if compared to a commercially available activated char when applied to remove micropollutants (MPs) from wastewater effluents. This indicates the need for alternative solutions to properly evaluate the potential of recovered cellulose biochar as a value-added sorbent.

Biological activation of biochar has been recently explored (Venditti et al., 2022a) as a successful and sustainable method to augment Nature-based Solutions (NBS) and boost their performance towards recalcitrant compounds as MPs for water purification purposes. Among NBS, Constructed Wetlands (CWs) proved to be an affordable, resilient and low-cost technology to be applied to small and medium-sized WWTPs in rural settlements. Passive CWs designs demonstrated to enhance their performance towards pollutant degradation when intensified for example with forced aeration or with the addition of admixtures (Nivala et al., 2018; Khan et al., 2023). When used as an admixture (Brunhoferova et al., 2022) in CWs, biologically activated char produced from plant residues was demonstrated to significantly contribute to compliance with legislation limits, e.g. for four selected mandatory compounds defined by the Luxembourgish Water Administration to be removed from municipal wastewater (AGE, 2020). The design of biochar production from cellulose for its local reuse with water or wastewater purification purposes as a circular systemic solution to be applied at regional level would be in line with the Circular City and Regional Initiative (CCRI) (EC, 2022) approach which promotes the development and implementation of circular initiatives within a territory.

This study aims to support all *three sustainability pillars* firstly by evaluating the suitability of biochar produced from recovered cellulose and activated biologically as an admixture in a CW in Vertical subsurface Flow (VF) configuration, which is applied as a post-treatment step for the removal of MPs (*environmental* benefit). Last, by conducting a circular approach assessing the feasibility of producing cellulose biochar in large WWTPs to subsequently use it as a mitigation measure in small WWTPs promoting *social inclusion* and *economic growth* in a territorial circular economy perspective.

Table 1
List of compounds.

Class	Substance	Law[a]	PNEC [µg L^{-1}][b]
P-Pharmaceuticals (13)			
Anti-inflammatories (2)	Diclofenac (CAS 15307-86-5)	L, RUWWTD	0.05
	Ibuprofen (CAS 15687-27-1)		1
Anaesthetics (1)	Lidocaine (CAS 137-58-6)		600
Antibiotics (4)	Ciprofloxacin (CAS 85721-33-1)		0.089
	Clarithromycin (CAS 81103-11-9)	L, RUWWTD	0.12
	N4-acetylsulfamethoxazole (CAS 21312-10-7)		2.38
	Sulfamethoxazole (CAS 723-46-6)		0.6
Beta-Blockers (2)	Atenolol (CAS 29122-68-7)		150
	Metoprolol (CAS 51384-51-1)	L, RUWWTD	8.6
Contrast media (2)	Amidotrizoic acid (CAS 117-96-4)		10,000
	Iomeprol (CAS 78649-41-9)		1,000,000
Lipid regulators (1)	Bezafibrate (CAS 41859-67-0)		2.3
Psychiatric drug (1)	Carbamazepine (CAS 298-46-4)	L, RUWWTD	0.05
H-Herbicides/Pesticides (7)			
	Aminomethylphosphonic acid (AMPA) (CAS 1066-51-9)		1500
	Deet (CAS 134-62-3)		88
	Diuron (CAS 330-54-1)		0.07
	Flufenacet (CAS 142459-58-3)		0.048
	Glyphosate (CAS 1071-83-6)		120
	Isoproturon (CAS 34123-59-6)		0.64
	Terbutryn (886-50-0)		0.065
Others (7)			
Antimycotic	Carbendazim (10605-21-7)		0.44
Corrosion inhibitor (2)	Benzotriazole (95-14-7)	L, RUWWTD	19
	Tolyltriazole (29385-43-1)		8
Flame retardant (1)	Tris(2-chloroisopropyl) phosphate (TCPP) (13674-84-5)		260
Fluorosurfactants (1)	Perfluorooctanesulfonic acid (PFOS) (1763-23-1)		0.002
Stimulants (1)	Caffeine (58-08-2)		87
Sweeteners (1)	Sucralose (56038-13-2)		29.7

[a] Indicator substances present in the Luxembourgish guidelines (L) (AGE, 2020) or in the revised Urban Wastewater Directive (RUWWTD) (EC, 2023).
[b] Supplementary information, Table S.1.

2. Materials and methods

2.1. Selection of the target compounds to be monitored

A total of 27 micropollutants have been chosen on different criteria for several catchments within the Greater Region encompassing the German federal states of Rhineland-Palatinate and Saarland, the Grand Duchy of Luxembourg, regions Wallonia and Lorraine from Belgium and France, respectively. This selection includes contrast media and sucralose, serving as main tracers for pharmaceuticals and domestic wastewater composition, respectively. The target compounds are given in Table 1 along with their CAS number and Predicted No Effect Concentration (PNEC) values.

The list comprises 13 pharmaceuticals spamming across 7 therapeutic classes, known for their highest excretion amounts within the Greater Region (i.e. antibiotics, beta-blockers, anti-inflammatories). Additionally, it comprises 7 herbicides of emerging concern (i.e. glyphosate and its degradation product, AMPA) along with those mandated by legal requirements (i.e. carbendazim, diuron, and isoproturon), a fluorosurfactant and other relevant compounds previously monitored for their occurrence (i.e. benzotriazole and tris(2-chloroisopropyl)phosphate) (Gallé et al., 2019).

2.2. Configuration of mesocosm CW systems

2.2.1. Characteristics of selected municipal wastewater

The wastewater used to operate the systems is a wastewater effluent weekly collected from the local biological WWTP Beringen, commune of Mersch (Luxembourg) with a design capacity of 70,000 PE and treating 11,373 m^3 d^{-1} (average 2022). The WWTP operated from the Syndicat Intercommunal de dépollution des eaux résiduaires de l'Ouest (SIDERO) was considered as an excellent candidate for the scope of this study because of its good effluent water quality resulting in: 12.3 mg L^{-1} COD, 2.9 mg L^{-1} Biological Oxygen Demand (BOD5), 8 mg L^{-1} Total Nitrogen (TN), 22.8 mg L^{-1} nitrate nitrogen (NO3-N), 1.7 mg L^{-1} ammonia nitrogen (NH4-N), 0.6 mg L^{-1} total phosphorous (Ptot) (average 2023). Although it can be classified as a medium-sized WWTP, the sewage treatment plant of Beringen is one of the biggest in Luxembourg.

The conventional activated sludge tank consists of 14,800 m^3 volume, for a total Sludge Retention Time (SRT) of 40 d and a Hydraulic Retention Time (HRT) between 12 and 41 h. The plant also uses a screen, a sand and grease trap preceding the primary clarifier and a digester as well as dewatering facilities.

2.2.2. Characteristics of the admixtures

Two biochar admixtures were produced by low temperature pyrolysis (750 °C) which is more effective to capture non-polar compounds. After carbonization, the biochar's are mixed with minerals (such as phosphate and carbonate salts), bacteria (such as *Lactobacillus*, *Rhodopseudomonas* and *Saccharomyces*) and yeast and left to ferment at a temperature ranging between 25 and 35 °C for four weeks (so called biological activation).

The difference between the two biochar can be described as following:

- EmiSûre-AC: purely produced from plant residues, it has been widely applied in previous studies, compared with more conventional substrates (i.e. zeolite) and tested from laboratory to pilot scale under controlled and real conditions producing reliable results that can be transferred and used as control in the current study (Brunhoferova et al., 2022; Venditti et al., 2022a; Venditti et al., 2022b);
- WOW-AC: produced from recovered cellulose. Rotating belt fine (RBF) sieves are used in the mechanical step of the WWTP to separate and filtrate cellulosic material from the wastewater influent stream. The pressed material is then dried at 60 °C producing a raw cellulose material with 65–70 % dry content. This material is converted into pellets with a diameter of 6 mm and further dried at 120 °C to reach a final 90 % dry content. Preliminary studies (Salmeron et al., 2023) indicated that biochar purely produced from cellulose (100 %) presents the lowest surface and micropore volume. Thus, a mixture with 50 % straw before pelletization has been selected to gain higher surface area measured by CO2 Brunauer-Emmett-Teller (BET) if compared to biochar from pure cellulose (249 and 211 m^2 g^{-1}, respectively).

Table 2
Operational parameters of the wetlands.

	Scenario 1	Scenario 2	Scenario 3
Characteristics	Batch	Batch	Continuous
Cycles	2× Every three days	2× Every three days	3× Every day
Test duration (days)	7	24	78
Hydraulic Loading Rate (HLR)			
Per irrigated surface			
L m^{-2} d^{-1} or mm d^{-1}	92.6	37	23.1
m^3 m^{-2} d^{-1}	0.09	0.04	0.02
L m^{-2} $batch^{-1}$	30.9	12.3	N.A.
Per volume of soil			
L m^{-3} d^{-1}	463	185.2	115.7
L m^{-3} $batch^{-1}$	154	61.7	N.A.
Measured retention volume (%)			
EmiSûre-AC	77.33	6.25	63.33
WOW-AC	81.66	5.83	62
Measured infiltration rate (L/min)			
EmiSûre-AC	0.0026	0.0125	0.00114
WOW-AC	0.0021	0.0125	0.00118

N.A. not applicable.

2.2.3. Experimental set-up

Two CWs in mesocosm scale were built with tanks of 27 cm length, 25 cm width and 30 cm height with 675 cm^2 of surface area and 20.25 l volume (Supporting information, Fig. S.1). The systems were filled, from the bottom to the top, with a 10 cm layer of gravel as drainage (6 cm of coarse 4–8 mm and 4 cm of fine 2–8 mm), and 20 cm of substrate, demonstrated to be the most active part of a VFCW according to previous studies (Pucher and Langergraber, 2019). The units consist on same support matrix structure, a naturally occurring sand (95 % Liapor sand, Germany) containing 55 % SiO_2, 24 % Al_2O_3, 14 % Fe_2O_3 and 5 % CaO, plus 5 % of activated biochar admixtures from different sources as follows: one containing EmiSûre-AC (plant residues) and the other containing WOW-AC (50 % cellulose/50 % straw). The test was designed to evaluate the performance of both admixture types in MPs' removal from a treated wastewater effluent using the same macrophytes, *Phragmites australis* and *Iris pseudacorusm*. The effluent of Beringen WWTP was used as influent to the units, weekly collected, kept cool at 4 °C to avoid degradation and pumped with a high precision two headed pump (Watson Marlow, Belgium). At each loading (in up-down intermittent regime), the wastewater flooded the mesocosms surface and drained by gravity through the depth. LED lamps were installed to provide 8 h of light per day.

2.2.4. Operation and sampling strategies

The mesocosms were operated in:

- Sequencing batch mode

The units were not fed every day but only 2 times per week in agreement to previous studies (Brunsch et al., 2018; Marcelino et al., 2020; Lei et al., 2022). Each watering cycle lasted three days including feeding (day 1) and draining (day 2 and 3). The feeding occurred twice in day 1, for 30 min. Samples were collected after the first and second feeding within 24 h. The applied batch volumes were 6 (SCENARIO 1) or 2.5 L (SCENARIO 2) per day which corresponded to 0.09 and 0.04 $m^3\,m^{-2}\,d^{-1}$ hydraulic load, respectively.

- Continuous mode

The units were fed twice a day for 30 min, every day (SCENARIO 3). Samples were collected weekly in relation to the change of the influent wastewater.

The resulting operation conditions for all 3 scenarios are provided in Table 2.

The Hydraulic Loading Rate (HLR) was selected based on previous studies: in Scenario 1 the HLR is similar to a previous lysimeter installation with EmiSûre-AC (Venditti et al., 2022a).

2.3. Analytical methods

2.3.1. Water quality parameters

Common parameters were routinely monitored. COD, TN, PO4-P, NH4-N and NO3-N were measured with Hach Lange cuvette tests while dissolved Total Carbon (DTC), Total Organic Carbon (DTOC) and Inorganic Carbon (DIC) with a TOC analyzer (Shimadzu, B). Oxidation-reduction potential, pH and conductivity were measured with conventional WTW (Xylem, UK) probes.

2.3.2. Micropollutants

Micropollutants were analysed by Liquid Chromatography coupled to tandem Mass Spectrometry (LC-MS/MS). It consists of an Agilent 1200 SL LC coupled with an Hybrid Quadrupole-Linear Ion Trap instrument (Sciex 4500 QTrap) with electrospray ionization in positive mode operated in Multiple Reaction Monitoring. All samples were pre-concentrated by solid phase extraction before their injection. Glyphosate and AMPA were analysed using chemical derivatization and on-line SPE-LC-MS/MS. The analyses were performed externally (Luxembourg Institute of Science and Technology LIST, Luxembourg) and the methodology has been previously described (Venditti et al., 2022a) (Supporting information, Table S.2).

2.4. Risk assessment

2.4.1. Individual compound risk assessment

The potential environmental risk of each analysed compound was evaluated via the calculation of the risk quotient (RQ) estimated as follows:

$$RQ = \frac{MEC}{PNEC} \qquad (1)$$

where MEC represents the Measured Environmental Concentration and PNEC represents the lowest values obtained from the most sensitive water species analysed in long-term exposure. PNEC values were derived using the NORMAN database or other literature sources (Table 1). The risks can be defined into four degrees according to the RQ values: i) RQ > 1 indicates that the potential ecological risk of the compound is very high, ii) 0.1 < RQ < 1 indicates that the compound could induce a medium potential risk, iii) 0.01 < RQ < 0.1 indicates that the potential risk of the compound is low and finally iv) RQ < 0.01 indicating negligible risk.

2.4.2. Mixture risk assessment

The risk posed by the mixture of 27 compounds is also estimated according to the concentration addition (CA) model (Gosset et al., 2021) which considers that individual chemicals even when detected below their own PNEC, can collectively pose toxic pressure to the ecosystem exceeding together the acceptable threshold limits (Spilsbury et al., 2024).

The overall risk posed by the mixture (RQmix) is calculated as the sum of individual risk quotients for compounds detected in WWTP influent, WWTP effluent, mesocosms with WOW-AC and EmiSûre-AC effluent samples as follows:

$$RQmix = \sum\nolimits_{1=1}^{n} \frac{MEC}{PNEC} \qquad (2)$$

This implies that the overall quotient increases with the number of compounds included. A conservative approach is adopted, and the risk posed to the overall mixture risk by individual compounds potentially present below their Limit of Quantification (LOQ) is considered: non-detected compounds are assumed to be present at their respective LOQ and their contribution to the mixture is calculated accordingly. Risk-driving compounds were identified by ranking the compounds according to their median RQ in each mixture. RQmix was used to estimate the global risk effect reduction when conventional activated sludge technology is applied and the additional benefit with CW as a post-treatment step. A default dilution factor of 10 (EMEA, 2006) is considered when estimating the environmental risk of receiving water from compounds present in effluent samples.

2.5. Implementation of a circular approach in the Blies catchment

Solutions for WOW-AC production (at large WWTPs) and subsequently use in CW as admixture (in small WWTPs) were developed for the Blies catchment area in Saarland (Germany).

2.5.1. Characteristics of the catchment

The Blies river, with a length of 100 km and covering a catchment area of 1960 km^2 (Supporting information, Fig. S.2), delineates the border between France and Germany before emptying into the Saar River in the French city of Sarreguemines. The Oster (30 km length), a tributary of the Blies, receives discharges from 14 WWTPs with capacity ranging from 30 to 4000 PE, for a total number of 17,777 PE. Out of 14 WWTPs, 7 are provided with Conventional Activated Sludge (CAS) process, two employ aerated pond plants and rotated disks, and 5 operate using Sequencing Batch Reactor (SBR).

2.5.2. Design of fine sieve and CW

The fine sieve was tailored to be implemented in large WWTPs accommodating a maximum influent water flow. The fine sieve's performance was considered similar to that of a primary clarifier, with a hydraulic retention time of 1.5–2 h according to (DWA, 2016).

To determine the necessary surface area of a CW (with WOW-AC), the following specifications were considered based on previous findings with EmiSûre-AC: 15 % AC and 85 % substrate composition, specific area of 0.4 $m^2\,PE^{-1}$, hydraulic load per irrigated surface ranging between 200 and 400 L $m^{-2}\,d^{-1}$. The dimensions of length and width were adjusted to fit the available space. A biochar density of 1500 kg m^{-3} was assumed.

2.5.3. Methodology

The Oster sub-catchment was chosen to investigate if i) sufficient cellulose for the production of WOW-AC can be recovered in the catchment ii) the quality criteria of diclofenac in the receiving water can be met by the implementation of CW with WOW-AC as admixture. Previous studies (Schmitt et al., 2019) identified diclofenac as the most relevant compound for the Blies catchment showing concentrations surpassing Environmental Quality Standard (EQS) already with the discharge from WWTP Haupersweiler, located at the outset of the river Oster's course. Consequently, diclofenac was chosen as the control parameter.

Cellulose is assumed to be recovered from fine sieve systems implemented at WWTP lacking primary clarifiers and sludge digestion to prevent depletion in biogas production. Additionally, it is assumed that a pyrolysis facility is located near the Ottweiler WWTP to minimize transportation costs of cellulose and produced WOW-AC. The harvested cellulose is dried and then pyrolyzed alongside straw to produce WOW-biochar. Two variants were investigated (Supporting information, Table S.3):

- Variant 1
  Cellulose recovery via *fine sieve technology* is implemented at three WWTPs for a total capacity of 13,863 PE: WWTP Haupersweiler, WWTP Sinnerthal and WWTP Ottweiler;
  Integration of CW as post-treatment step is applied at three WWTPs for a total capacity of 7783 PE: i) Haupersweiler, chosen for its demonstrated impact on diclofenac emissions, ii) Saal, scheduled for conversion to a CAS system within the next decade iii) Lautenbach, which discharges into a small tributary vulnerable to urban emission;
- Variant 2
  All facilities eligible for post-treatment steps (9 WWTPs with a capacity of 13,863 PE) are considered to optimize micropollutant reduction. Consequently, higher amount of WOW-AC is requested. Cellulose is recovered at five WWTPs with a connected population of 61,436 PE.

3. Results and discussion

3.1. Performance evaluation of the mesocosms systems

3.1.1. Occurrence of MPs in the WWTP of Beringen

Out of 27 compounds examined, 24 and 21 were detected with concentrations above the limit of quantification at the least once in the WWTP influent and effluent samples, respectively (Supporting information, Table S.3). During the conventional biological treatment, a limited number of compounds (caffeine, ibuprofen, DEET, iomeprol and atenolol) were removed with a relative elimination exceeding 80 %, while the majority of the compounds exhibited minimal removal (with a relative elimination below 20 %). This aligns with findings from other studies which report over 90 % elimination for both caffeine and ibuprofen (Stamatis and Konstantinou, 2013).

However, for few compounds a negative elimination was calculated related to higher effluent concentrations compared to influent values. Negative removals can be associated to the sampling methodology when grab sampling does not consider residence time distribution, conjugated/deconjugated reactions, or matrix interference particularly in the quantification of influent because of the higher pollutant load. This phenomenon is observed for sulfamethoxazole, where its metabolite acetyl-sulfamethoxazole undergoes breakdown during the biological treatment process, regenerating the mother compound. Similarly, conjugated forms of glyphosate may cleave into its transformation product AMPA (Aslam et al., 2023; Venditti et al., 2023), resulting in a notable increase in effluent concentration. A zero elimination was assumed for those compounds known to be persistent and hardly removed from the conventional activated sludge treatment (i.e. benzotriazole, carbamazepine, clarithromycin, lidocaine and metoprolol) (Ternes, 1998; Bahlmann et al., 2014; Falås et al., 2016).

Compounds exhibiting relatively high concentrations (exceeding the average value of 0.5 μg L^{-1}) in the effluent samples include sucralose, benzotriazole, AMPA, diclofenac and TCPP. To comply with the guidelines established by the Luxembourgish government (AGE, 2020) for the safe discharge of treated water into receiving bodies, four indicator substances defined as mandatory (carbamazepine, diclofenac, benzotriazole and clarithromycin) need to be eliminated by 80 % on average across the entire treatment process including post-treatment. Therefore, considering these results, upgrading the WWTP with a post-treatment step is necessary.

3.1.2. Performances of cellulose versus plant residue admixtures

To assess the suitability of WOW-AC as CW admixture, the experimental runs were designed with EmiSûre-AC as a benchmark for comparison due to its well-established and demonstrated performances. In particular, two feeding regimes (i.e. sequencing batch and continuous) were selected to test WOW-AC improving the removal of MPs and to get insights for future full-scale design. Results showed that there is not a significant difference between operating CW with short or long resting time (from 12 to 72 h) in terms of MPs elimination. SCENARIO 1 and 2 depict a full elimination already with the first flash occurring after 4 h from the watering cycle (Supporting information, Fig. S.3). Additionally, lower HLR for SCENARIO 2 did not bring benefit to the average removal of MPs (Supporting information, Figs. S.4. and S.5) with the only exception of the beta-blocker atenolol for which higher contact time (proportional to faster infiltration rates and lower retained volume of water, Table 2) seems to lead to higher elimination. Measured retained water and infiltration rate look similar if the same volume of water is applied during the first day of the batch (SCENARIO 1) or distributed along three days (SCENARIO 3), in line with the HLR (30.9 L m^{-2} $batch^{-1}$ and 23.1 L m^{-2} d^{-1}, respectively).

The findings suggest that a higher load can be planned and released during the first day of the flush for the same achieved elimination and that a design similar to the one proposed from (Brunsch et al., 2018) could be adopted.

When looking at the continuous mode operandi (SCENARIO 3) (Fig. 1), the studied mesocosm systems showed an overall elimination higher than 80 % for most analysed MPs, with the only exception of the flame retardant TCPP and the beta blocker atenolol. Our results are comparable to previous studies where CWs have shown low capacity to remove chemical substances with slow or non-biological degradability as TCPP (Liu et al., 2022; Tondera et al., 2019) and for which degradation pathways rather involve carboxylation, hydroxylation and dichlorination processes. Atenolol removal has been observed variable depending on CW configuration and type of substrate, particularly enhanced by soil organic matter due to electrostatic interactions.

The WOW-AC based system showed elimination values similar to those achieved with the application of EmiSûre-AC (average of 91.5 and 89.1 % when 15 relevant compounds are considered). This indicates that that biological activation significantly enhances the value of the produced biochar compared to physical or chemical activation methods. Consequently, it produces a high value-added sorbent that is suitable as admixture in CW applied for MPs removal from municipal wastewater

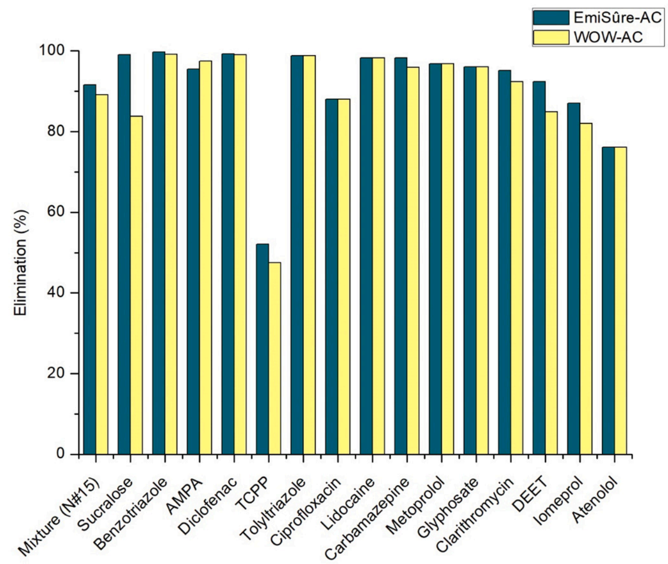

Fig. 1. Average elimination values of 15 MPs by plant and cellulose residues-based admixture (EmiSûre-AC and WOW-AC, respectively), from the most to the less abundant in the WWTP effluent, left to right.

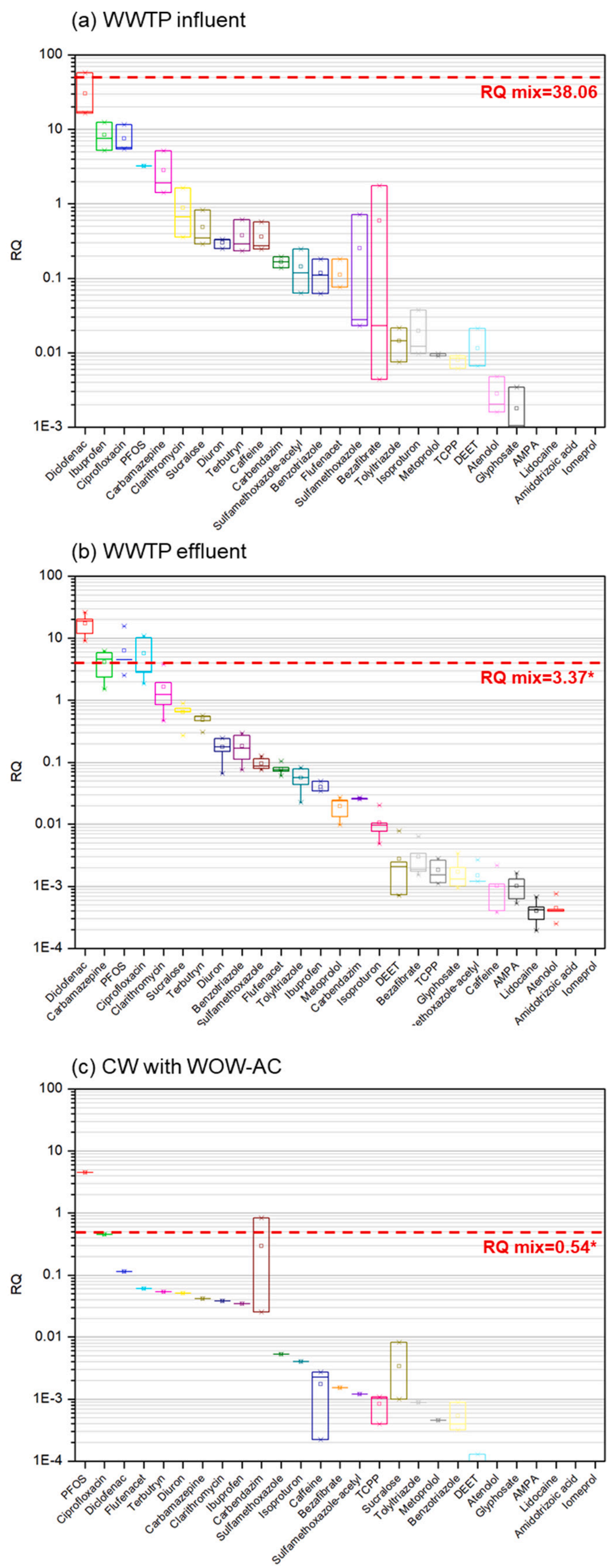

Fig. 2. Risk driving compounds ranked by median RQ (from highest to lowest value, left to right) in the (a) WWTP influent, (b) WWTP effluent and (c) WWTP effluent treated using a CW with WOW-AC as admixture.

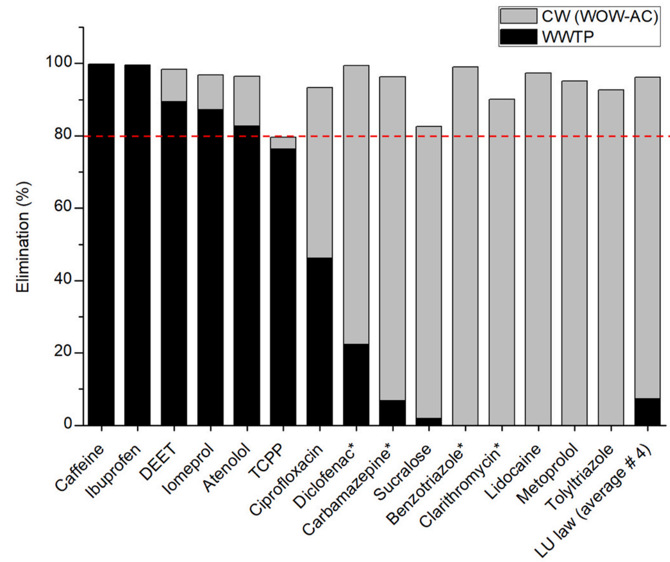

Fig. 3. Relative contributions of the CW with WOW-AC and the conventional WWTP to the overall global average removal efficiencies (from highest to lowest WWTP elimination value, left to right).

effluents.

3.1.3. Risk reduction

Diclofenac, ibuprofen, ciprofloxacin, PFOS and carbamazepine had median RQs of 17.2, 7.5, 5.6, 3.2 and 1.8 respectively demonstrating to be the risk drivers in the influent samples and contributing to its overall mixture risk by 93 % (RQmix influent = 38.06) (Fig. 2 a). Activated sludge technology at Beringen WWTP reduced the median risk of the mixture down to RQmix effluent 33.7. If a default dilution factor of 10 is applied, the environmental risk for receiving waters from the cocktail of 27 compounds is reduced to 3.37 indicating the need of a post-treatment as risk mitigation measure. The prominent risk compounds in the Beringen WWTP resulted to be diclofenac, carbamazepine, PFOS, ciprofloxacin and clarithromycin (posing all a very high risk with RQ > 1) (Fig. 2 b) in line with literature data (Spilsbury et al., 2024).

The use of CW with cellulose derived admixture showed that most compounds were reduced to below detection limit and that the technology with WOW-AC reduces the risk from compounds cocktail below maximum acceptable level. These results are encouraging and strongly support the use of WOW-AC as admixture in conventional CW's substrate. However, the risk assessment is based on uncertain PNEC values from several literature sources which may lead to different conclusions when the approach is used to trigger decisions if a technology should be applied or not. Moreover, PNEC values of transformation products detected in effluent are mostly not ecotoxicologically tested and thus cannot be considered in cumulative risk assessment. Nonetheless, this approach gives a magnitude order about the impact of CW with WOW-AC as admixture on the environmental protection.

3.1.4. Policy implementation

When the removal contributions of the two treatments steps (conventional WWTP and additional CW with plant or cellulose residue-based admixtures, Fig. S6 of Supporting information and Fig. 3 respectively) to the overall elimination of the selected compounds is plotted, the CW resulted to be:

- a non-significant contributor in the elimination of those compounds highly degraded from the WWTP (i.e. caffeine, ibuprofen, DEET etc.);
- a strong contributor in the elimination of antibiotics (i.e. clarithromycin and ciprofloxacin);

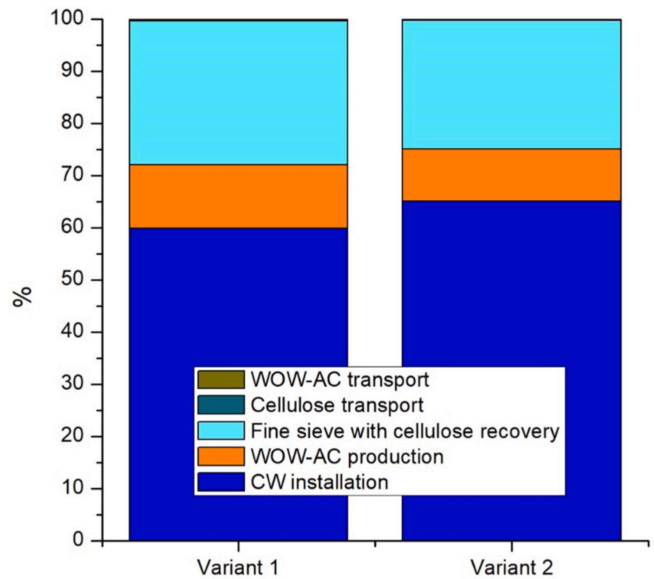

Fig. 4. Capex of the installation of cellulose recovery and constructed wetlands with WOW biochar for Variant 1 and Variant 2.

- the dominant treatment in the elimination of those compounds that are known to be persistent and hardly removed in conventional activated sludge treatment such as lidocaine, carbamazepine.

Since there are not significant differences between EmiSûre-AC and WOW-AC performances, it is possible to affirm that the use of CW with WOW-AC as an admixture in a CW allows to comply with the 80 % removal threshold for the four mandatory compounds (AGE, 2020). The goal of 80 % elimination for defined compounds is also integrated into the proposal for the revised UWWTD.

3.2. *Circular approach in the Blies catchment*

Results showed that with a specific cellulose load of 32 g PE^{-1} d^{-1}, an equal amount of straw and an 80 % loss during pyrolysis, up to 1,08 and 1,98 million kg of WOW-AC can be produced for Variant 1 and Variant 2, respectively. A period of about eight years is required to produce sufficient WOW-biochar from wastewater for both variants. The integration of a fine sieve can additionally lead to a beneficial reduction in the inlet COD load to the biological stage, resulting in a subsequent 20 % decrease in the demand for aeration.

When the produced WOW-AC is applied as admixture in CW installed as post-treatment step, the required surface area is estimated to be 7400 m^2 and 13,545 m^2 for Variant 1 and Variant 2, respectively. However, this estimation assumes a reduction in infiltration water to 20 % prior to CW installation.

Upon conducting a technical design of the additional treatment steps a total Capital expenditure (Capex), (Table S6, Supporting information), which includes installation of cellulose recovery, production of WOW-AC involving pyrolysis, installation of CW and transportation costs, of 8.8 and 19.8 million € for Variant 1 and Variant 2, respectively was calculated.

The main cost blocks are related to the production of the biochar and to the construction of the CWs (Fig. 4). However, these costs can be reduced if higher HLR are achieved in practical operation.

When utilizing diclofenac concentration as quality criterion and assuming a conservative elimination rate of 80 % in CWs, the impact of the two mitigation strategies on the river can be evaluated.

Through the construction of three CWs (Variant 1), the EQS for diclofenac can be nearly met along the entirety of the Oster River's flow path (Fig. 5). Alternatively, by installing CWs at all small WWTPs, diclofenac concentration decreases below the EQS (Variant 2).

Implementing a circularity approach at territory level demonstrates that integrating cellulose recovery with fine sieves to provide WOW Biochar for CWs for MP removal in a river catchment is feasible. Despite the modest reduction in MP-load from small WWTP in comparison to the overall load from all WWTP in the catchment, the impact on the river quality is significant, particularly for small, sensitive waterbodies in rural areas.

4. Conclusions

On the basis of the data set collected the following conclusions are drawn:

- the biological activation of biochar by fermentation produced from recovered cellulose demonstrated to be a valid alternative to conventional physical and chemical activation processes and allowed to fully exploit its potential as a value-added sorbent;
- WOW-AC proved to be an excellent admixture in CW to increase the elimination of MPs when applied as post-treatment step in small catchments. This demonstrated its viability as alternative to more conventional admixture;
- post-treatment CW with WOW-AC as admixture is an effective measure to reduce the risk to the environment from the cocktail of compounds to safe level (RQmix<1). Diclofenac, carbamazepine, PFOS, ciprofloxacin and clarithromycin have been identified as the main risk drivers;

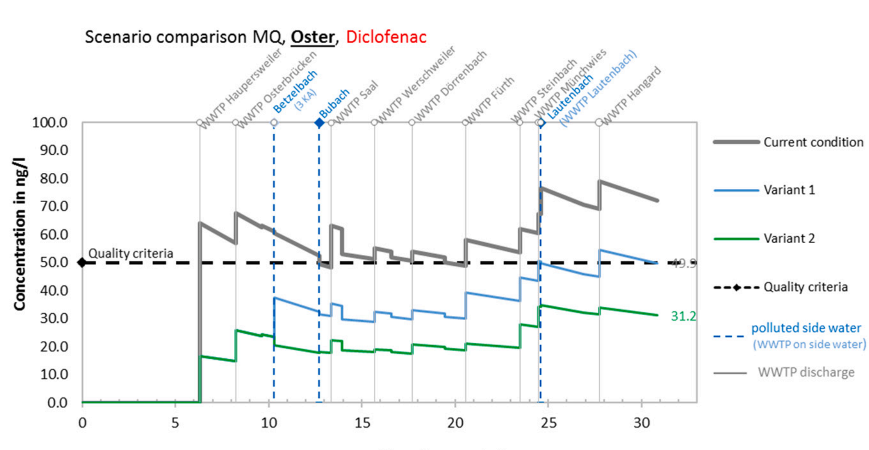

Fig. 5. Diclofenac concentration of the river Oster for the current conditions and for Variant 1 and 2.

- >80 % removal has been achieved for the most recalcitrant compounds (i.e. carbamazepine and diclofenac) complying with the target imposed by national legislation and in line with the revised UWWTD;
- cellulose recovery with fine sieve (from large WWTPs) and the subsequent application of produced biochar for micropollutant mitigation (to small WWTPs) in the same catchment is feasible (circular approach) and the modelled impact on the water body quality is high. This creates an ideal closing loop where the former waste material `cellulose` is locally recovered and valorised, allowing the geographical cohesion and providing solution to environmental issues all at once;
- in future studies an optimization of the maximum achievable hydraulic load shall be evaluated. The impact of recovering cellulose from wastewater influent to the management of activated sludge for further dewatering and biogas potential should be better understood. Finally costs and GHG emissions related to the produced biochar should be included in the economic assessment.

CRediT authorship contribution statement

Silvia Venditti: Writing – original draft, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization. **Irene Salmeron:** Writing – review & editing, Visualization, Methodology, Data curation, Conceptualization. **Paula Nunez Tafalla:** Writing – review & editing, Visualization, Methodology, Data curation, Conceptualization. **Inka Hobus:** Writing – review & editing, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Gerd Kolisch:** Writing – review & editing, Visualization, Methodology, Formal analysis, Data curation, Conceptualization. **Joachim Hansen:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.172055.

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