Interreg North-West Europe
WOW!
European Regional Development Fund

Report on the characterization of biochar obtained from recovered cellulose and evaluation of its potential for water purification.

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NAME: Technical report on lab-scale experiments with non-activated and activated Biochar (WOW-AC) including determination of physical-chemical characteristics and MP-elimination capacity

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SUBJECT: Lab-scale results of WOW!-AC

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1. Introduction

1.1. Context

Sewage contains valuable substances that can be used as raw materials for biobased products. However, to date this potential has hardly been exploited to its full potential in North-West Europe. This results in loss of valuable materials, CO_2-emmissions and less efficient use of natural resources. The Interreg North-West Europe project WOW! - Wider business Opportunities for raw materials from Wastewater (sewage) - aims to develop three value chains for the recovery of carbon-based elements from sewage (see figure 1):

1. **The production of biodiesel**. The sewage inflow is used to cultivate *Microthrix p.* which can accumulate lipids. The lipids are extracted, processed and transformed to biodiesel.
2. **The production of bio-oil, biochar and acetic acid**. The screening material which mainly consists of cellulose material (toilet paper) is dewatered and dried. In a thermal degradation process (pyrolysis) the dried cellulose material is converted into biochar, bio-oil and acetic acid.
3. **The production of PHA (bioplastic)**. For this the primary sludge is used. In a biological process, PHA is enriched and extracted. Then the PHA is compounded and processed to an end product.

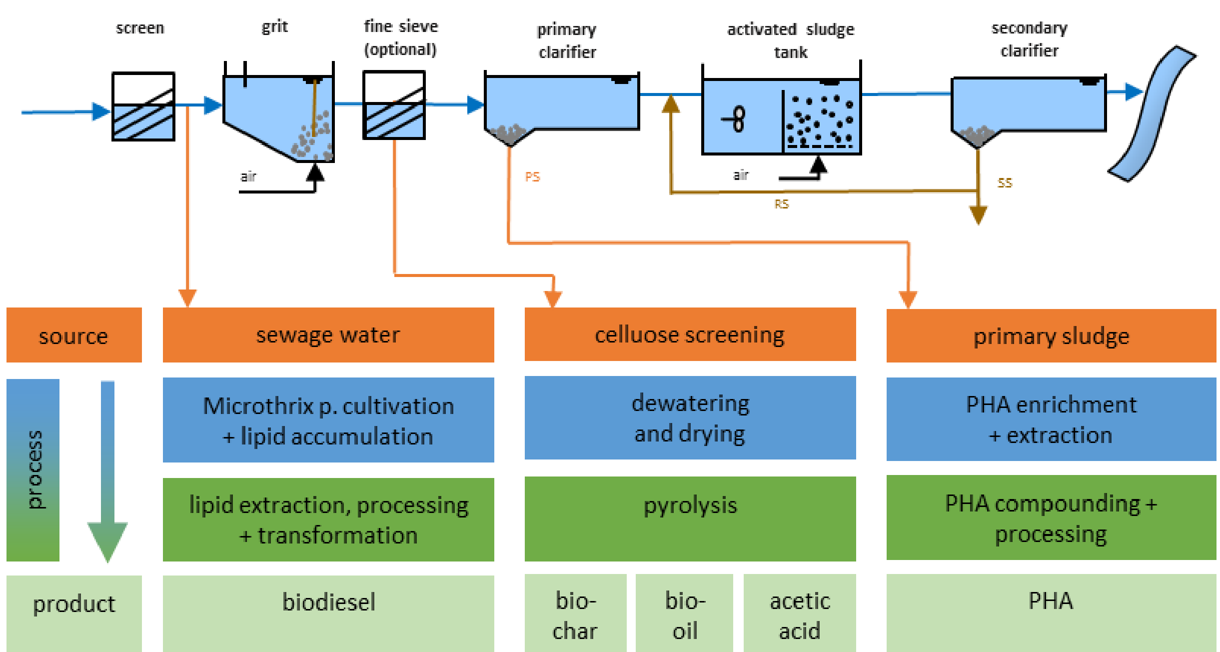


Figure 1. Recovery of carbon-based elements from sewage in WoW!

One of the main activities of the project was to demonstrate the technical feasibility of these three value chains in three pilots with a focus on optimisation of the different recovery and upcycling techniques and tailoring the products to market needs.

1.2. Biochar potential

Biochar is defined by the International Biochar Initiative (IBI, 2015) as the solid material obtained from the thermochemical conversion of biomass in an oxygen-limited environment. This material is considered to have multiple applications environmentally advantageous:

- It is consider a Greenhouse emissions controller by the sequestration of the CO_2 captured by the vegetable biomass source used to produce it (Garcia et al., 2022).
- It has several applications in agriculture as soil amendment, peat substitute or additive.
- A huge number of articles reported its high capability as sorbent applied in water and soil decontamination, being able to remove organic pollutant, dyes and even heavy metals (Mohan et al., 2014).

Considering their possibilities, the biochar produced from the recovered cellulose aims to be used as substrate for Constructed Wetlands. This technology is a nature-based water treatment in which the synergy of multiple mechanisms acts simultaneously for the removal of pollutants (Venditti et al., 2022). The processes involved in constructed wetlands are the phytoremediation using specific species, biological degradation by micro-organisms growing in the soil associated with plant roots and, the main one, the adsorption on a specific substrate which commonly is a mix of sand and biochar.

In this context and as first step to assess its suitability as adsorbent for water depuration purposes, this report focusses on the production and characterization of activated biochar from recovered cellulose as well as the analysis of their pollutant's removal capacity.

1.3. Biochar production

Cellulose was recovered and dried by CirTec B.V. (Figure 2a and b) at the wastewater treatment plant (WWTP) of Ede (The Netherlands) (Khan et al., 2022), obtain as raw material the cellulose pellets shown in Figure 2c.

a) b) c)

Figure 2. a) Recovered cellulose from toilet paper, b) detail of the raw cellulose c) dried pellets

These first pellets were sent to Klimafarmer® (Germany) for their carbonization. It was noticed that the raw cellulose pellets were inhomogeneous and partly mouldy/wet thus the cellulose was reprocessed obtaining homogeneous pellets of 8 mm suitable for their further carbonization (Figure 3a). Klimafarmer® has a great knowledge about the production and applications of this kind of substrates thus to guarantee that the material would be suitable for a subsequential biological activation, it was proposed to mix the cellulose with other 2 materials commonly used to produce biochar, straw and wood chips (Figure 3 b and c).

a) b) c)

Figure 3. Pellets of a) 100% cellulose, b) 50% cellulose-50% straw c) 50% cellulose-50% wood

Together with the carbon source, the pyrolysis temperature is the factor that will determine the absorption capacity of the material. Biochar produced at 400 °C are more effective on the capture of polar compounds, that are adsorbed by H bonding between the compounds and the O containing moieties of the biochar (Sun et al., 2011). Biochar produced at higher temperature have a higher surface area and a well-developed micropore structure being more effective for organic pollutants removal. In fact, high aromaticity and low polarity of the biochas produced at 700 °C allows non-polar compounds to access hydrophobic sites on biochar surfaces in the absence of H bonding between water and O containing (Ahmad et al., 2014)

Bearing in mind that the produced biochar will be used for organic compounds removal, the three different kinds of pellets were carbonized at 750°C for 210 minutes, obtaining the biochar below (Figure 4).

a) **b)** **c)**

Figure 4. Biochar after pellets carbonization. a) 100% cellulose, b) 50% cellulose-50% straw c) 50% cellulose-50% wood

After this, the three materials are activated via an anaerobic fermentation. The biochars obtained in the previous step are mixed with minerals, a nutrient substrate and microorganisms, as bacteria and yeast. These substrates are fermented between 25 and 35 °C for a time period of 2 - 4 weeks. The biologically activated biochar is then ready to use. (Figure 5).

a) **b)** **c)**

Figure 5. Biologically activated biochar pellets. a) 100% cellulose, b) 50% cellulose-50% straw c) 50% cellulose-50% wood

2. Materials and methods

2.1. Physical characterization

The characterization of the material was performed by 3P INSTRUMENTS (Germany). Density was measured by Helium pycnometry following DIN 66137-2. For that, pellets were dried at 105°C during 16h and, after reach room temperature in a desiccator, they were measured with a 3P densi instrument. Brunauer–Emmett–Teller (BET) surface area and micropore analysis are usually performed with N_2 at 77K, however the 3 biochar types showed kinetics inhibitions. To prevent this problem, analysis were performed with CO_2 at 273 K, applying for the micropore analysis the Monte-Carlo Software. The disadvantage of using CO_2 is that the impossibility to measure pores with a diameter higher than 1.5 nm.

2.2. Adsorption test

2.2.1. Biochar fractions

As said in the previous section, 3 different types of non-activated and activated biochar were tested regarding their composition: 100% cellulose, 50% cellulose-50% straw and 50% cellulose-50% wood. It is known that, for a sphere, the ratio between volume and surface is 3:1 meaning that the volume grows 3 times faster than its surface. As adsorption is a surface phenomenon, to compare the different biochar properly it is necessary to have similar particle size. The pellets of the 3 biochar were crushed and sieved obtaining 3 fractions of each: pellets of 8 mm diameter, grains between 100 and 500 µm and powder below 100 µm (Figure 6).

a) **b)** **c)**

Figure 6. Different particles sizes tested. a) Pellets, b) 100 - 500µm c) Powder <100µm

Biologically activated biochars had a humidity content after fermentation of the 20 %, thus before their fractionation they were dried at 106°C during 16h.

2.2.2. Batch mode test

This are one of the most common tests used to measure adsorption equilibrium and kinetics from solutions. Setup consists of reservoirs contained a contaminated solution and biochar disposed on a shaking table (Figure 7), which are stirring till reach the breakthrough. The main disadvantage is that it needs a long time to define the adsorption curve, in the range of weeks or months.

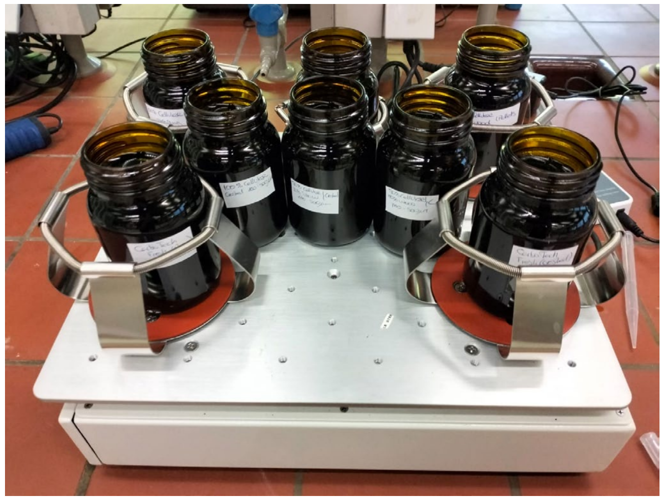


Figure 7. Setup of batch experiments

With this system, the removal of a dye (indigo carmine) and micropollutants (Benzotriazole, Carbamazepine, Clarithromycin, DEET and Diclofenac) was studied. The conditions for each are in the table below (Table 1):

Table 1. Experimental conditions applied according to the target contaminant in batch experiments

	Dye	**Micropollutants**
Concentration	5 mg/L	1-2µg/L each
Water matrix	Ultrapure water	Ultrapure water
Adsorbent	1g/L	1g/L
Particle size tested	Pellets and 100-500 µm	100-500 µm

Note: Not possible to do the test with powder due to the interference of the suspended particles in the measurements.

2.2.3. Continuous mode test with Rapid Small-Scale Columns

Rapid small-scale columns (RSSC) (Figure 8) reproduce big scale systems but with a very small bed volume. The equipment used in this study was designed according to previous studies (Zietzschmann et al., 2014) and constructed by HiTec Zang (Germany). It allows to reach the breakthrough in 1-2 days of operation.

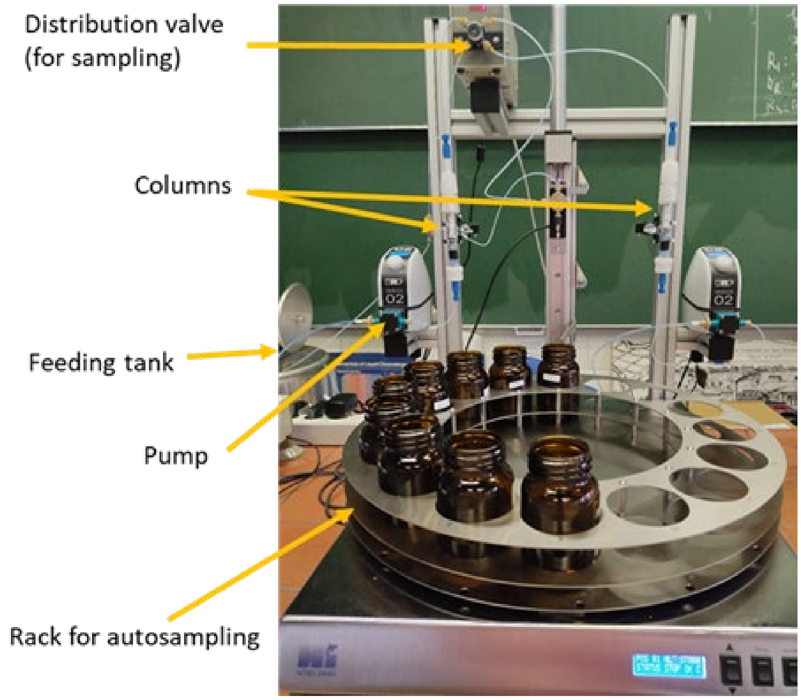


Figure 8. RSSC installed at University of Luxembourg facilities

The removal of both, dye and micropollutants, was studied with this setup according to the conditions described in Table 2:

Table 2. Experimental conditions applied for each the target contaminant in continuous mode experiments

	Dye	**Micropollutants**
Concentration	5 mg/L	1-2µg/L each
Water matrix	Ultrapure water	Real WWTP effluent
Adsorbent	400 mg	1900 mg
Height	1 cm	5.1-5.3 cm
Bed Volume	0.8 mL	4mL
Particle size tested	100-500 µm and powder	100-500 µm

Note: Not possible to do the test with pellets. Due to the column internal diameter, it is necessary a small particle size.

The performance of the columns is the opposite of the batch system. In the reservoirs we have a certain concentration of pollutants that are in contact with the biochar, being absorbed over time thus decreasing the amount of pollutant in the solution. On the opposite, the columns contain biochar through which a solution with pollutants is continuously passed. Initially all the pollutants will be absorbed by the biochar, but as the column is fed, biochar will become saturated and a residual concentration will appear, increasing over time until it is completely saturated and the pollutants are not removed.

2.3. Biological activity

Biologically activated version of the biochars contained microorganisms which, potentially, can play an important role in the removal of the pollutants. As there is no established protocol to analyse such activity, to identify their influence, three different tests were performed applying in each case a different method to obtain the micro-organisms:

- By vortex agitation of the pellets following Piai et al., 2020.
- Via de preparation of a microorganisms stock solution (Figure 9): Fresh liquid cultures were prepared and mixed with each kind of biologically activated biochar, being incubated during 24 h at 37 ◦C Bacterial suspensions were harvested by centrifugation at 3000 rpm for 10 min. Then, the pellet containing microorganisms were resuspended in Phosphate Buffer Saline (PBS) solution and added directly into the polluted water.
- Direct use of the humid pellets of biologically activated biochar, without drying (adsorption + biological activity)

a) **b)** **c)** **d)**

Figure 9. Steps for inoculum preparation. a) Culture medium, b) Bacterial suspension after incubation c) Pellet of microorganisms after centrifugation d) Resuspension in PBS

The removal the dye (5 mg/L) and micropollutants (1-2 µg/L each) were studied in batch mode in 1L of simulated WWTP effluent with constant temperature (25 °C) and agitation. The simulated WWTP effluent had the following composition: 96 mg/L of $NaHCO_3$, 51 mg/L of $CaCl_2{\cdot}H_2O$, 60 mg/L of $MgSO_4$, 4 mg/L KCl 1.8 mg/L of Beef Extract, 2.7 mg/L of Peptone, 23.6 mg/L of $(NH_4)SO_4$ and 7 mg/L of K_2HPO_4 . Adapted from (Maniakova et al., 2021).

3. Results

3.1. Biochar characterization

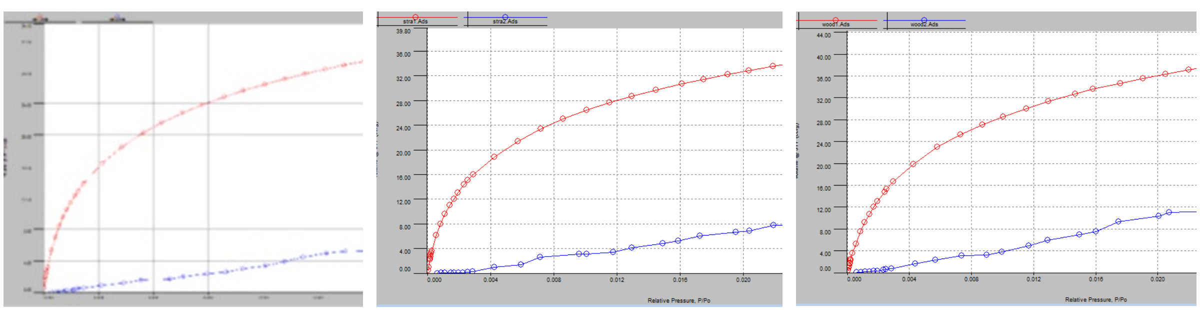
Results obtained from the physical analysis performed by 3P instrument are summarized in Table 3.

Table 3. Main physical parameters of the pellets of the different non activated biochar

	100% cellulose	50% cellulose-50% straw	50% cellulose-50% wood
Helium-Density (g/cm^3)	2.072	2.004	1.958
CO_2 BET surface area (m^2/g)	211	249	280
Monte-Carlo micropore surface area (m^2/g)	298	345	388
Monte-Carlo micropore volume (cm^3/g)	0.082	0.094	0.111

Biochar consisting of 100% cellulose presented the lowest surface and micropore volume thus the mixture with straw and wood would entail an enhancement having more surface area available to interact with the organic compounds present in the water to be treated.

However, after biological activation, biochars reported a huge change in their structure. BET and micropore analysis were not possible to calculate since the isotherms were not stable. Moreover, their values were always lower than the non-activated ones so the adsorption capacity is significantly reduced.



a) **b)** **c)**

Figure 10. Isotherms of the BET analysis with CO_2 at 273K, non-activated (red) vs biologically activated biochar (blue). a) 100% cellulose, b) 50% cellulose-50% straw c) 50% cellulose-50% wood

3.2. Pollutants adsorption

3.2.1. Batch mode

The adsorption of the dye -indigo carmine- for each non activated and biologically activated biochar is presented in Figure 11 for the pellets (a and b) and the fraction between 100-500 µm (c and d). Considering the CO_2 BET surface area of **non-activated materials**, it could be expected that the biochar 50% cellulose-50% wood presented more adsorption capacity due to its higher surface. However, this material had the lowest one with a significant difference regarding the other biochars, reaching higher removal with the mixture 50% cellulose-50% straw presenting just a slight difference with 100% cellulose (lower than 10%).

Biologically activated materials revealed a very low dye absorption capacity. Mixtures with straw and wood show the same trend, and pure cellulose is clearly the best option with a limited removal of the 20% in pellets format and less than 40% in the fraction between 100 and 500 µm. Therefore, this confirms what was previously detected in their physical characterization, that the activation via fermentation does not produce an increase in surface area or improvement in its adsorbent capacity.

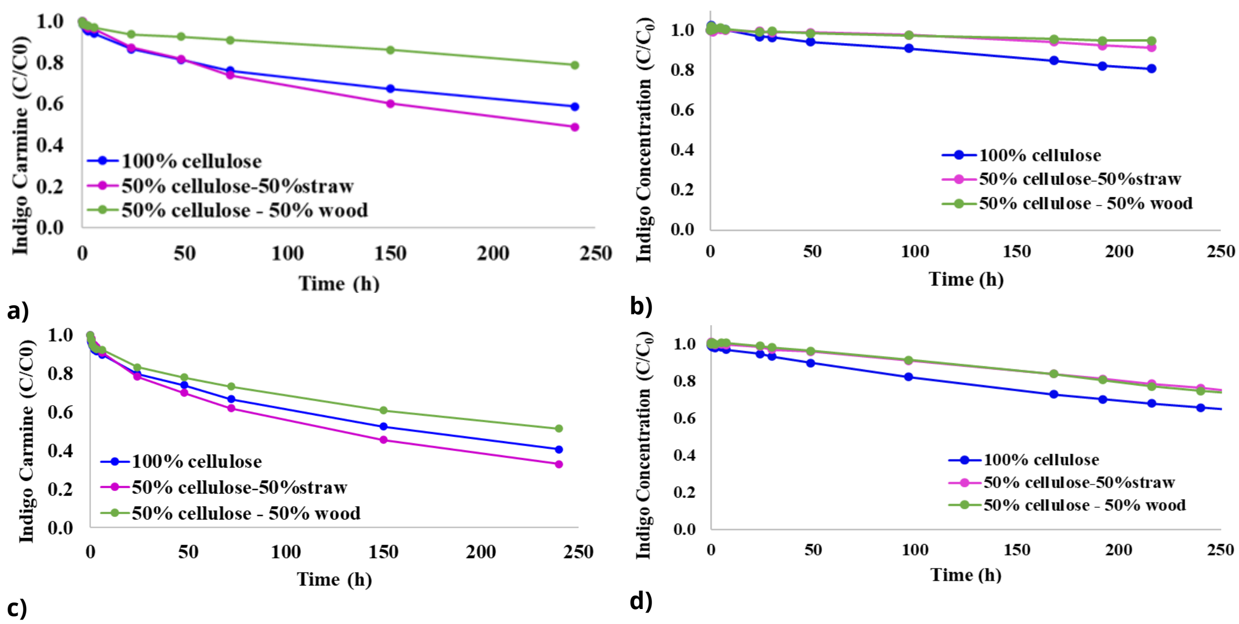


Figure 11. Removal of the dye with the 3 biochar in batch test, being a) non activated pellets b) biologically activated pellets, c) non activated fraction between 100-500 µm and d) biologically activated fraction between 100-500 µm

Results obtained from micropollutants removal (Figure 12) evidenced the same behavior than the dye. 50% cellulose-50% wood had the lowest adsorption capacity for all the compounds and 100% cellulose and 50% cellulose-50% straw presented quite similar profiles.

The most remarkable finding was the low DEET removal capacity of the 50% cellulose-50% wood biochar, being in the best case the 50% while the others biochar got a 75%.

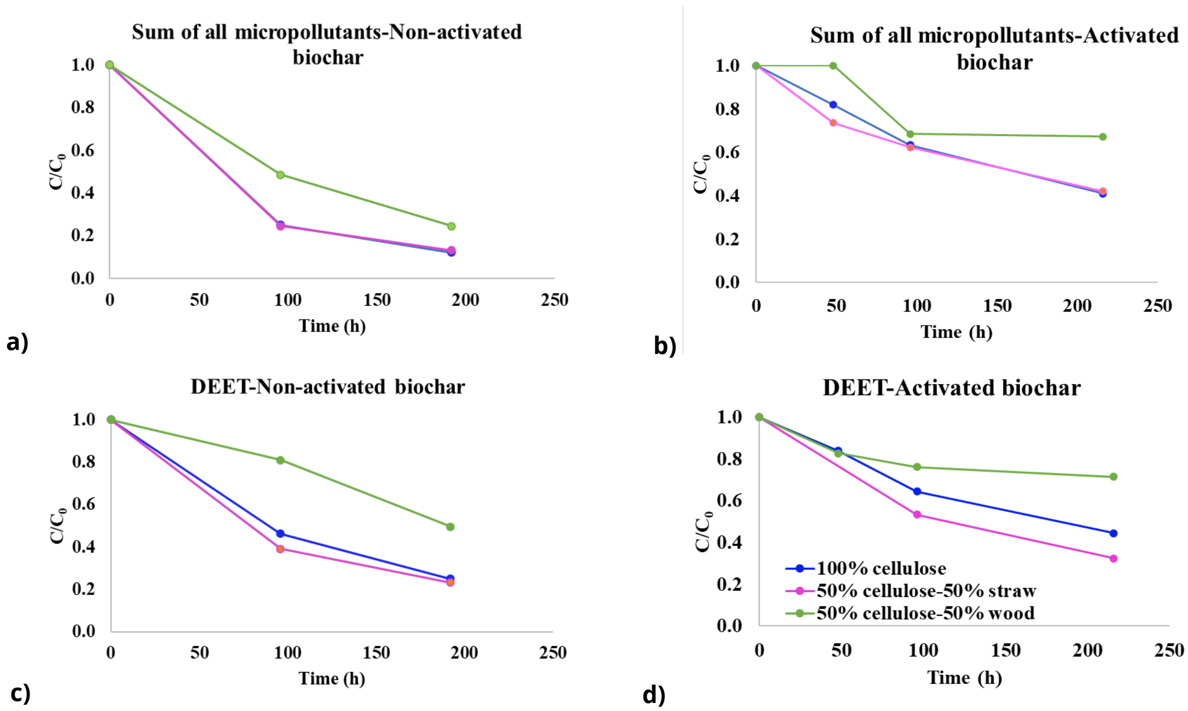
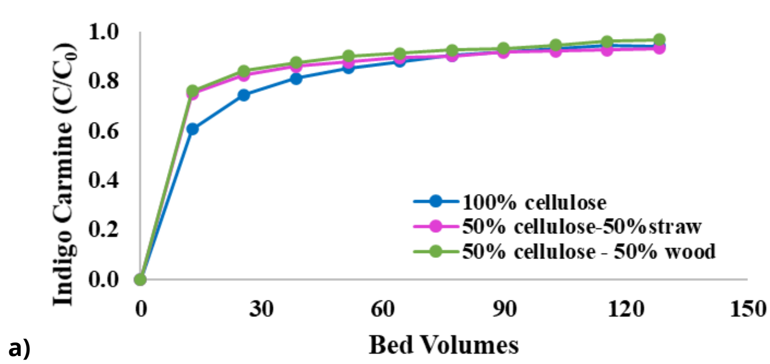


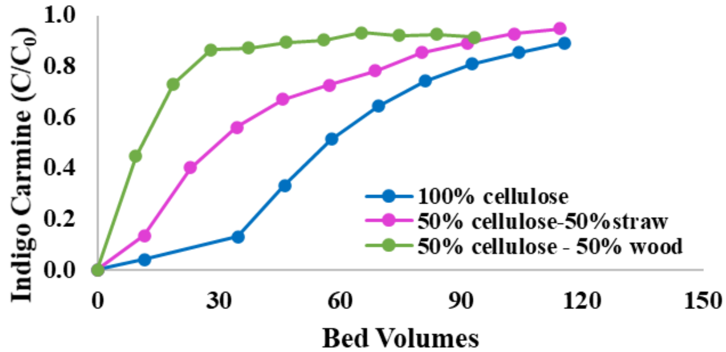
Figure 12. Micropollutants removal with the fraction between 100 – 500 µm of the different mix of activated and non-activated biochar

3.2.2. Continuous mode

On the columns, the absorption of the dye was studied in the lowest particle sizes. In Figure 10a is shown the trends obtained with the 100-500 µm fraction, getting almost the same profiles for all biochar. 100% cellulose showed higher absorption capacity at the first stages of the process but reaches the same saturation as the rest after only 40 BV.

Differences are considerably greater with powdered biochar (Figure 10b), and 100% cellulose demonstrated a much higher dye absorption capacity with the lowest release of dye in the treated solution for almost 120 BV.





b)

Figure 13. Removal of the dye in the RRSC a)100-500 µm and b)powder

For the analysis of micropollutants (Figure 14), data evaluation is not conclusive because of the high analytical error (low volume of sample for solid phase extraction + uncertainties of the method) but are crucial to establish and calibrate the tests to be done in the future with the biologically activated biochar.

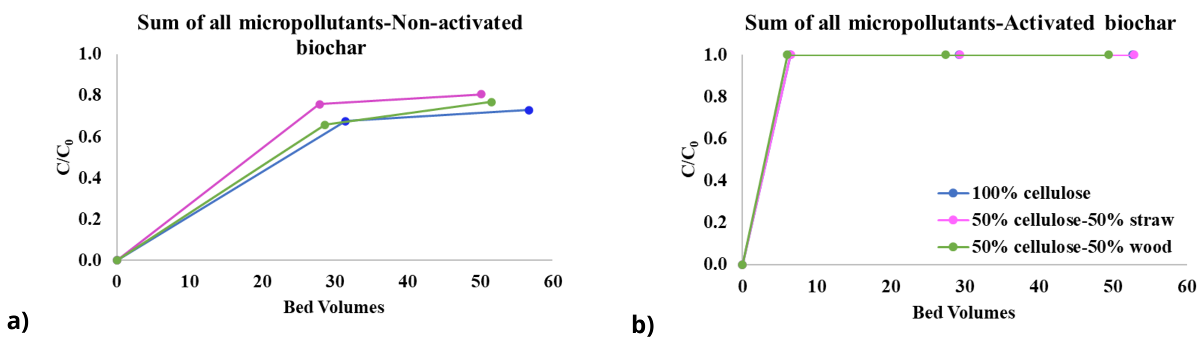


Figure 14. Micropollutants removal in RSSC with real wastewater as matrix in the biochar fraction of 100-500 µm

3.3 Removal by microorganisms

During the fermentation of the biochar, micro-organisms not only produce changes in the physical structure of the biochar, but also part of these micro-organism communities grow using the material as a support. Therefore, it is not correct to consider only the capacity to adsorb pollutants, but also the ability to remove them via the biological processes. First, the removal of the dye by microorganisms was studied, by differentiating the three procedures described in Section 2.3 (Figure 15).

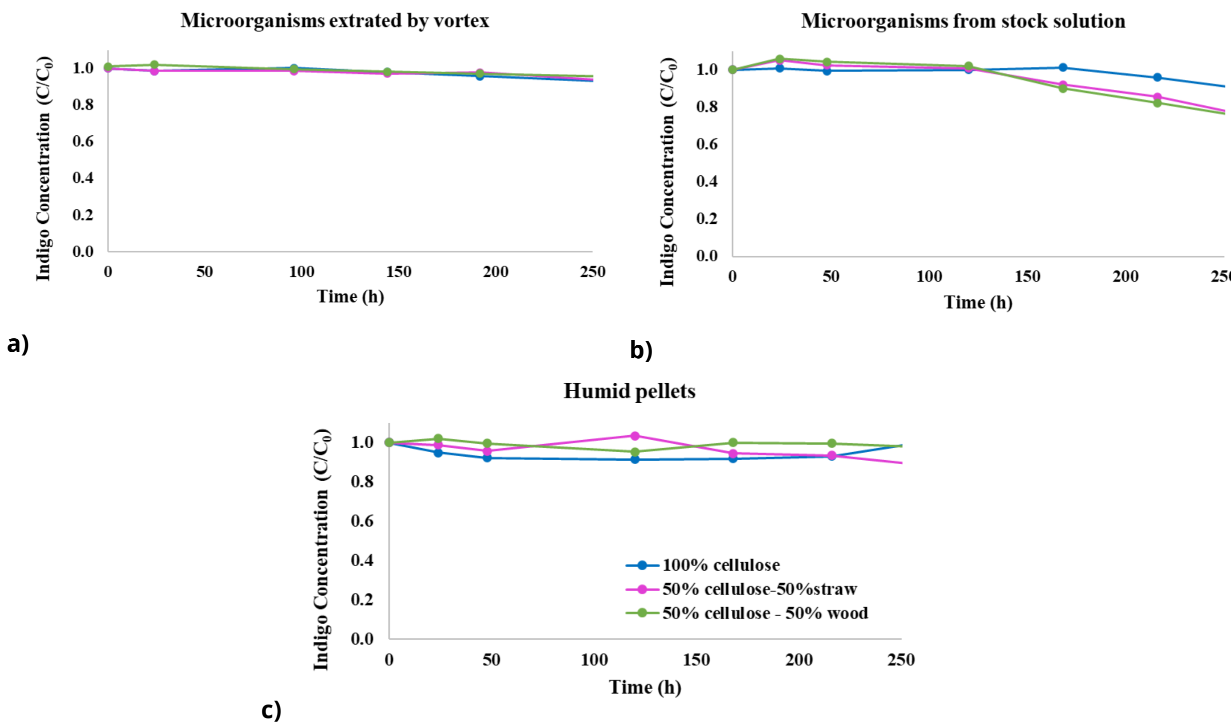


Figure 15. Dye removal by microorganisms in batch mode with simulated WWTP effluent as matrix.

When extracting the microorganisms in the pellets via vortex and applying humid pellets without pretreatment, results did not show any removal of the dye or a significant difference in the efficiency in between materials. The concentration of the microorganisms under both methods would be the same and, probably, low. In fact, with humid pellets some adsorption phenomena could be expected, however the removal was lower than in the previous adsorption test developed with dry materials presented in section 3.2.1. Only by increasing microorganisms concentration via incubation (Figure 15b) the removal efficiency could be evaluated. At the end of the experience, mixes with straw and wood reached a dye removal 15% higher than the 100% cellulose.

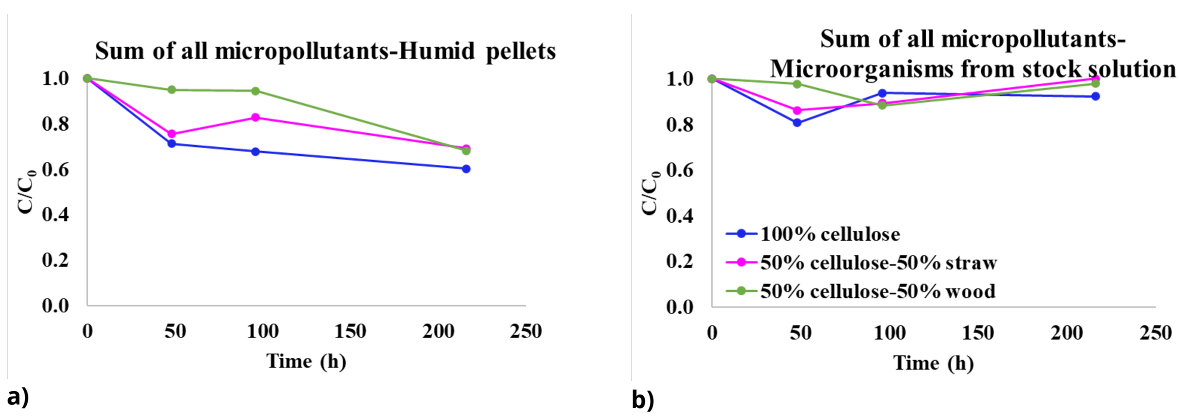


Figure 16. Micropollutants removal by microorganisms in batch mode with simulated WWTP effluent as matrix.

As the extraction via vortex was not successful in the previous test, for the evaluation of micropollutants removal this procedure was discarded. In contrast to the results obtained with the dye, incubated microorganisms were not able to remove any micropollutants (Figure 16b), probably due to their toxic and non-biodegradable character which hinders any biological degradation. The humid pellets (Figure 16a) of 50% cellulose-50% wood reported the slower removal rate, mostly at the beginning of the process, while 100% cellulose and 50% cellulose-50% straw had similar trends. This fact is consistent with results obtained in absorption test, thus any of this two are suitable options to be implemented in constructed wetlands.

4. Conclusions

After the first evaluation of the different biochar produced from cellulose before and after their biological activation, the following conclusions have been identified:

- Despite the characterisation of the 50% cellulose-50% wood mixture indicating that it exhibited the highest adsorption potential due to its larger surface area, batch and continuous experiments evidenced the opposite, being the material that removed the lowest amount of contaminants - dye and micropollutants - from the solution.
- The 100% cellulose biochar demonstrates the same absorption capacity as the straw mixture, even though it has a smaller surface area. In fact, its powder fraction shows much higher absorption capacity than the rest of the materials.
- Biological activation modifies the physical properties of the material but does not increase the adsorption capacity.
- A proper assessment of the microbiological activity after biological activation via fermentation is necessary to take an adequate decision concerning their suitability for water depuration.
- Biodegradable contaminants, as dyes, are well removed by microorganisms coming from material fermentation, while recalcitrant and non-biodegradable micropollutants need the combination of adsorption and biological degradation for their purification.
- Globally, after the full characterization, 100% cellulose and the mixture 50% cellulose-50% straw reported similar behavior. To guarantee the efficiency of the biologically activated biochar in a real scenario, minimizing risks while increasing the circularity of the material, the the mixture 50% cellulose-50% straw was selected to be implemented in the substrate of constructed wetlands.

5. References

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