Journal Pre-proofs

Comparative environmental assessment of end-of-life carbonaceous water treatment adsorbents

Ivan Kozyatnyk, Dalia M.M. Yacout, Jo Van Caneghem, Stina Jansson

PII: S0960-8524(20)30135-8
DOI: https://doi.org/10.1016/j.biortech.2020.122866
Reference: BITE 122866

To appear in: *Bioresource Technology*

Received Date: 6 November 2019
Revised Date: 17 January 2020
Accepted Date: 20 January 2020

Please cite this article as: Kozyatnyk, I., Yacout, D.M.M., Van Caneghem, J., Jansson, S., Comparative environmental assessment of end-of-life carbonaceous water treatment adsorbents, *Bioresource Technology* (2020), doi: https://doi.org/10.1016/j.biortech.2020.122866

Comparative environmental assessment of end-of-life carbonaceous water treatment adsorbents

Ivan Kozyatnyk[1], Dalia M. M. Yacout[1], Jo Van Caneghem[2], Stina Jansson[1]*

[1] *Department of Chemistry, Umeå University, SE-901 87 Umeå, Sweden*

[2] *TC Materials Technology, KU Leuven, Group T Leuven Campus, Andreas Vesaliusstraat 13, 3000 Leuven, Belgium*

Abstract

This study evaluates and compares the environmental impacts arising from the disposal of different carbonaceous sorbents used for wastewater treatment. Three different adsorption materials were considered, i.e. activated carbon, biochar and hydrochar, and three end-of-life management approaches, i.e. incineration, regeneration and landfilling. The highest overall environmental impact of *Carcinogenic effects* and *Freshwater Ecotoxicity* was due to emission of heavy metals during production of all types of sorbents. The use of materials with higher adsorption capacities and regeneration of carbonaceous materials were considered and shown to be an efficient way for reducing the overall environmental impacts of the different adsorbents. The compensation of fossil fuel incineration by using recovered heat led to negative impacts in all categories. Recirculation of HTC process water reduced the impact on *Freshwater Ecotoxicity* and *Eutrophication*.

*Corresponding author: E-mail address: stina.jansson@umu.se (S. Jansson), +46907867622.

Keywords: Life-cycle assessment, Activated carbon, Biochar, Hydrochar, Hydrothermal carbonisation

1. Introduction

Carbon-based adsorbents are known to be very efficient in wastewater treatment. Activated carbon (AC) is the most widely used; it has a high specific surface area and pore volume and has therefore a high adsorption capacity for many organic and inorganic pollutants (Dias et al., 2007). Because AC has generally been a fossil-based product, several low-cost bio-based residues from agriculture and industry have been examined as possible replacements (Thompson et al., 2016). One such group of materials is lignocellulosic biomass, which has been used as a feedstock for the production of AC, biochar (BC) and hydrochar (HC) that can be used as low cost and efficient adsorbents in environmental applications (Mohan et al., 2014; Thompson et al., 2016).

The thermal treatment of biomass under low-oxygen conditions generates a carbonaceous material, BC, which has an abundance of oxygen-containing functional groups and aromatic entities on its surface (Lehmann et al., 2006). Depending on the conditions during the carbonisation process, and the chemical and physical characteristics of the starting material, BCs have a relatively high surface-to-volume ratio and an extensive surface area. BCs have been used in many different applications including as adsorbents for purifying wastewater (Mohan et al., 2014). In addition, the use of locally or regionally available low-cost bio-based residues would probably be more advantageous from an economic and environmental point of view than conventional fossil-based adsorbent materials (Mohan et al., 2014; Weidemann et al., 2018).

An elevated moisture content is a major limiting factor for the successful conversion of biomass to BC by conventional thermal carbonisation processes (Owsianiak et al., 2016), and pre-drying of moist biomass requires a high amount of energy. Wet pyrolysis techniques, such as hydrothermal carbonisation (HTC), have therefore been recommended as efficient methods for converting high-moisture biomass and biomaterials into carbonaceous materials referred to as HC, thereby avoiding energy intensive and costly pre-drying steps (Owsianiak et al., 2016). In HTC, the feedstock and water are heated in a closed vessel; this generates products in the form of gases, an aqueous fraction, and the solid HC. Reaction temperatures are in the range of 180 °C - 260 °C, and the self-generated pressure is maintained above the saturation pressure to maintain water in its liquid state (Libra et al., 2011). Previous studies have argued that HTC can convert bio-based residues into energy-efficient biocompatible products that can replace traditional fossil fuels in energy production (Zeymer et al., 2017), or can be used in various types of environmental applications, e.g. as (waste)water purification adsorbents (Mohan et al., 2014).

For most areas of application, proper end-of-life management of BC, HC and AC adsorbents is an important issue that should be addressed but is often neglected (Rosales et al., 2017). Currently, the most common end-of-life treatments for AC, BC and HC adsorption materials are regeneration and recycling of the adsorbent, incineration for energy recovery, and being sent to landfill (Mohammadi et al., 2019). In order to comply with legislation in some EU countries (including Sweden), many industries will need to close their internal landfills by 2020, which implies that incineration may become increasingly attractive as an end-of-life treatment option (Libra et al., 2011; Zeymer et al., 2017). It also means that there is an urgent need for new technically and economically feasible end-of-life treatments for carbonaceous adsorbents to be

developed and assessed. The environmental impacts of AC and BC adsorbents used for tertiary wastewater treatment have been compared by Thompson et al. (2016) have reported low capacity BC (used in doses of 600 mg BC L^{-1} of wastewater) to have a lower environmental impact than AC, in the sense that BC had lower impacts than AC on global warming, respiratory effects, and carcinogenic potential.

To date, the environmental impacts of different end-of-life treatment options for AC and wood-based carbonaceous adsorbents have received little attention. Furthermore, the potential environmental benefits and related end-of-life impacts from using renewable materials, such as BC and HC, for water treatment applications remain unclear in the literature. Most existing studies focus on the environmental impacts from either production (Arena et al., 2016; Berge et al., 2015; Liu et al., 2017; Thompson et al., 2016; Zeymer et al., 2017) or use (Liu et al., 2017; Sparrevik et al., 2013; Thompson et al., 2016; Zeymer et al., 2017) of carbonaceous adsorbents. Therefore, the current study determines and evaluates, by means of a life-cycle assessment (LCA) approach, the environmental impacts of different end-of-life scenarios for three carbonaceous adsorbent materials (AC, BC and HC). The end-of-life treatments include incineration, landfilling, regeneration, and reactivation. Sending incineration ash to landfill is one of the most common practices in Sweden as well as other EU countries (Mohammadi et al., 2019). In Sweden, depositing organic material in landfill sites is not permitted; however, carbonaceous adsorbents can be used as cover on landfill sites (Chen et al., 2016). AC is reactivated by thermal regeneration: the spent AC is heated up to 700 °C, then activated through vaporisation at 800 °C – 1000 °C (Álvarez et al., 2004). Regeneration is done by means of acid solution (Li et al., 2015) and can be performed on the same material up to four times. By comparing the different end-of-life treatments, the approach with the lowest environmental impact can be identified.

2. Materials and Methods

An LCA was employed to assess and compare the environmental impacts for the-end-of life of the three carbonaceous adsorbent materials: AC, BC and HC. Two of them (BC and HC) are produced from wood biomass while AC is produced from black charcoal, which was used as a baseline. The end-of-life treatment options were incineration, landfill, elution regeneration, and thermal reactivation. The three scenarios 'incineration', 'landfill', and 'elution regeneration' were assessed for all carbonaceous adsorbent materials, whereas the thermal reactivation scenario was assessed only for AC. A total of ten end-of-life scenarios were thus defined and compared through this LCA (see Table 1).

The LCA followed the International Organization for Standardization (ISO) 14040/44 guidelines, which incorporate four phases: (1) goal and scope definition, (2) life-cycle inventory, (3) life-cycle impact assessment, and (4) interpretation (ISO 14040, 2006). LCA modelling was performed using Umberto LCA+ software (ifu Hamburg, Germany). As advised by the Joint Research Centre (JRC), and the European Commission's science and knowledge service, the environmental impact assessment was performed according to the International Reference Life Cycle Data System (ILCD) v2.0 2018 Midpoint. The relative importance of the score derived for each impact category, as obtained with ILCD by means of the Umberto LCA+ software, is difficult to interpret because it is not placed in an appropriate environmental context (Sleeswijk et al., 2008). A normalisation step was therefore introduced to translate the impact score for each impact category into the contribution of the life-cycle relative to a reference

situation. In the present study the global normalisation factors were used for each impact category as provided by Sala et al. (2017).

2.1. Goal and scope

The main goals of the present study were to identify which end-of-life treatment for adsorbents used in industrial wastewater treatment applications has the lowest environmental impact, and to enhance the understanding of the environmental impacts of various end-of-life options when using BC and HC as alternatives to AC. The environmental impacts of the life-cycles of AC, BC and HC with four alternative end-of-life treatments were modelled and compared. The considered end-of-life treatments were: 1) Incineration; 2) Landfilling; 3) Regeneration; 4) Reactivation. A total of ten different end-of-life scenarios were defined and compared (Table 1).

The scope of the present study was established as a cradle-to-grave approach to include the following stages in the life-cycle of adsorbents: production; use in wastewater treatment; and end-of-life treatment. The avoided production and incineration of primary fuels (coal and natural gas) was included because of potential energy generation from incineration of spent adsorbents. Transportation of the adsorbents from their production site to the wastewater treatment facility, and from there to the end-of-life facility were not included. According to Yacout et al. (2016) transportation is case-specific, it adds to the overall environmental impacts, and it is not recommended to use specific data to develop a generic estimate. Since part of the goal of this study was to identify the preferred approach for adsorbents' end-of-life management using generic data for Sweden, transportation was not included. The manufacturing of filters and other parts of the wastewater treatment process were

deemed beyond the scope of the present study and were therefore not taken into consideration. Infrastructure and construction of the end-of-life facility were also excluded.

2.2. Functional unit and system boundaries

Since carbonaceous adsorbents for wastewater treatment were considered in the study, the functional unit was defined as being the treatment by carbon-based adsorbents (AC, BC or HC) of 100 m^3 tertiary wastewater polluted with pharmaceuticals and contaminants of emerging concern (CECs). Tertiary wastewater treatment is an advanced treatment in wastewater plants that enables the treated water to be fit for recycling after chemical oxidation, pressurised sand filtration, and adsorption (Mareddy et al., 2017).

The adsorption capacity of the respective carbonaceous materials determines the amount required for the treatment of the defined volume of wastewater. In this study, to determine the adsorption capacity of AC, BC and HC for pharmaceuticals solutions of 10 mg L^{-1} was used, which is commonly found to be the concentration of pharmaceuticals in the wastewater effluents from production plants (Fick et al., 2009). Adsorption data were collected for CECs (caffeine (Bernardo et al., 2017; Sotelo et al., 2012), carbamazepine (Chen et al., 2017; Ncibi & Sillanpää, 2017; Román et al., 2018), bisphenol A (Bautista-Toledo et al., 2005; Li et al., 2017; Román et al., 2018) and triclosan (Oh & Seo, 2016; Román et al., 2018)) onto the carbonaceous adsorbents. These compounds represent pharmaceutical and industrial pollutants with different hydrophilic-hydrophobic properties (octanol-water partition coefficients) and are organic compounds of importance for adsorption onto carbonaceous materials (Li et al., 2018) (see Table 2).

The adsorption capacity of AC is much higher than that of either BC or HC. Based on the data in Table 2, the average adsorption capacities used in the present study were 220 mg g^{-1} for AC, 5.5 mg g^{-1} for BC and 4.0 mg g^{-1} for HC. Naturally, the adsorption of other CECs than those included in this study can differ from the set selected here. The influence of adsorption capacity on environmental impact is therefore specifically addressed in the Sensitivity Analysis (see Section 3.8 below).

The system boundaries are presented in Fig. 1, which includes AC production from fossil black charcoal, or alternatively BC or HC production from wood biomass, as well as the use-phases of the different adsorbents (adsorption of pharmaceuticals from wastewater), the end-of-life treatment, and related emissions to air, water discharge, and solid wastes.

2.3. End-of-life scenarios

A total of ten end-of-life scenarios were evaluated in the present study. Details of each scenario are given in Table 1.

2.3.1. Activated carbon end-of-life scenarios (AC I, AC L, AC Rg, AC Ra)

These scenarios consider AC produced from black charcoal by pyrolysis and steam activation. After use as an adsorbent during the use-phase, the spent AC is disposed of by incineration in a coal-fired power plant (*AC I*). In the case of scenario *AC L*, the spent AC is disposed of in landfill.

Regeneration of spent AC was considered in scenario *AC Rg*. Regeneration of AC refers to the restoration of its available surface area and its adsorption sites (Nasruddin et al., 2018). Regeneration can significantly improve the lifetime of adsorption materials and it is in general cheaper to regenerate AC than to replace it (Álvarez et al., 2004).

Adsorption capacity recovery by chemical regeneration relies on the use of various solvents (Goncharuk et al., 2007; Li et al., 2015). The main advantages of chemical regeneration are the possibility to extract valuable substances, and a low loss of weight of the adsorbent (Nasruddin et al., 2018). However, chemical regeneration to recover valuable products from AC usually requires additional treatment of the extraction liquid (Rinkus et al., 1997). In the current study, the end-of-life scenario is the regeneration of AC adsorbent for re-use in the use-phase without considering the recovery of valuable substances.

One of the most commonly used techniques for regeneration is thermal regeneration by pyrolysis (Álvarez et al., 2004). In this case spent carbonaceous sorbents are regenerated in the presence of a mildly oxidising atmosphere, usually steam or carbon dioxide at temperature of about 800 °C. Adsorbed organic substances are degraded by oxidation and the original carbon-pore structure is thus restored (Álvarez et al., 2004). In this scenario (*AC Ra*) spent AC is reactivated by thermal regeneration: the spent AC is heated to 700 °C, then activated through vaporisation at 800 °C – 1000 °C (Álvarez et al., 2004). Loss of carbon as a result of oxidation increases with increasing duration and temperature of the process. In most industrial installations, these regeneration losses range from 5% - 15 % per cycle. Despite the relatively large losses of the sorbent and the consumption of fuel (natural gas, liquid fuel) to maintain the desired high temperature, which leads to additional costs, the method of thermal high-temperature regeneration has become the most widely used process (Álvarez et al., 2004). This type of reactivation by thermal regeneration was not considered for BA and HC, since high temperature pyrolytic treatment of these materials can significantly change their adsorption properties (Leng & Huang, 2018).

2.3.2. Biochar end-of-life scenarios (BC I, BC L, BC Rg)

BC is produced from a mixture of hardwood and softwood biomass processed through a pyrolysis process at > 350 °C and under low-oxygen conditions (Lehmann et al., 2006). In the case of Scenario *BC L*, the spent BC was disposed of in a landfill; for *BC I* the spent BC was incinerated; for *BC Rg* the spent BC sorbent was chemically regenerated.

2.3.3. Hydrochar end-of-life scenarios (HC I, HC L, HC Rg)

HC end-of-life treatments were as for BC, viz. spent sorbents from *HC I, HC L, and HC Rg* were incinerated, sent to landfill, and chemically regenerated, respectively. The total organic carbon content in the HTC process water has been reported as high as in the order of grams per litre (Fettig et al., 2019). Naturally, process water with this composition cannot be discharged directly to the environment and would instead need to be either recirculated in the HTC process (Kambo et al., 2018) or subjected to some form of wastewater treatment (Fettig et al., 2019). Therefore, biological treatment of the HTC process water was set as a baseline scenario for the production of HC from wood biomass.

2.4. Life-cycle inventory

Inventory background data for the various scenarios were either calculated from experimental results or collected from life-cycle inventory studies and the literature. Foreground data were retrieved from the Ecoinvent 3.5 database. The AC dataset is based on data sourced from the literature for European production. For the production of the BC, the process ‘Charcoal production’ was used, the dataset also being sourced from literature published on European production. Since the HC production process does not

exist in the available LCI databases it was developed from data in previously published studies (Benavente et al., 2017; Berge et al., 2015; Liu et al., 2017; Owsianiak et al., 2016; Zeymer et al., 2017). Specific details associated with each process, including process material, energy needs, and operational parameters, can be found in the Appendix (Table A1). The process 'Treatment of wastewater, average, capacity 1E9l/year [Europe without Switzerland]' from the Ecoinvent 3.5 database was used for HTC process water treatment.

The geographical location of the case study was assumed to be in Sweden. In order to model landfill of spent adsorbents the Ecoinvent 3.5 activity 'Waste treatment by sanitary landfill' was used as it is the closest representation to landfill waste treatment in other European countries. For the incineration of AC, the process 'Heat production, at hard coal industrial furnace 1-10 MW' was used. For the incineration of BC and HC, 'Treatment of biowaste, municipal incineration' was employed. The thermal regeneration of AC was modelled as 'Treatment of spent activated carbon, granular from hard coal, reactivation'. Electricity consumption was estimated as the average of annual production for the middle voltage level in Sweden. This includes: the production and transmission of 1kWh electricity at middle voltage, starting from its feed into the low voltage transmission network; transportation in the production and transmission network over aerial lines and cables; direct emissions to air; and electricity losses during transmission (Ecoinvent 3.5).

2.5. Impact Assessment

Six impact categories related to the ILCD were evaluated and compared in this work: *Climate Change* impacts over a time horizon of 100 years (as recommended by the IPCC (2015); *Freshwater and Terrestrial Acidification*; *Freshwater Eutrophication*

Potential; *Freshwater Ecotoxicity*; *Carcinogenic Effects*; and *Non-carcinogenic Effects*. Each method was calculated according to Benini et al. (2014). These categories were chosen because they are environmentally relevant and internationally accepted in accordance with ISO 14040:2006 (ISO, 2006). The total environmental impacts were normalised in order to give a visual representation of the overall environmental impacts with reference to the level of impacts at the global scale. Normalisation was achieved by dividing the sum of the direct and indirect environmental impacts by the normalisation factors provided by Sala et al. (2017).

2.6. Compensation of fossil fuel incineration

Many countries use incineration of fossil fuels such as black coal and natural gas for energy production. The important environmental impacts related to this have been highlighted in previous studies (Mohammadi et al., 2019; Thompson et al., 2016). However, fossil fuels can, in many cases, be substituted by carbon-rich materials produced from renewable resources. In order to understand the related impacts in greater depth, the environmental impacts of two types of fossil fuels (black coal and natural gas) were analysed. For each of these substitutes, the environmental impacts were compared to those of the base case scenario without energy recovery. The following activities from the Ecoinvent 3.5 database were used: 'Heat and power co-generation, natural gas, conventional power plant, 100 MW electrical [SE]' and 'Heat and power co-generation, hard coal [SE]'. These processes are also representative of the situations in other European countries.

2.7. Sensitivity analysis

Different manufacturing processes and feedstock properties result in materials that differ in their adsorption capacities for organic compounds (Hagemann et al., 2018). Data uncertainties can arise due to the large variation in the assumed adsorption capacities of AC, BC and HC. AC usually has a more developed porosity and thus a greater adsorption capacity than BC and HC (Table 2). A smaller amount of material with high adsorption capacity would thus be required to treat the same volume of contaminated water. This in turn leads to higher environmental impacts from BC and HC during production and end-of-life stages. However, it has recently been shown that the adsorption capacity of BC and HC can be increased by activation or surface functionalisation. The adsorption capacity for such improved materials was considered to be 20 mg L^{-1} (Paunovic et al., 2019). An important aspect of the sensitivity analysis is thus to reflect any changes in the environmental impacts as they might relate to the changes in the adsorption capacities of BC and HC.

Another case considered in the sensitivity analysis was the management of process water generated during HTC treatment. Therefore, the production of 1 kg of HC from wood biomass was considered with three alternatives routes for the process water: (1) without treatment; (2) biological wastewater treatment (baseline scenario); and (3) recirculation. The uncertainty on the obtained results was evaluated according to the classification provided by Hauschild et al. (2011).

3. Results and discussion

3.1. Overall environmental impacts

Life-cycle assessment results are presented in Figs 2, 3 and in Appendix Table A2. Fig. 2 shows the overall normalised environmental impacts for the different end-of-life scenarios. *Carcinogenic effects* (Thompson et al., 2016) and *Freshwater Ecotoxicity*

(Kambo et al., 2018) had the highest normalised environmental impacts due to emission of heavy metals during production of all types of sorbents mainly due to consumption of electricity for the production of these sorbents (Arena et al., 2016). Fig. 3 shows the detailed impacts of each LCA stage (production, use-phase, end-of-life) on each environmental impact with respect to the different scenarios. The production stage of the different adsorption materials was the main contributor to most of the environmental impacts of the different scenarios (Arena et al., 2016), followed by the end-of-life stage (Fig. 3.).

3.2. Climate Change

Impacts in this category were mainly caused by the emissions of carbon dioxide and methane at the production stage of the different adsorption materials (Fig. 3). For the first two scenarios (*AC I, AC L*), the production and activation of AC from fossil hard coal contributed the most to the total impact in this category. In the case of the *BC I* and *BC L* scenarios, the high impact resulted from the emissions generated from burning fossil fuels to maintain a suitable production process that yields a stable BC material (high temperatures of 400 °C - 700 °C for long periods) as well as the low adsorption capacity of the BC compared to AC (Leng & Huang, 2018). The re-use of AC, BC, and HC through regeneration or reactivation processes was an efficient way to reduce the overall emissions related to the production stage of these materials (Scenarios *AC Rg, AC Ra, BC Rg,* and *HC Rg*). In agreement with Álvarez et al. (2004) the regeneration process reduced the consumption of natural gas and liquid fuel, which leads to large energy and cost savings, in addition to the reduction of the related environmental impacts. Furthermore, the incineration technology employed in the case of *BC I* and *HC I* also had a high impact on *Climate Change*. This can be reduced by

employing an energy recovery option such as generation of electricity only or cogeneration of heat and power (Berge et al., 2015; Owsianiak et al., 2016).

3.3. Freshwater and terrestrial acidification

Acidification is mainly caused by emissions of sulphur dioxide and nitrogen oxides. In agreement with Arena et al. (2016), energy consumption played a key role in the overall impact found in this category. The venting of emissions to air from the incineration of fossil fuels used for the production of AC, BC and HC, and for maintaining the pyrolysis process conditions for BC production, and the incineration of the chars in the end-of-life process, were the main sources of acidifying gases in the respective scenarios (*AC I*, *AC L*, *BC I* and *BC L*).

The regeneration treatments of AC, BC and HC (Scenarios *AC Rg*, *BC Rg*, and *HC Rg*) had a notable impact in this category, attributable to the use of hydrochloric acid in the regeneration process. Furthermore, the use of aluminum and ferric salts in the wastewater treatment process during the use-phase stage also had an impact on the different scenarios in this category. These chemicals are used to coagulate and flocculate colloidal and fine suspended matter, as well as to precipitate dissolved matter (Yoo et al., 2001). The production of these salts generates emissions of nitrogen and sulphur oxides that contribute to acidification (Renou et al., 2008).

3.4. Freshwater eutrophication

Nitrogen and phosphorus in effluents were the main factors influencing *Freshwater Eutrophication*. HTC generates a substantial amount of wastewater with a high level of phosphates, which is responsible for its impact on *Freshwater Eutrophication* (Libra et al., 2011). As shown in Fig. 3, the highest impact on this

category were those related to HC production (*HC I, HC L* and *HC Rg*). However, recirculating and re-using the liquid discharge of the HTC process in the same production process, or applying additional wastewater treatments before discharge to the environment, can reduce the overall impacts. According to Kambo et al. (2018), using pure water in the HTC process is not suitable and can be a disadvantage. By recycling and re-using the HTC process water, environmental benefits are gained from reducing water use and consequently minimising the impact on *Freshwater Eutrophication* (Kambo et al., 2018). For a more detailed discussion about management alternatives of HTC process water, see Section 3.8 below.

3.5. Freshwater Ecotoxicity

Freshwater Ecotoxicity was quite sensitive to inputs of phosphorous and heavy metals. Heavy metals emissions from BC production and discharges after HTC process water treatment were the main sources of impact on this category (scenarios *BC I, BC L, BC Rg, HC I, HC L* and *HC Rg*). It is recommended that process water is recirculated as this will increase the overall efficiency of the system and reduce both the operating costs and the overall environmental impact (Kambo et al., 2018). For a more detailed discussion about management alternatives of HTC process water, see Section 3.8 below.

3.6. Carcinogenic and Non-carcinogenic effects

Heavy metals from both the production and end-of-life phases in the different scenarios contributed to both *Carcinogenic* and *Non-carcinogenic Effects*. In agreement with Thompson et al. (2016), high electricity consumption caused the greatest impacts. The emissions from the combustion of fossil fuels in generating electricity to power

process equipment, maintain process conditions, and power incineration processes, contributed most to these impact categories.

In the *BC I* and *HC I* scenarios, chromium from the combustion of fossil fuels during incineration was the main contributor to *Carcinogenic Effects* (Fig. 3). The incineration of adsorption materials used to treat 100 m^3 of wastewater, generated 1.46 x 10^{-6} and 2.01 x 10^{-6} CTUh, in the *BC I* and *HC I* scenarios, respectively. Zinc from the AC, BC and HC production processes contributed most to the impact on the *Non-carcinogenic Effects* category. An additional load from the *BC I* and *HC I* scenarios came from arsenic and mercury emitted during incineration. Overall impacts in these categories can be reduced by using regenerated AC, BC and HC materials.

3.7. Compensation of fossil fuel incineration

The LCA results presented in Fig. 3 showed that the adsorbent production stage was the most influential parameter on the overall impacts in the different scenarios. The high carbon content of the adsorbent materials makes them suitable for incineration with energy or heat recovery (Leng & Huang, 2018). An end-of-life management approach which includes an energy recovery step may replace other heat production processes that use fossil fuels like black charcoal or natural gas in those countries where these processes are used for energy production (Berge et al., 2015; Owsianiak et al., 2016). Fig. 4 shows how excluding the incineration of fossil black charcoal or natural gas affects the environmental impacts of the different scenarios. The basic scenario, without compensation of environmental impact from fossil fuel incineration, should be considered for countries like Sweden where the production of energy from municipal solid waste prevails. It should be noted that the use of energy recovery leads to negative impacts in different scenarios of all categories. *Climate Change* was sensitive to

emissions of fossil CO_2, CH_4 and N_2O being excluded. *Freshwater Eutrophication*, and *Freshwater and Terrestrial Acidification* were mainly influenced by nitrogen oxide emissions. At the same time, *Freshwater Eutrophication* was more sensitive to phosphorus emissions. Excluding sulphur oxide emissions from coal incineration played a major role in the impact on *Freshwater and Terrestrial Acidification*. As seen in Fig. 4, in most impact categories the compensation effects were greater on coal than on gas incineration.

3.8. Sensitivity analysis

Within the framework of this LCA study, adsorption capacity was found to be the most influential parameter. Increasing the adsorption capacity of these materials resulted in both economic and environmental benefits, since higher adsorption capacity allows smaller amounts of the adsorption materials to be used. This in turn can reduce the costs and the environmental impacts during production (Hagemann et al., 2018) and end-of-life processing. The adsorption properties of BC and HC can be improved by activation or functionalisation (Paunovic et al., 2019). These methods increase the capacity of materials to adsorb organic substances by enhancing porosity or by introducing surface functionality allowing a more efficient adsorption of specific groups of compounds.

In the sensitivity analysis, the impacts of using BC and HC with a higher adsorption capacity were considered and compared in order to quantify how the use of improved materials affects their environmental impact. The results of the sensitivity analyses for the ten end-of-life scenarios on the different environmental impacts are presented in Fig. 5. It is clear that the use of these improved adsorption materials (BC

and HC with high adsorption capacity) reduced the impacts in all scenarios and all impact categories. The introduction of new BC and HC technology requires further investigation to improve their adsorption capacity and evaluate the economic aspects related to the direct and indirect costs of producing and reusing such materials. Related social benefits such as the creation of new employment opportunities should also be considered.

The sensitivity analysis also considered different management options for dealing with the HTC process water with respect to the two most sensitive categories *Freshwater Ecotoxicity* and *Eutrophication* (Fig. 6). It was considered purification of the process water by either biological wastewater treatment or recirculation in the HTC process. Biological wastewater treatment substantially decreased the impacts on *Freshwater Ecotoxicity* and *Eutrophication*. Recirculation of the process water allowed a reduction of these impacts by several orders of magnitude and is thus the most effective strategy for water use in the HTC process (Stemann et al., 2013).

3.9. Uncertainty analysis

The uncertainties on the environmental impacts were evaluated based on the classification provided by Hauschild et al. (2011). *Climate Change* is classified as a level I method which is recommended and satisfactory for characterisation, with a low uncertainty on the characterization factors, since they are based on the heat absorption capacity of greenhouse gases, which is a physical characteristic that can be determined quite accurately. *Freshwater and Terrestrial Acidification*, and *Freshwater Eutrophication* are classified as level II being recommended with some improvements needed. For these impact categories the uncertainty on the characterization factors is mainly due to special and temporal variation. Hence it is important to mention that the

results obtained and discussed in this work (Sections 3.2 to 3.8) only apply within the spatial and temporal boundaries implied in the ILCD methodology. *Freshwater Ecotoxicity*, and *Carcinogenic Effects*; and *Non-carcinogenic Effects* belong to level III which are recommended, but to be applied with caution. Indeed, for these impact categories the uncertainties on the characterization factors are mainly due to uncertainty on degradation rates and toxicity data. The uncertainty on the individual characterization factors is estimated at 2 orders of magnitude (Hauschild et al., 2011). This implies that for these impact categories, the absolute value of the differences in impacts between the different scenarios (Fig. 3 to 5) is not relevant. A conclusion can only be drawn on the relative trend, e.g. the impact of one scenario being lower of higher than the impact of another scenario.

4. Conclusions

The environmental impacts arising from end-of-life management approaches of carbonaceous wastewater treatment adsorbents were evaluated. The highest overall environmental impact of *Carcinogenic effects* and *Freshwater Ecotoxicity* was due to emission of heavy metals during production of all types of sorbents. The use of materials with higher adsorption capacities and regeneration of carbonaceous materials were considered and shown to be an efficient way for reducing the overall environmental impacts of the different adsorbents. It was also shown that recirculation of HTC process water reduced the impact on *Freshwater Ecotoxicity* and *Eutrophication.*

Acknowledgements

This work was supported by Bio4Energy (www.bio4energy.se), a strategic research environment appointed by the Swedish government and The Kempe Foundation [grant number SMK-1552].

References

1. Álvarez, P.M., Beltrán, F.J., Gómez-Serrano, V., Jaramillo, J., Rodríguez, E.M. 2004. Comparison between thermal and ozone regenerations of spent activated carbon exhausted with phenol. *Water Res.*, **38**(8), 2155-2165.

2. Arena, N., Lee, J., Clift, R. 2016. Life cycle assessment of activated carbon production from coconut shells. *J. Clean. Prod.*, **125**, 68-77.

3. Bautista-Toledo, I., Ferro-García, M.A., Rivera-Utrilla, J., Moreno-Castilla, C., Vegas Fernández, F.J. 2005. Bisphenol A Removal from Water by Activated Carbon. Effects of Carbon Characteristics and Solution Chemistry. *Environ. Sci. Technol.*, **39**(16), 6246-6250.

4. Benavente, V., Fullana, A., Berge, N.D. 2017. Life cycle analysis of hydrothermal carbonization of olive mill waste: Comparison with current management approaches. *J Clean Prod*, **142**(Part 4), 2637-2648.

5. Benini, L., Mancini, L., Sala, S., Manfredi, S., Schau, E.M., Pant, R. 2014. Normalisation method and data for Environmental Footprints. European Commission, Joint Research Center, Institute for Environment and Sustainability.

6. Berge, N.D., Li, L., Flora, J.R.V., Ro, K.S. 2015. Assessing the environmental impact of energy production from hydrochar generated via hydrothermal carbonization of food wastes. *Waste Manag.*, **43**, 203-217.

7. Bernardo, M.M.S., Madeira, C.A.C., dos Santos Nunes, N.C.L., Dias, D.A.C.M., Godinho, D.M.B., de Jesus Pinto, M.F., do Nascimento Matos, I.A.M., Carvalho,

A.P.B., de Figueiredo Ligeiro Fonseca, I.M. 2017. Study of the removal mechanism of aquatic emergent pollutants by new bio-based chars. *Environ. Sci. Pollut. Res.*, **24**(28), 22698-22708.

8. Chen, J., Zhang, D., Zhang, H., Ghosh, S., Pan, B. 2017. Fast and slow adsorption of carbamazepine on biochar as affected by carbon structure and mineral composition. *Sci. Total Environ.*, **579**, 598-605.

9. Chen, X.-W., Wong, J.T.-F., Ng, C.W.-W., Wong, M.-H. 2016. Feasibility of biochar application on a landfill final cover—a review on balancing ecology and shallow slope stability. *Environ. Sci. Pollut. Res.*, **23**(8), 7111-7125.

10. Dias, J.M., Alvim-Ferraz, M.C.M., Almeida, M.F., Rivera-Utrilla, J., Sánchez-Polo, M. 2007. Waste materials for activated carbon preparation and its use in aqueous-phase treatment: A review. *J. Environ. Manage.*, **85**(4), 833-846.

11. Dutta, T., Kim, T., Vellingiri, K., Tsang, D.C.W., Shon, J.R., Kim, K.-H., Kumar, S. 2019. Recycling and regeneration of carbonaceous and porous materials through thermal or solvent treatment. *Chem. Eng. J.*, **364**, 514-529.

12. Fettig, J., Austermann-Haun, U., Meier, J.-F., Busch, A., Gilbert, E. 2019. Options for removing refractory organic substances in pre-treated process water from hydrothermal carbonization. *Water*, **11**(4), 730.

13. Fick, J., Söderström, H., Lindberg, R.H., Phan, C., Tysklind, M., Larsson, D.G.J. 2009. Contamination of surface, ground, and drinking water from pharmaceutical production. *Environ. Toxicol. Chem.*, **28**(12), 2522-2527.

14. Goncharuk, V.V., Kozyatnik, I.P., Klimenko, N.A., Savchina, L.A. 2007. Natural bioregeneration of activated carbons in filters for add-on treatment of drinking water during their continuous operation. *J. Water Chem. Tech.*, **29**(6), 300-306.

15. Hagemann, N., Spokas, K., Schmidt, H.-P., Kägi, R., Böhler, M., Bucheli, T. 2018. Activated carbon, biochar and charcoal: linkages and synergies across pyrogenic carbon's ABCs. *Water-Sui*, **10**(2), 182.

16. Hauschild, M., Goedkoop, M., Guinee, J., Heijungs, R., Huijbregts, M., Jolliet, O., Margni, M., De Schryver, A. 2011. *International Reference Life Cycle Data System (ILCD) Handbook- Recommendations for Life Cycle Impact. Assessment in the European context. First ed*. Publications Office of the European Union, Luxemburg.

17. IPCC. 2015. *Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*. IPCC, Geneva, Switzerland.

18. ISO. 2006. ISO 14040: Environmental Management -Life Cycle Assessment - Principles and Framework., International Organization for Standardization. Geneva, Switzerland, pp. 20.

19. Kambo, H.S., Minaret, J., Dutta, A. 2018. Process water from the hydrothermal carbonization of biomass: a waste or a valuable product? *Waste Biomass Valorization*, **9**(7), 1181-1189.

20. Lee, T., Zubir, Z.A., Jamil, F.M., Matsumoto, A., Yeoh, F.-Y. 2014. Combustion and pyrolysis of activated carbon fibre from oil palm empty fruit bunch fibre assisted through chemical activation with acid treatment. *J. Anal. Appl. Pyrol.*, **110**, 408-418.

21. Lehmann, J., Gaunt, J., Rondon, M. 2006. Bio-char sequestration in terrestrial ecosystems – a review. *Mitig. Adapt. Strateg. Glob. Chang.*, **11**(2), 403-427.

22. Leng, L., Huang, H. 2018. An overview of the effect of pyrolysis process parameters on biochar stability. *Bioresour. Technol.*, **270**, 627-642.

23. Li, H., Cao, Y., Zhang, D., Pan, B. 2018. pH-dependent K_{OW} provides new insights in understanding the adsorption mechanism of ionizable organic chemicals on carbonaceous materials. *Sci. Total Environ.*, **618**, 269-275.

24. Li, J., Liang, N., Jin, X., Zhou, D., Li, H., Wu, M., Pan, B. 2017. The role of ash content on bisphenol A sorption to biochars derived from different agricultural wastes. *Chemosphere*, **171**, 66-73.

25. Li, Q., Qi, Y., Gao, C. 2015. Chemical regeneration of spent powdered activated carbon used in decolorization of sodium salicylate for the pharmaceutical industry. *J. Clean. Prod.*, **86**, 424-431.

26. Libra, J.A., Ro, K.S., Kammann, C., Funke, A., Berge, N.D., Neubauer, Y., Titirici, M.M., Fühner, C., Bens, O., Kern, J., Emmerich, K.H. 2011. Hydrothermal carbonization of biomass residuals: A comparative review of the chemistry, processes and applications of wet and dry pyrolysis. *Biofuels*, **2**(1), 71-106.

27. Liu, X., Hoekman, S.K., Farthing, W., Felix, L. 2017. TC2015: Life cycle analysis of co-formed coal fines and hydrochar produced in twin-screw extruder (TSE). *Environ. Prog. Sustain.*, **36**(3), 668-676.

28. Liu, Z., Fei, B., Jiang, Z., Liu, X. 2014. Combustion characteristics of bamboo-biochars. *Bioresour. Technol.*, **167**, 94-99.

29. Mareddy, A.R., Shah, A., Davergave, N. 2017. *Environmental impact assessment: theory and practice*. Butterworth-Heinemann, Oxford, UK.

30. Mohammadi, A., Sandberg, M., Venkatesh, G., Eskandari, S., Dalgaard, T., Joseph, S., Granström, K. 2019. Environmental analysis of producing biochar and energy recovery from pulp and paper mill biosludge. *J. Ind. Ecol.*, **23**(5), 1039-1051.

31. Mohan, D., Sarswat, A., Ok, Y.S., Pittman, C.U. 2014. Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent – A critical review. *Bioresour. Technol.*, **160**, 191-202.

32. Nasruddin, M.N., Fahmi, M.R., Abidin, C.Z.A., Yen, T.S. 2018. Regeneration of spent activated carbon from wastewater treatment plant application. *J. Phys. Conf. Ser.*, **1116**(3), 1-8.

33. Ncibi, M.C., Sillanpää, M. 2017. Optimizing the removal of pharmaceutical drugs Carbamazepine and Dorzolamide from aqueous solutions using mesoporous activated carbons and multi-walled carbon nanotubes. *J. Mol. Liq.*, **238**, 379-388.

34. Oh, S.Y., Seo, Y.D. 2016. Sorption of halogenated phenols and pharmaceuticals to biochar: affecting factors and mechanisms. *Environ. Sci. Pollut. Res.*, **23**(2), 951-961.

35. Owsianiak, M., Ryberg, M.W., Renz, M., Hitzl, M., Hauschild, M.Z. 2016. Environmental performance of hydrothermal carbonization of four wet biomass waste streams at industry-relevant scales. *ACS Sustain. Chem. Eng.*, **4**(12), 6783-6791.

36. Paunovic, O., Pap, S., Maletic, S., Taggart, M.A., Boskovic, N., Turk Sekulic, M. 2019. Ionisable emerging pharmaceutical adsorption onto microwave functionalised biochar derived from novel lignocellulosic waste biomass. *J. Colloid Interface Sci.*, **547**, 350-360.

37. Renou, S., Thomas, J.S., Aoustin, E., Pons, M.N. 2008. Influence of impact assessment methods in wastewater treatment LCA. *J. Clean. Prod.*, **16**(10), 1098-1105.

38. Rinkus, K., Reed, B.E., Lin, W. 1997. NaOH regeneration of Pb and phenol-laden activated carbon. I. Batch study results. *Sep. Sci. Technol.*, **32**(14), 2367-2384.

39. Román, S., Libra, J., Berge, N., Sabio, E., Ro, K., Li, L., Ledesma, B., Álvarez, A., Bae, S. 2018. Hydrothermal carbonization: modeling, final properties design and applications: a review. *Energies*, **11**(1), 216.

40. Rosales, E., Meijide, J., Pazos, M., Sanromán, M.A. 2017. Challenges and recent advances in biochar as low-cost biosorbent: From batch assays to continuous-flow systems. *Bioresour. Technol.*, **246**, 176-192.

41. Sala, S., Crenna, E., Secchi, M., Pant, R. 2017. *Global normalisation factors for the Environmental Footprint and Life Cycle Assessment*. Publications Office of the European Union, Luxembourg.

42. Sleeswijk, A.W., van Oers, L.F.C.M., Guinée, J.B., Struijs, J., Huijbregts, M.A.J. 2008. Normalisation in product life cycle assessment: An LCA of the global and European economic systems in the year 2000. *Sci. Total Environ.*, **390**(1), 227-240.

43. Sotelo, J.L., Rodríguez, A., Álvarez, S., García, J. 2012. Removal of caffeine and diclofenac on activated carbon in fixed bed column. *Chem. Eng. Res. Des.*, **90**(7), 967-974.

44. Sparrevik, M., Field, J.L., Martinsen, V., Breedveld, G.D., Cornelissen, G. 2013. Life cycle assessment to evaluate the environmental impact of biochar implementation in conservation agriculture in Zambia. *Environ. Sci. Technol.*, **47**(3), 1206-1215.

45. Stemann, J., Putschew, A., Ziegler, F. 2013. Hydrothermal carbonization: Process water characterization and effects of water recirculation. *Bioresour. Technol.*, **143**, 139-146.

46. Thompson, K.A., Shimabuku, K.K., Kearns, J.P., Knappe, D.R.U., Summers, R.S., Cook, S.M. 2016. Environmental comparison of biochar and activated carbon for tertiary wastewater treatment. *Environ. Sci. Technol.*, **50**(20), 11253-11262.

47. Weidemann, E., Niinipuu, M., Fick, J., Jansson, S.J.E.S., Research, P. 2018. Using carbonized low-cost materials for removal of chemicals of environmental concern from water. *Environ. Sci. Pollut. Res. Int.*, **25**(16), 15793-15801.

48. Yacout, D.M.M., Abd El-Kawi, M.A., Hassouna, M.S. 2016. Cradle to gate environmental impact assessment of acrylic fiber manufacturing. *Int. J. Life Cycle Ass.*, **21**(3), 326-336.

49. Yoo, C.K., Kim, D.S., Cho, J.-H., Choi, S.W., Lee, I.-B. 2001. Process system engineering in wastewater treatment process. *Korean J. Chem. Eng.*, **18**(4), 408-421.

50. Zeymer, M., Meisel, K., Clemens, A., Klemm, M. 2017. Technical, economic, and environmental assessment of the hydrothermal carbonization of green waste. *Chem. Eng. Technol.*, **40**(2), 260-269.

Figure 1. Material flow and system boundaries of the life-cycle of wastewater treatment with AC, BC or HC adsorbents and their different end-of-life treatments.

Figure 2. Overall normalised environmental impacts of the ten end-of-life scenarios (Normalisation, ILCD 2018)

AC – Activated Carbon; BC – Biochar; HC – Hydrochar.

I – Incineration; L – Landfilling; Rg – Regeneration; Ra – Reactivation.

Figure 3. Environmental impacts of the ten end-of-life scenarios (ILCD 2018)

AC – Activated Carbon; BC – Biochar; HC – Hydrochar.

I – Incineration; L – Landfilling; Rg – Regeneration; Ra – Reactivation.

Figure 4. Compensation of fossil fuel incineration.

AC – Activated Carbon; BC – Biochar; HC – Hydrochar.

I – Incineration; L – Landfilling; Rg – Regeneration; Ra – Reactivation.

Figure 5. Sensitivity analysis of the ten end-of-life scenarios on the different environmental impacts

AC – Activated Carbon; BC – Biochar; HC – Hydrochar.

I – Incineration; L – Landfilling; Rg – Regeneration; Ra – Reactivation.

Figure 6. Sensitivity analysis of alternative management options for process water after HTC.

HTC – Hydrothermal Carbonisation (baseline case); HTC wwt – Hydrothermal Carbonisation with wastewater treatment; HTC rec – Hydrothermal Carbonisation with process water recirculation.

51.

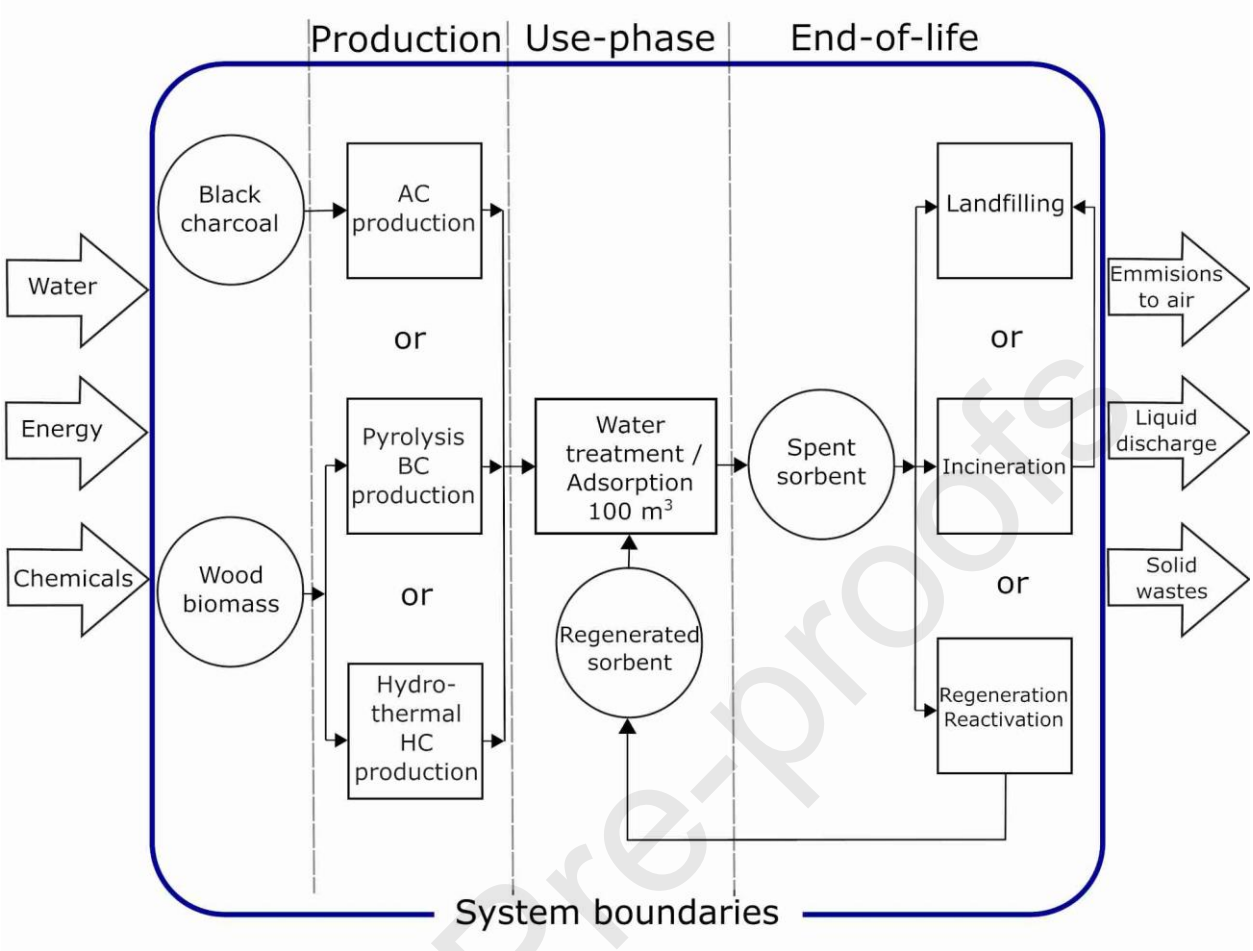


Figure 1

52.

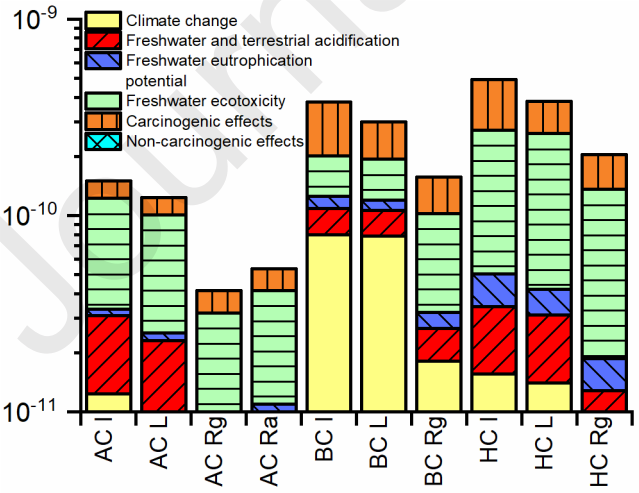


Figure 2.

53.

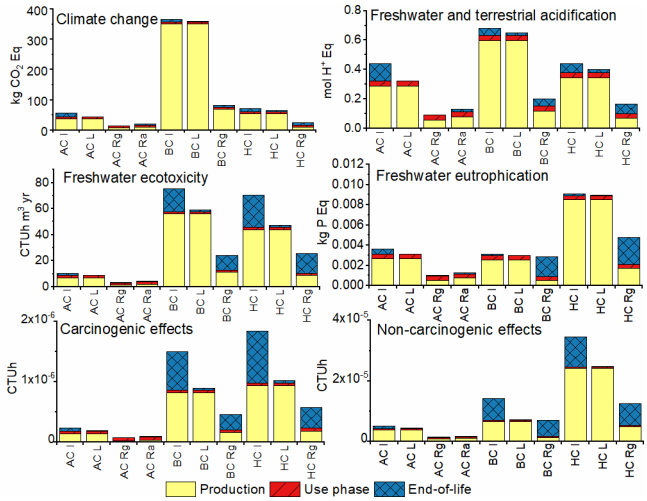


Figure 3.

54.

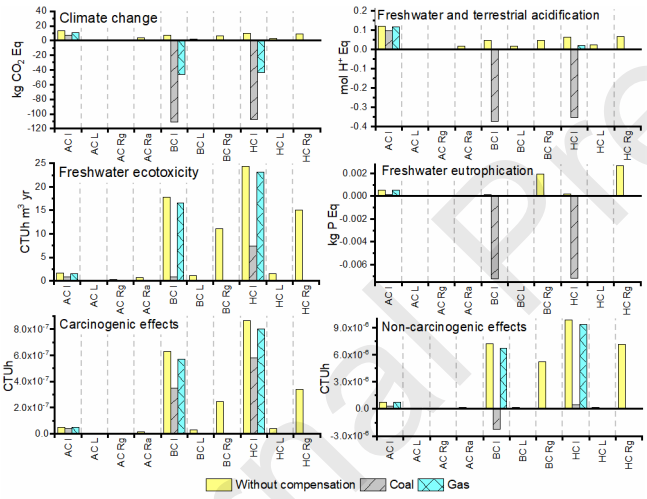


Figure 4.

55.

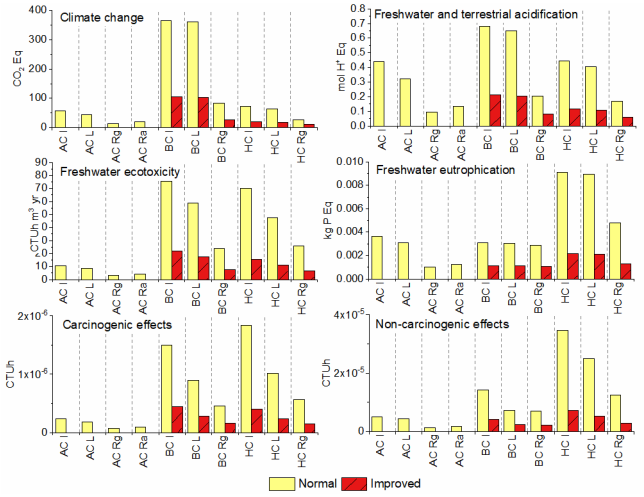


Figure 5.

56.

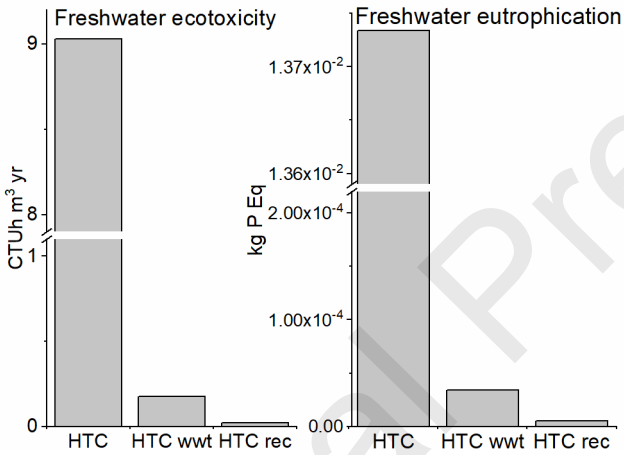


Figure 6.

57.

Table 1. Details of End of life Scenarios

Scenario (Used Term)	Adsorption material	End of life	Remarks
Scenario 1, (*AC I*)	AC	Incineration	AC combustion efficiency was considered 80.2% and related emissions of CO_2, non-fossil (air/urban air close to the ground) were assumed to be 1.52 kg (Lee et al., 2014)
Scenario 2, (*AC L*)	AC	Landfill	The Ecoinvent 3.5 activity "Treatment of inert waste, sanitary landfill" was used which represents Europe cases without Switzerland
Scenario 3, (*AC Rg*)	AC	Regeneration	The regeneration of the AC is done by means of a 0.1 M HCl solution in ratio 1:10 (sorbent: regeneration solution) by mass and four cycles of

Scenario (Used Term)	Adsorption material	End of life	Remarks
			regeneration are considered (Li et al., 2015; Nasruddin et al., 2018).
Scenario 4, (*AC Ra*)	*AC*	Reactivation	Reactivation of AC is done by thermal regeneration, the spent AC is heated up to 700 °C, then activated through vaporisation at 800 – 1000 °C (Álvarez et al., 2004).
Scenario 5, (*BC I*)	BC	Incineration	The modelling dataset considers the production of charcoal from wood as a pre-product for technical processes. The carbon content of the charcoal ranges between 78 and 90-wt % and is assumed 80 %. The heating value of charcoal ranges between 29 and 33MJ kg^{-1}. The hardwood used in the charcoal production is from forest plantations with full CO_2 uptake assumed (Ecoinvent 3.5).
Scenario 6, (*BC L*)	BC	Landfill	The Ecoinvent 3.5 activity "Treatment of inert waste, sanitary landfill" was used which represents Europe cases without Switzerland
Scenario 7, (*BC Rg*)	BC	Regeneration	
Scenario 8, (*HC I*)	HC	Incineration	Assumed complete combustion of 1 kg of HC yields 1.89 kg of carbon dioxide. Related emissions of CO_2, non-fossil (air/urban air close to the ground) were assumed to be 1.2 kg (Liu et al., 2014)
Scenario 9, (*HC L*)	HC	Landfill	The Ecoinvent 3.5 activity "Treatment of inert waste, sanitary landfill" was used which represents Europe cases without Switzerland
Scenario 10, (*HC Rg*)	HC	Regeneration	This was done according to recent studies that considered the regeneration of HC (Dutta et al., 2019).

58.

Table 2. Adsorption capacity of AC, BC and HC for contaminants of emerging concern

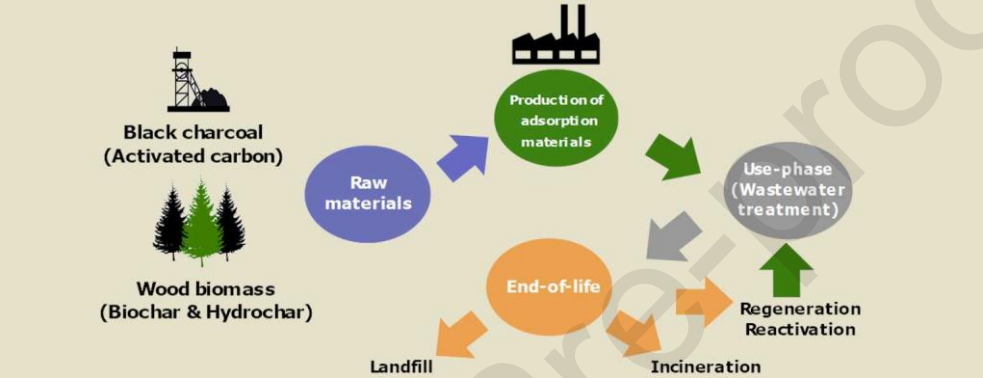
Substance	Adsorption capacity, mg g-1		
	AC	BC	HC
Caffeine	239	8.0	8.0
Carbamazepine	223	2.3	2.3-4.3
Bisphenol A	263	5.6	2.3-3.4
Triclosan	277	4.0	4.3-5.3

59.

- BC and HC combined with regeneration can be feasible alternative to AC

- Emissions from production of sorbents caused the highest environmental impacts
- Highest impacts were seen for Carcinogenic Effect and Freshwater Ecotoxicity
- Materials with higher adsorption capacities had lower overall environmental impact

60.



61.

Ivan Kozyatnyk - Writing - Original Draft; Conceptualization; Methodology (LCA modeling); Data analysis.

Dalia M. M. Yacout - Writing - Original Draft; Methodology (LCA modeling); Data analysis.

Jo Van Caneghem - Funding acquisition; Supervision; Writing - Review & Editing; Conceptualization; Data analysis.

Stina Jansson - Funding acquisition; Supervision; Writing - Review & Editing; Conceptualization

All authors read and approved the manuscript.

62.