THE UNIVERSITY *of* EDINBURGH

Edinburgh Research Explorer

Feedstock doping using iron rich waste increases the pyrolysis gas yield and adsorption performance of magnetic biochar for emerging contaminants

Citation for published version:

Wurzer, C, Wurzer, C & Masek, O 2021, 'Feedstock doping using iron rich waste increases the pyrolysis gas yield and adsorption performance of magnetic biochar for emerging contaminants', *Bioresource technology*, vol. 321, 124473. <https://doi.org/10.1016/j.biortech.2020.124473>

Digital Object Identifier (DOI):

[10.1016/j.biortech.2020.124473](https://doi.org/10.1016/j.biortech.2020.124473)

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Peer reviewed version

Published In:

Bioresource technology

General rights

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.

Feedstock doping using iron rich waste

Formatted: Not Highlight

increases the pyrolysis gas yield and
adsorption performance of magnetic biochar
for emerging contaminants

*Christian Wurzer † *, c.wurzer@ed.ac.uk*

Ondřej Mašek ‡, ondrej.masek@ed.ac.uk

† UK Biochar Research Centre, School of GeoSciences, University of Edinburgh,
Alexander Crum Brown Road, Edinburgh, EH9 3FF, United Kingdom

* Corresponding author: Christian Wurzer, email: c.wurzer@ed.ac.uk

Formatted: No underline, Font color: Auto

Paper type: Original research article

ABSTRACT

Magnetic carbons can significantly lower the costs of wastewater treatment due to easy separation of the adsorbent. However, current production techniques often involve the use of chlorinated or sulfonated Fe precursors with an inherent potential for secondary pollution. In this study, ochre, an iron-rich waste stream was investigated as a sustainable Fe source to produce magnetic activated biochar from two agricultural feedstocks, softwood and wheat straw. Fe-doping resulted in significant shifts in pyrolysis yield distribution with increased gas yields (+50 %) and gas energy content (+40 %) lowering the energy costs for production. Physical activation transformed ochre to magnetite/maghemite resulting in activated magnetic biochars and lead to a 4-fold increase in the adsorption capacities for two common micropollutants – caffeine and fluconazole. The results show that Fe doping not only benefits the adsorbent properties but also the production process, leading the way to sustainable carbon adsorbents.

Keywords

Catalytic pyrolysis; Gas energy content; Agricultural biomass; Magnetic biochar; Wastewater treatment

Formatted: Not Highlight

Formatted: Not Highlight

1. Introduction

Emerging contaminants such as pharmaceuticals, personal care products, and pesticides have become a growing concern in wastewaters with increasing usage leading to higher pollutant discharge into the environment (Dulio et al., 2018). In their study, Alygizakis et al. (2019) detected over 280 chemicals of emerging concern in effluents of wastewater treatment plants discharging into the Danube river basin. One of the most effective removal techniques is adsorption on porous materials such as activated carbon, however, widespread adoption in wastewater treatment plants is hindered by high production and operational costs (Sophia A. and Lima, 2018). As activated carbon is predominantly produced from fossil coal or increasingly scarce resources such as coconut shells, research is focusing on alternative feedstocks from agricultural and forestry waste (Correa and Kruse, 2018). Biochar, a closely related class of materials produced from renewable resources, presents a promising alternative as it is generally considered more sustainable and less expensive (Ahmed et al., 2015). Various modification methods can be used to improve the physicochemical characteristics of biochar (Wang et al., 2020). A promising method is the addition of metallic species such as Fe, Cu or Mg into the carbon structure of biochars to modify its functional properties (Li et al., 2018). Especially Fe oxide species receive increasing attention due to their non-toxicity, abundance, and selective sorption capacity towards organic contaminants (X. Li et al., 2020). Additionally, certain Fe species such as magnetite and maghemite can introduce magnetic characteristics to biochar (R. Li et al., 2020). Therewith, main operational costs in wastewater filtration applications can be reduced through

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Formatted: Not Highlight

Field Code Changed

Field Code Changed

Formatted: Not Highlight

separation of the exhausted adsorbent from the liquid phase by applying an external magnetic field (X. Li et al., 2020).

Field Code Changed

Fe oxides can be incorporated in biochar by a variety of methods and are well explained in recent reviews (X. Li et al., 2020; Rocha et al., 2020). The use of iron salts such as FeCl_3 or FeSO_4 to impregnate the biomass precursor is the most common technique, however, the use of these precursors can lead to secondary pollution during production and application (Damertey et al., 2020; Hagemann et al., 2020). Few studies proposed the use of solid-phase precursors such as hematite or goethite as environmentally sound alternatives (Damertey et al., 2020; Wang et al., 2015). The use of a solid Fe precursor sourced from currently unutilised waste streams could further increase the sustainability of the process. We hypothesize that ochre can be an alternative sustainable Fe source. Ochre is a waste mineral produced in coal mine drainage systems with an estimated production of around 4,500 t (dry basis – d.b.) per year in the UK alone. Pre-treated ochre sludge is currently being landfilled with costs between £ 70-149 per ton (Sapsford et al., 2015). Solid dewatered ochre consists of a mixture of goethite, ferrihydrite, and low amounts of organic carbon, and was already considered as a sustainable additive for biochar production (Shepherd et al., 2016), as water treatment reagent (Sapsford et al., 2015), and for the production of catalysts (Perera-Solis et al., 2019). To our knowledge, no published study on the use of ochre for the production of magnetic biochar exists.

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

The presence of Fe in biomass pyrolysis not only affects the properties of the solid product, but changes the product distribution between solid, liquid and gaseous yields (Xia et al., 2019). These catalytic effects could provide opportunities to

Field Code Changed

enhance the efficiency of the overall pyrolysis process beyond the solid product characteristics. Combustion of the pyrolysis gas can be an efficient way to reduce the overall energy costs of the process as it can provide heat for the pyrolysis process, and excess heat can be used for additional purposes such as feedstock drying (Huang et al., 2015). While bio-oil could be used as a feedstock for the synthesis of green chemicals, tar production can also cause operational problems in pyrolysis reactors (Paethanom et al., 2013). A higher relative gas yield and gas energy content might therefore be more beneficial for the overall process efficiency. While previous studies found a relative increase in CO₂ and H₂ yield in the presence of Fe, CO and CH₄ as the other main constituents of pyrolysis gas decreased (Collard et al., 2012; Xia et al., 2019). With generally higher gas yields the impact of Fe on the gas energy content remains inconclusive and needs further investigation to evaluate potential cost savings for Fe catalysed biochar production.

Field Code Changed

Field Code Changed

Field Code Changed

This study aims at obtaining synergistic benefits by the catalytic activity of Fe on the solid and gaseous products of biomass pyrolysis. Softwood and wheat straw pellets were selected as regionally available biomass and mixed with ochre as an environmentally sound Fe source for the production of magnetic activated biochar. The effects of Fe on the pyrolysis process were analysed by comparing product yield distributions and compositions. Gas composition analysis was used to evaluate the possibility of a self-sustaining pyrolysis process by utilising the gas fraction. Finally, the adsorptive performance of the produced biochars for wastewater treatment was assessed using batch adsorption tests of two emerging contaminants, caffeine and fluconazole. Caffeine is one of the most widely consumed psychoactive substances

Formatted: Not Highlight

Formatted: Not Highlight

and commonly found in wastewater treatment plant effluents (Paíga et al., 2019; Yang et al., 2017). Studies showed negative impacts of even marginal levels of caffeine on aquatic organisms (Cruz et al., 2016). Fluconazole is a widely used anti-fungal pharmaceutical, harmful to fish and aquatic life and presents low removal efficiencies in current wastewater treatment plants (Chen and Ying, 2015; Östman et al., 2017).

Field Code Changed

Field Code Changed

Field Code Changed

2. Material and methods

2.1 Feedstock preparation

Softwood pellets (SWP) and wheat straw pellets (WSP) were obtained from commercial suppliers (Puffin Pellets, and Agripellets), and had previously been used as feedstocks for the UKBRC Standard biochars (Mašek et al., 2018).

Field Code Changed

Lignocellulosic composition of the feedstocks was determined by a commercial laboratory (Celignis, Ireland). Ochre was obtained from the Coal Authority Minto mine water treatment scheme in Fife, Scotland.

Softwood and wheat straw pellets were dried at 105 °C overnight, crushed using a blender, and sieved to obtain a particle size of 1-2 mm. Ochre was dried and sieved to a particle size smaller than 0.5 mm. Ochre suspensions were prepared by adding 500 mL of deionised water to a predefined amount of ochre and sonicated for 30 min to achieve a homogenous mixture. The suspensions containing 5 % and 10 % ochre (wt. d.b.) were mixed with 500 g dried softwood or wheat straw, respectively, regularly stirred during the first hour and left to sorb overnight. After sorption, the mixtures were dried at 105 °C overnight and sieved again to remove small particles and obtain a feedstock particle size of 1-2 mm. Samples were named according to

their feedstock source (SWP, WSP) followed by an abbreviation to indicate the initial ochre suspension concentration i.e. SWP 5 for softwood mixed with a 5 % (wt. d.b.) ochre suspension.

2.2 Pyrolysis and activation

Pyrolysis was carried out using a vertical batch reactor as described in [Crombie et al. \(2013\)](#). Dry feedstock (30 g - 50 g) was first flushed with N₂ for 10 min to remove residual oxygen, heated in N₂ (800 mL min⁻¹) to a highest treatment temperature (HTT) of 550 °C at 15 °C min⁻¹ with a residence time of 45 min at HTT. Physical activation (HTT of 800 °C, 25 °C min⁻¹, residence time 60 min) was conducted in the same reactor set-up in CO₂ (550 mL min⁻¹). Condensable liquids were collected using a series of four condensation traps at the outlet of the reactor. Gaseous emissions were analysed continuously with one measurement per second using a multigas-analyser equipped with an infrared sensor (CO, CO₂), tuneable laser diode (CH₄), and thermal conductivity detector (H₂).

Pyrolysis and activation yields were determined by weight difference of the reactor (solid char yield), the condensation traps and the connection parts (condensable liquid yield) before and after the pyrolysis runs. Total solid yields were calculated as weight difference (wt. % d.b.) between feedstock and unwashed activated biochars. Accordingly, solid carbon yield was calculated as the mass difference of carbon in the feedstock and unwashed activated biochar. Total gas yield was determined by subtracting the solid and liquid yield from the dry feedstock mass. Lower Heating Value (LHV) of the pyrolysis gas was calculated according to [Alipour Moghadam et al. \(2014\)](#) assuming only H₂, CO and CH₄ as relevant constituents.

Field Code Changed

Field Code Changed

2.3 Biochar characterisation

Biochar characterisation was done on washed and sieved (0.125-0.5 mm) samples to remove weakly attached mineral particles and achieve a defined particle size of 0.125-0.5 mm to avoid particle size effects during adsorption (Kårelid et al., 2017). Biochars were washed using 2 g of char in 40 mL of deionised water and shaken for 2 hours on an orbital shaker at 180 rpm. Ultimate and proximate analysis, pH, and EC measurements were done on washed and sieved as well as untreated samples to observe the influence of the sample homogenisation treatment.

Volatile matter (VM), fixed carbon (FC) and ash content were determined by thermogravimetric analysis as described in Crombie et al. (2013). C, H, N, and S composition of the biochars was determined by ultimate analysis using flash combustion, oxygen content was calculated by difference. Total metal content was analysed by inductively coupled plasma optical emission spectrometry (ICP-OES) as described by Buss et al. (2016). Sample preparation was done according to the modified dry-ashing method proposed by Enders and Lehmann, (2012).

Surface elemental analysis was performed using a scanning electron microscope at an acceleration voltage of 15 kV - 20 kV equipped with EDX. Prior to the analysis, the samples were sputter coated with a gold layer to reduce particle charging. Crystalline structures of the samples were analysed using continuous scan XRD with a Cu K-alpha X-radiation source at diffraction angles from 2 - 65 degrees. Mass specific magnetic susceptibility of the biochar samples was measured using a magnetic susceptibility meter at 4.6 kHz.

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Textural properties were analysed by N₂ adsorption at -195.8 °C in the pressure range 0.01-0.99 after degassing at 150 °C for 10 hours. Quenched solid density functional theory (QSDFT) assuming slit/cylindrical pores was used to calculate the specific surface area (SSA), pore size distribution and average pore diameter (Thommes et al., 2015). Total pore volume was determined at a relative pressure point of 0.99.

Field Code Changed

Single compound batch adsorption experiments using caffeine (extra pure, Fisher Chemical UK) and fluconazole (> 98%, Acros Organics UK) were conducted to assess the adsorption capacity in the concentration range of 15-320 mg L⁻¹ (fluconazole) and 5-500 mg L⁻¹ (caffeine). For the adsorption experiments, 25 mg of biochar (wt. % d.b.) were mixed with 25 mL of pharmaceutical solution, shaken for 24 hours on an orbital shaker at 180 rpm before filtering through 0.45 µm hydrophilic PTFE syringe filters. All experiments were conducted at room temperature of 20 °C. The supernatants were analysed by UV-Vis spectrophotometry at 260 nm for both contaminants, with linear calibration ranges of 10–100 mg L⁻¹ (Fluconazole) and 2-125 mg L⁻¹ (Caffeine). Equilibrium concentrations were calculated according to Yan et al. (2015). The obtained isotherm data was fitted using the non-linear forms of the Langmuir and Freundlich isotherm models to calculate the adsorption capacity (Kumar, 2006).

Formatted: Not Highlight

Formatted: Not Highlight

Formatted: Not Highlight

Formatted: Not Highlight

Field Code Changed

Field Code Changed

3. Results and discussion

3.1 Feedstock characterisation

Characterisation of the softwood and wheat straw pellets highlights the main differences between the two feedstocks, with ash contents of 1.9 % (SWP) and 7.9 % (WSP) and a lower FC content for softwood than wheat straw (8.6 % and 15.2 %). Lignocellulosic composition of softwood pellets shows the main components to be cellulose and lignin (53 % and 27 %), while wheat straw pellets have a lower content of cellulose (36 %), but higher hemicellulose content (22.2 %). Carbon contents of 49.05 % and 43.89 %, and Fe contents of 0.01 % and 0.02 %, respectively, are similar between the feedstocks. The mineral additive ochre exhibits an ash content of 84.9 % with a total amount of 55.3 % Fe and a carbon content of 1.58 %. XRD analysis identified ochre to consist primarily of goethite. Final feedstock-ochre mixtures before pyrolysis contained 2.46 % and 3.9 % (SWP 5, SWP 10), and 6.9 % and 8.36 % (WSP 5, WSP 10) ash, respectively.

3.2. Pyrolysis

Solid pyrolysis yields of the softwood feedstock series showed only minor changes with ochre amendment, while yield distribution shifted from condensable liquids (bio-oil) to non-condensable gas production with increasing ochre addition (Table 1).

The ratio of liquid to gas yield changed from 1.96 (SWP) to 1.54 (SWP 10). Increased emissions of non-condensable gases are likely caused by the catalytic effect of Fe on the cellulose and lignin constituents of the biomass. Collard et al. (2012) observed similar results for the pyrolysis of Fe impregnated beech wood. Beside higher gas yields for ochre amended samples, differences in the gas emission patterns confirmed changed decomposition patterns due to Fe-doping (Figure 1).

Formatted: Not Highlight

Field Code Changed

While SWP exhibits a clear CO and CO₂ peak at approx. 380 °C, ochre amendment decreased the intensity of this first emission peak which is indicative for hemicellulose decomposition reactions. Contrastingly, the second peak which can be assigned to reactions with cellulose and lignin was increased in the presence of Fe.

As the softwood used in this study contains around 53% cellulose, this emission pattern is dominated by interactions of Fe with cellulose, although primary and secondary decomposition products and interactions from all lignocellulosic components influence the total gas emissions (Collard et al., 2015). For cellulose, Fe can inhibit depolymerisation at low temperatures by increasing dehydration and rearrangement reactions. Subsequent depolymerisation at higher temperatures above 300 °C is followed by tar cracking reactions and an increase in CO, CH₄ and H₂ emissions. Increased tar cracking reactions with ochre amendment are confirmed by decreasing condensable gas yields (Table 1). The appearing shoulders in gas emission patterns (Figure 2) for ochre amended samples resemble the effects of Fe on catalysed cellulose decomposition as observed in similar emission patterns published for Fe-impregnated cellulose (Collard et al., 2015). Fe doping also shifts gas emission peaks to lower temperature ranges, especially for H₂, from 550 °C to 460 °C (SWP and SWP 5 / SWP 10). The occurrence of H₂ emission peaks simultaneously to increased CO and CH₄ emissions is another indicator for tar cracking reactions from cellulose depolymerisation. However, increases in H₂ yields have also been reported for metal-impregnated lignin as the other main lignocellulosic constituent of softwood (Collard et al., 2012). Nevertheless, the influence of Fe-catalysed lignin rearrangements is unlikely the main factor due to the

Formatted: Not Highlight

Formatted: Not Highlight

Formatted: Not Highlight

Formatted: Not Highlight

Formatted: Not Highlight

Formatted: Not Highlight

Formatted: Not Highlight

relatively low pyrolysis temperature of 550 °C. This can be seen in the less pronounced but broad H₂ emissions peak for non-amended softwood, which can be assigned to beginning lignin rearrangement reactions (Huang et al., 2011). Total gas composition displays lower relative CH₄, CO₂ and CO emissions while the H₂ emissions increase with ochre amendment, which is in line with previously reported results for Fe impregnated beech wood (Collard et al., 2012).

Formatted: Not Highlight

Formatted: Not Highlight

Formatted: Not Highlight

Field Code Changed

For wheat straw, the solid yield increased with increasing ochre amendment from 29.6% (WSP) to 30.4% (WSP 5) to 31.3% (WSP 10). In contrast to softwood, wheat straw contained a higher proportion of hemicellulose, which shows different decomposition reactions than cellulose in the presence of Fe (Collard et al., 2012).

Field Code Changed

Therefore, the shoulder in gas emissions seen for Fe catalysed cellulose pyrolysis is less pronounced. Instead the condensable gas yield increased from 43.4 % to 46 % with ochre amendment (Table 1), indicating less tar cracking activity than in softwood pyrolysis. This is further confirmed by the lower CH₄ emissions with ochre amendment, indicative for Fe-catalysed hemicellulose decomposition. In contrast to softwood pyrolysis, H₂ emissions for Fe-doped wheat straw were not accompanied by a simultaneous increase in CO, CO₂ or CH₄ emissions. This indicates that the increase in H₂ for doped wheat straw samples was due to enhanced rearrangement reactions of lignin rather than tar cracking. Different H₂ emission sources can be identified by the missing first H₂ emission peak as seen for Fe-doped softwood, with wheat straw only displaying a broad peak at higher temperatures.

Formatted: Not Highlight

As pyrolysis gas can be combusted to self-sustain the pyrolysis process and excess heat used for feedstock preparations such as feedstock drying, the LHV and the gas

energy content are important for the overall process efficiency (Crombie and Mašek, 2014). LHV of the ochre amended samples decreased marginally compared to the non-amended samples from 10.3 MJ /m³ (SWP) to 9.9 MJ /m³ and 9.7 MJ /m³ (SWP 5 and SWP 10, respectively). This can be attributed to the lower amount of CH₄, which was only partly compensated for by the significant increase in H₂ yield. However, due to the increase in the total gas yield, the gas energy content of the ochre amended softwood samples increased to 115% (1.179 MJ kg⁻¹) for SWP 5, and 141% (1.434 MJ kg⁻¹) for SWP 10 compared to SWP (Figure 2).

Field Code Changed

Crombie and Mašek (2014) reported comparable values for the same feedstock under different pyrolysis conditions, with a reported lower energy limit of 1.05 MJ kg⁻¹ for a self-sustaining pyrolysis process. Therefore, the increase in gas energy content due to ochre amendment can provide significant excess heat beside sustaining the pyrolysis process.

Field Code Changed

For wheat straw pyrolysis, the LHV showed a similar but more pronounced trend with increasing Fe content, lowering the LHV from 9.1 MJ / m³ (WSP) to 7.9 MJ / m³ (WSP 5 and WSP 10, respectively). Here, the gas energy content of 0.97 MJ kg⁻¹ was further decreased by ochre amendment due to the lower gas yields. WSP 5 showed a reduction to 72.9 % (0.70 MJ kg⁻¹) compared to WSP, while the gas energy content for WSP 10 was reduced to 70.6% (0.68 MJ kg⁻¹). In contrast to Fe-doped softwood biochar, only the gas energy content of the unamended sample is above the self-sustaining limit of 0.95 MJ kg⁻¹ (Crombie and Mašek, 2014). While ochre amendment increased both the solid yield and the gas energy content for the softwood feedstock, the influence of Fe on wheat straw pyrolysis only increased the

Field Code Changed

char yield while decreasing the gas energy content. This confirms observations by [Collard et al. \(2012\)](#) about the determining influence of the lignocellulosic composition of the feedstock on the effects of Fe addition on the pyrolysis process.

Field Code Changed

3.3 Physical activation in CO₂

Formatted: Not Highlight

Solid activation yields showed only small differences between the two feedstocks (Table 1, S2). Minor effects of ochre addition on activation yields for SWP 5 and WSP 5 could be observed with solid yields changing from 74 % (SWP) to 72.9 % (SWP 5) and 78.2 % (WSP) to 81.2 % (WSP 5) respectively. However, for both feedstocks' solid yields decreased significantly for 10 % amended samples, indicating a non-linear effect of Fe-doping on carbon burn-off with solid yields of 57.7 % and 58.8 % (SWP and WSP). As stated by [Zhou et al. \(2012\)](#), Fe accelerates the reactivity of the carbon matrix with CO₂ by a two-step oxygen transfer mechanism, which results in carbon burn-off and increased CO emissions. Gas emission patterns for softwood activation confirmed the increased reactivity of the ochre amended samples during the whole activation run (Figure 3).

Field Code Changed

The CO emissions for softwood activation started at similar temperatures around 540 °C, but with different intensity at 0.012 mmol g⁻¹ s⁻¹ (SWP), 0.019 mmol g⁻¹ s⁻¹ (SWP 5), and 0.044 mmol g⁻¹ s⁻¹ (SWP 10). A similar trend was observed for the wheat straw series with CO emissions starting around 550 °C with CO peaks of 0.024 mmol g⁻¹ s⁻¹ (WSP) and 0.052 mmol g⁻¹ s⁻¹ (WSP 5). No emission pattern for WSP 10 could be obtained due to operational errors. The steeper decrease of CO emissions after peaking might be explained by the higher initial ash content of wheat straw and a lower absolute amount of available carbon in the samples. [Qian et al.](#)

Field Code Changed

(2016) observed that higher FeCl_3 amendments decreased the optimal activation temperature for a maximised surface area. Therefore, optimising the Fe loading by lowering the activation temperature or time might have prevented the high burn-off for WSP 10 and SWP 10 without compromising the characteristics of the biochars (Hagemann et al., 2020).

Field Code Changed

Due to the increased reactivity of Fe-amended biochars during activation, both feedstocks series showed decreasing total solid yields (Table 1). Similarly, the total solid carbon yield for SWP of 33 % of the total carbon input, decreased to 28.3 % (SWP 5) and 19.3 % (SWP 10). Although the trend for the wheat straw series was comparable, the relative loss of carbon with ochre amendment was lower, likely because of the higher initial ash content of the feedstock. The solid carbon yield decreased from 31 % (WSP) to 23.66 % (WSP10). Lower solid carbon yields affect the carbon sequestration potential of the activated biochars and therefore the environmental impact of the process. While decreased solid carbon yields could at least be partly compensated by the increased gas energy content, the characteristics of the activated biochars are determining the overall efficiency of the ochre amendment.

3.4 Activated biochar characterisation

Activated biochars were washed and sieved to obtain homogenous samples and to achieve a defined particle size of 0.125 - 0.5 mm to avoid a particle size effects in micropollutant adsorption (Kårelid et al., 2017). During the homogenisation, the carbon content increased for all samples (except for SWP 5) due to the loss of mineral matter. However, ICP-OES analysis of the supernatants showed no relevant

Field Code Changed

losses of the Fe, indicating a stable incorporation into the carbon structure. For all samples, Ca, K, and Mg showed minor leaching during water washing as common for biochars (Angst and Sohi, 2013). Feedstock doping lead to a relative reduction in mineral leaching for ochre amended biochars. Proximate analysis before and after the washing and sieving steps revealed that higher amounts of ash fraction were removed during sieving rather than washing. This was confirmed by different ash contents for the particles < 0.125 mm and the fraction between 0.125 - 0.5 mm.

Proximate analysis was used to assess the stability of the samples as the fixed carbon (FC) content is an indication for the graphitisation degree of biochar. For both feedstocks, an increase of volatile matter content and a parallel decrease of fixed carbon content with increasing ochre addition was observed (Table 2). While Fe is known to enhance graphitisation during pyrolysis in an inert atmosphere, it also acts as a catalyst for gasification reactions at higher temperatures in CO₂ atmosphere (Xia et al., 2019). Evaluation of the carbon stability was based on an ash-free basis to give a more accurate picture of the carbon stability as the ash content increased to 17.1 % for SWP 10 and 35.2 % for WSP 10 due to the ochre amendment. The fixed carbon content (ash-free basis) decreased from 93 % (SWP) to 87 % (SWP 5) and 81 % (SWP10). Similar results were found for the wheat straw series with 90 % (WSP), 81 % (WSP5) and 75 % (WSP10).

To confirm the impregnation of Fe into the biochar structure, ICP-OES was used to analyse total Fe content. For softwood biochars, the Fe content increased from 0.08 % (SWP) to 2.51 % (SWP 5) and 3.56 % (SWP 10) and for wheat straw biochars from 0.7 % (WSP) to 3.73 % (WSP 5) and 6.23 % (WSP 10) (Table 2). The higher

Formatted: Not Highlight

Formatted: Not Highlight

Formatted: Not Highlight

Field Code Changed

Fe content in the wheat straw series can be explained by a better impregnation efficiency for mineral rich feedstocks (Collard et al., 2012). Fe speciation was investigated by XRD. All activated ochre amended biochar samples showed main peaks at 29.95 °, 35.25°, 42.9°, 56.9°, and 62.4°, identified as magnetite (Fe₃O₄) or maghemite (γ-Fe₂O₃), which cannot be differentiated in XRD with certainty (Dastgheib et al., 2014). The XRD spectra confirm the successful thermal reduction of goethite to magnetite/maghemite during pyrolysis of biomass. No metallic Fe speciation was identified, which verifies that CO₂ prohibits iron oxide reduction during subsequent physical activation (Qian et al., 2016). Additional broad peaks at 15-30° were attributed to amorphous carbon while the peak at 40-50° was assigned to graphite structures (Xia et al., 2019). The lower intensity of these peaks for ochre amended samples confirms the decreased carbon stability measured by proximate analysis. This can be expected due to the high reactivity of Fe during activation as seen in the increased carbon burn-off and significantly decreased activation yields.

Mass specific magnetic susceptibility (Table 2) was analysed to test if the magnetic properties were sufficient for the separation of the magnetic activated biochars from wastewater. While WSP and SWP showed no relevant magnetic susceptibility, all ochre amended activated biochars showed ferrimagnetic properties sufficient for good separability in wastewater with values ranging from 25,450 x 10⁻⁶ m³ kg⁻¹ (WSP 5) to 47,722 x 10⁻⁶ m³ kg⁻¹ (SWP 10) (Damertey et al., 2020). SEM and EDX analysis confirmed irregularly distributed magnetite or maghemite particles on the surface of the ochre amended biochars. Fe was mainly found in larger cavities of the biochar structure with agglomerated spherical shapes of sizes up to 20 µm.

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Formatted: Not Highlight

Field Code Changed

Specific surface area (SSA) of the softwood series increased with the addition of ochre, following the order SWP < SWP 5 < SWP 10 (Table 2). The SSA increase was accompanied by a rise of the average pore diameter from 1.95 nm for SWP and 2.02 nm (SWP 5) displaying dominantly microporous materials. SWP 10 showed an average pore diameter in the small mesoporous range of 3.21 nm, which corresponds to a rise of 64 %. Additionally, the total pore volume of SWP 10 ($0.584 \text{ cm}^3 \text{ g}^{-1}$) doubled in comparison to SWP ($0.29 \text{ cm}^3 \text{ g}^{-1}$). This increase in pore diameter and volume is especially important for the adsorption performance as contaminants often cannot enter narrow micropores (Bentley and Summers, 2020). The differential pore volume in the narrow micropore region of 1-1.2 nm also increased substantially for SWP 5 and 10, indicating a more pronounced creation of micropores by CO_2 (Figure 4). The additional increase in the mesoporous range at around 5 nm in ochre amended samples could be due to the direct carbon burn-off by the reaction of Fe_3O_4 with CO_2 to CO similar to results obtained by (Cazetta et al., 2016).

The wheat straw series showed the opposite trend in SSA and pore volume with WSP > WSP 5 > WSP 10. However, the average pore diameter increased with ochre addition, from 1.93 nm (WSP) to 2.42 nm (WSP 10). In the case of ash-rich wheat straw, the additional mineral input from ochre might have resulted in pore blocking by iron particles as the reduction in the 5 nm pore range indicates. At the same time, WSP 10 increased the differential pore volume in the narrow micropore range, again confirming the enhanced reactivity of CO_2 with Fe to create new micropores.

3.5 Adsorption performance

Field Code Changed

Field Code Changed

Formatted: Not Highlight

To evaluate the adsorption performance, batch adsorption tests for caffeine were conducted using concentrations between 5 - 500 mg L⁻¹. Isotherm data was best fitted by the Langmuir model indicating monolayer adsorption of caffeine. The maximum adsorption capacity ($q_{\max}$) for the softwood series was higher than for wheat straw, with increasing values for ochre amended samples for both feedstocks. While SWP exhibited an adsorption capacity $q_{\max}$ of 135 mg g⁻¹, it increased to 173 mg g⁻¹ for SWP 5 and 227 mg g⁻¹ for SWP 10 (+ 68%). A similar trend could be observed for wheat straw with 42 mg g⁻¹ for WSP, 123 mg g⁻¹ for WSP 5, similar to WSP 10 (+ 193 %). The maximum adsorption capacity of activated carbons for caffeine is often correlated to the micropore volume, caused by the small critical diameter of 0.45 nm (Galhetas et al., 2014). The activated biochars in this study showed similar or higher adsorption capacity towards caffeine (except WSP) compared to values reported for activated carbons in a recent review (Anastopoulos et al., 2020). Compared to values obtained by Beltrame et al. (2018) of 155 mg g⁻¹ for activated carbon with a higher SSA_{BET} (1031 m² g⁻¹) but lower micropore volume (0.05 cm³ g⁻¹), the importance of the latter for caffeine adsorption can be highlighted. However, when comparing materials with similar SSA, pore volume and micropore volume such as SWP and WSP from this study, SWP still shows a threefold increase in adsorption capacity. One decisive factor could be the ash content of 21 % for WSP in comparison to 1.9 % for SWP. When further comparing WSP and WSP 5, the adsorption capacity increases even as the SSA and micropore volume decreases, suggesting a dominant influence of Fe loading. However, the equivalent adsorption capacity between WSP 5 and WSP 10 indicates additional factors counteracting the

Field Code Changed

Field Code Changed

Field Code Changed

Formatted: Not Highlight

beneficial effects of higher Fe contents. These could be due to the further decrease in SSA and pore volume, or an agglomeration of Fe particles on WSP 10. For the softwood series, the increased adsorption capacity for ochre amended samples confirms the more pronounced influence of Fe doping on caffeine adsorption, despite decreasing micropore volumes.

As for caffeine, the Langmuir model provided better data fitting ($R^2 > 0.91$) indicating monolayer adsorption of fluconazole. Fluconazole adsorption showed a similar trend as caffeine with higher adsorption capacities for the softwood series (58.8 mg g^{-1} – SWP and 18.1 mg g^{-1} - WSP), which further increased with ochre amendment (SWP 5 - 95.0 mg g^{-1} , SWP 10 – 116.7 mg g^{-1}). While the unamended biochars showed significant differences, Fe doping had a similar influence on the adsorption capacity for both samples. With every 1 % increase in total Fe content relative to the unamended biochar, an increase of 14.9 mg g^{-1} (SWP 5), 16.6 mg g^{-1} (SWP 10) and 15.1 mg g^{-1} (WSP 5) could be observed. WSP 10 showed a lower increase of 9.8 mg g^{-1} per 1 % additional iron content, probably due to the agglomeration of Fe particles and therefore less active Fe surface for adsorption. Due to the lack of comparable literature data on fluconazole adsorption on biochars or activated carbons, activated carbon (Aquasorb 2000, Jacobi Carbon) was analysed for comparison. The coal-based powdered activated carbon with superior surface area ($962 \text{ m}^2 \text{ g}^{-1}$) and pore volume ($0.625 \text{ cm}^3 \text{ g}^{-1}$) constitutes a commercial benchmark material optimised for wastewater filtration. It showed an adsorption capacity of 279.6 mg g^{-1} , which is a 2.4-fold higher capacity than SWP 10, and a 3.9-fold increase compared to WSP 10.

While the benchmark activated carbon proves to be superior in terms of adsorption capacity for fluconazole, magnetic activated biochar showed similar performance to fossil activated carbons in the case of caffeine (Anastopoulos et al., 2020; Kozyatnyk et al., 2020).

Field Code Changed

The adsorption capacity is a determining factor to evaluate the environmental impact of carbon adsorbents. Biochars typically outperform fossil based activated carbons in the production phase due to their biomass feedstock source and less energy intensive processing, but the higher adsorption capacity for activated carbons often reverses the outcome through lower dose requirements in wastewater treatment scenarios (Kozyatnyk et al., 2020). However, even moderate capacity biochars with 20 % adsorption capacity of activated carbon can provide environmental benefits as shown by Thompson et al. (2016). Therefore, the lower capacity for fluconazole of 40 % for SWP 10 might be environmentally competitive to fossil carbon adsorbent as the activated biochar is produced from sustainable biomass mixed with mineral waste. Additionally, the increase in pyrolysis gas energy content through the catalytic effects of Fe-doping will further decrease the global warming impact by enabling a self-sustaining pyrolysis process (Kozyatnyk et al., 2020; Thompson et al., 2016).

Field Code Changed

Field Code Changed

Field Code Changed

Beside the energetic benefits in production, the magnetic properties provide additional cost reductions in wastewater treatment due to the facilitation of separation of the adsorbent from the liquid phase. To evaluate the overall performance of magnetic activated biochars, a comparative life-cycle analysis could provide important insights for future research and applications.

4. Conclusions

The lignocellulosic feedstock composition determined the catalytic effects of ochre on all three product fractions, showing the potential to optimise the yield distribution by targeted feedstock selection. For softwood, ochre led to a favourable increase of the gas energy content, enabling cost-savings for this feedstock. However, physical activation conditions must be optimised to achieve increased adsorption performance of the produced biochars while avoiding excessive burn-off. A parallel focus on the production efficiency and product performance can lead to additional synergies in magnetic biochar production and should be used for the development of sustainable, yet efficient carbon adsorbents for wastewater treatment.

Appendix

E-supplementary data of this work can be found in online version of the paper.

Acknowledgements

The authors thank Daniela Polic and Clare Peters for help with the manuscript. This project received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 721991.

References

1. Ahmed, M.B., Zhou, J.L., Ngo, H.H., Guo, W., 2015. Adsorptive removal of

Field Code Changed

- antibiotics from water and wastewater: Progress and challenges. *Sci. Total Environ.* 532, 112–126. <https://doi.org/10.1016/j.scitotenv.2015.05.130>
2. Alipour Moghadam, R., Yusup, S., Azlina, W., Nehzati, S., Tavasoli, A., 2014. Investigation on syngas production via biomass conversion through the integration of pyrolysis and air-steam gasification processes. *Energy Convers. Manag.* 87, 670–675. <https://doi.org/10.1016/j.enconman.2014.07.065>
 3. Alygizakis, N.A., Besselink, H., Paulus, G.K., Oswald, P., Hornstra, L.M., Oswaldova, M., Medema, G., Thomaidis, N.S., Behnisch, P.A., Slobodnik, J., 2019. Characterization of wastewater effluents in the Danube River Basin with chemical screening, in vitro bioassays and antibiotic resistant genes analysis. *Environ. Int.* 127, 420–429. <https://doi.org/10.1016/j.envint.2019.03.060>
 4. Anastopoulos, I., Pashalidis, I., Orfanos, A.G., Manariotis, I.D., Tatarchuk, T., Sellaoui, L., Bonilla-Petriciolet, A., Mittal, A., Núñez-Delgado, A., 2020. Removal of caffeine, nicotine and amoxicillin from (waste)waters by various adsorbents. A review. *J. Environ. Manage.* 261. <https://doi.org/10.1016/j.jenvman.2020.110236>
 5. Angst, T.E., Sohi, S.P., 2013. Establishing release dynamics for plant nutrients from biochar. *GCB Bioenergy* 5, 221–226. <https://doi.org/10.1111/gcbb.12023>
 6. Beltrame, K.K., Cazetta, A.L., de Souza, P.S.C., Spessato, L., Silva, T.L., Almeida, V.C., 2018. Adsorption of caffeine on mesoporous activated carbon fibers prepared from pineapple plant leaves. *Ecotoxicol. Environ. Saf.* 147, 64–71. <https://doi.org/10.1016/j.ecoenv.2017.08.034>
 7. Bentley, M.J., Summers, R.S., 2020. Ash pretreatment of pine and biosolids produces biochars with enhanced capacity for organic micropollutant removal from

- surface water, wastewater, and stormwater. *Environ. Sci. Water Res. Technol.* 6, 635–644. <https://doi.org/10.1039/c9ew00862d>
8. Buss, W., Graham, M.C., Shepherd, J.G., Mašek, O., 2016. Suitability of marginal biomass-derived biochars for soil amendment. *Sci. Total Environ.* 547, 314–322. <https://doi.org/10.1016/j.scitotenv.2015.11.148>
 9. Cazetta, A.L., Pezoti, O., Bedin, K.C., Silva, T.L., Paesano Junior, A., Asefa, T., Almeida, V.C., 2016. Magnetic Activated Carbon Derived from Biomass Waste by Concurrent Synthesis: Efficient Adsorbent for Toxic Dyes. *ACS Sustain. Chem. Eng.* 4, 1058–1068. <https://doi.org/10.1021/acssuschemeng.5b01141>
 10. Chen, Z.F., Ying, G.G., 2015. Occurrence, fate and ecological risk of five typical azole fungicides as therapeutic and personal care products in the environment: A review. *Environ. Int.* 84, 142–153. <https://doi.org/10.1016/j.envint.2015.07.022>
 11. Collard, F.X., Bensakhria, A., Drobek, M., Volle, G., Blin, J., 2015. Influence of impregnated iron and nickel on the pyrolysis of cellulose. *Biomass and Bioenergy* 80, 52–62. <https://doi.org/10.1016/j.biombioe.2015.04.032>
 12. Collard, F.X., Blin, J., Bensakhria, A., Valette, J., 2012. Influence of impregnated metal on the pyrolysis conversion of biomass constituents. *J. Anal. Appl. Pyrolysis* 95, 213–226. <https://doi.org/10.1016/j.jaap.2012.02.009>
 13. Correa, C.R., Kruse, A., 2018. Biobased functional carbon materials: Production, characterization, and applications-A review. *Materials* (Basel). <https://doi.org/10.3390/ma11091568>
 14. Crombie, K., Mašek, O., 2014. Investigating the potential for a self-sustaining slow pyrolysis system under varying operating conditions. *Bioresour. Technol.* 162,

- 148–156. <https://doi.org/10.1016/j.biortech.2014.03.134>
15. Crombie, K., Mašek, O., Sohi, S.P., Brownsort, P., Cross, A., 2013. The effect of pyrolysis conditions on biochar stability as determined by three methods. *GCB Bioenergy* 5, 122–131. <https://doi.org/10.1111/gcbb.12030>
 16. Cruz, D., Almeida, Â., Calisto, V., Esteves, V.I., Schneider, R.J., Wrona, F.J., Soares, A.M.V.M., Figueira, E., Freitas, R., 2016. Caffeine impacts in the clam *Ruditapes philippinarum*: Alterations on energy reserves, metabolic activity and oxidative stress biomarkers. *Chemosphere* 160, 95–103. <https://doi.org/10.1016/j.chemosphere.2016.06.068>
 17. Damertey, D., Nguyen, H., Ohemeng-boahen, G., Han, S., 2020. Science of the Total Environment Facile magnetic biochar production route with new goethite nanoparticle precursor. *Sci. Total Environ.* 717, 137091. <https://doi.org/10.1016/j.scitotenv.2020.137091>
 18. Dastgheib, S.A., Ren, J., Rostam-Abadi, M., Chang, R., 2014. Preparation of functionalized and metal-impregnated activated carbon by a single-step activation method. *Appl. Surf. Sci.* 290, 92–101. <https://doi.org/10.1016/j.apsusc.2013.11.005>
 19. Dulio, V., van Bavel, B., Brorström-Lundén, E., Harmsen, J., Hollender, J., Schlabach, M., Slobodnik, J., Thomas, K., Koschorreck, J., 2018. Emerging pollutants in the EU: 10 years of NORMAN in support of environmental policies and regulations. *Environ. Sci. Eur.* 30. <https://doi.org/10.1186/s12302-018-0135-3>
 20. Enders, A., Lehmann, J., 2012. Comparison of Wet-Digestion and Dry-Ashing Methods for Total Elemental Analysis of Biochar. *Commun. Soil Sci. Plant Anal.* 43, 1042–1052. <https://doi.org/10.1080/00103624.2012.656167>

21. Galhetas, M., Mestre, A.S., Pinto, M.L., Gulyurtlu, I., Lopes, H., Carvalho, A.P., 2014. Chars from gasification of coal and pine activated with K₂CO₃: Acetaminophen and caffeine adsorption from aqueous solutions. *J. Colloid Interface Sci.* 433, 94–103. <https://doi.org/10.1016/j.jcis.2014.06.043>
22. Hagemann, N., Schmidt, H.P., Kägi, R., Böhrer, M., Sigmund, G., Maccagnan, A., Mc Ardell, C.S., Bucheli, T.D., 2020. Wood-based activated biochar to eliminate organic micropollutants from biologically treated wastewater. *Sci. Total Environ.* 730, 138417. <https://doi.org/10.1016/j.scitotenv.2020.138417>
23. Huang, Y., Anderson, M., McIlveen-Wright, D., Lyons, G.A., McRoberts, W.C., Wang, Y.D., Roskilly, A.P., Hewitt, N.J., 2015. Biochar and renewable energy generation from poultry litter waste: A technical and economic analysis based on computational simulations. *Appl. Energy* 160, 656–663. <https://doi.org/10.1016/j.apenergy.2015.01.029>
24. Huang, Y.F., Kuan, W.H., Chiueh, P.T., Lo, S.L., 2011. Pyrolysis of biomass by thermal analysis-mass spectrometry (TA-MS). *Bioresour. Technol.* 102, 3527–3534. <https://doi.org/10.1016/j.biortech.2010.11.049>
25. Kårelid, V., Larsson, G., Björleinius, B., 2017. Pilot-scale removal of pharmaceuticals in municipal wastewater: Comparison of granular and powdered activated carbon treatment at three wastewater treatment plants. *J. Environ. Manage.* 193, 491–502. <https://doi.org/10.1016/j.jenvman.2017.02.042>
26. Kozyatnyk, I., Yacout, D.M.M.M., Caneghem, J. Van, Jansson, S., Van Caneghem, J., Jansson, S., 2020. Comparative environmental assessment of end-of-life carbonaceous water treatment adsorbents. *Bioresour. Technol.* 302, 122866.

- <https://doi.org/10.1016/j.biortech.2020.122866>
27. Kumar, K.V., 2006. Comparative analysis of linear and non-linear method of estimating the sorption isotherm parameters for malachite green onto activated carbon. *J. Hazard. Mater.* 136, 197–202.
<https://doi.org/10.1016/j.jhazmat.2005.09.018>
28. Li, R., Wang, J.J., Gaston, L.A., Zhou, B., Li, M., Xiao, R., Wang, Q., Zhang, Z., Huang, Hui, Liang, W., Huang, Heteng, Zhang, X., 2018. An overview of carbothermal synthesis of metal–biochar composites for the removal of oxyanion contaminants from aqueous solution. *Carbon N. Y.* 129, 674–687.
<https://doi.org/10.1016/j.carbon.2017.12.070>
29. Li, R., Zhang, Y., Deng, H., Zhang, Z., Wang, J.J., Shaheen, S.M., Xiao, R., Rinklebe, J., Xi, B., He, X., Du, J., 2020. Removing tetracycline and Hg(II) with ball-milled magnetic nanobiochar and its potential on polluted irrigation water reclamation. *J. Hazard. Mater.* 384, 121095.
<https://doi.org/10.1016/j.jhazmat.2019.121095>
30. Li, X., Wang, C., Zhang, J., Liu, J., Liu, B., Chen, G., 2020. Preparation and application of magnetic biochar in water treatment: A critical review. *Sci. Total Environ.* 711, 134847. <https://doi.org/10.1016/j.scitotenv.2019.134847>
31. Mašek, O., Buss, W., Roy-Poirier, A., Lowe, W., Peters, C., Brownsort, P., Mignard, D., Pritchard, C., Sohi, S., 2018. Consistency of biochar properties over time and production scales: A characterisation of standard materials. *J. Anal. Appl. Pyrolysis* 132, 200–210. <https://doi.org/10.1016/j.jaap.2018.02.020>
32. Östman, M., Lindberg, R.H., Fick, J., Björn, E., Tysklind, M., 2017. Screening of

- biocides, metals and antibiotics in Swedish sewage sludge and wastewater. *Water Res.* 115, 318–328. <https://doi.org/10.1016/j.watres.2017.03.011>
33. Paethanom, A., Bartocci, P., D'Alessandro, B., D'Amico, M., Testarmata, F., Moriconi, N., Slopicka, K., Yoshikawa, K., Fantozzi, F., 2013. A low-cost pyrogas cleaning system for power generation: Scaling up from lab to pilot. *Appl. Energy* 111, 1080–1088. <https://doi.org/10.1016/j.apenergy.2013.06.044>
 34. Paíga, P., Ramos, S., Jorge, S., Silva, J.G., Delerue-Matos, C., 2019. Monitoring survey of caffeine in surface waters (Lis River) and wastewaters located at Leiria Town in Portugal. *Environ. Sci. Pollut. Res.* 26, 33440–33450. <https://doi.org/10.1007/s11356-019-06168-w>
 35. Perera-Solis, D.D., Pimlott, M., Fidment, E., Whiting, A., Greenwell, H.C., 2019. Adding value to waste minerals in a circular economy framework: Ochre-derived layered double hydroxide catalysts in fatty acid ketonisation. *Minerals* 9, 7–9. <https://doi.org/10.3390/min9110681>
 36. Qian, F., Zhu, X., Liu, Y., Hao, S., Ren, Z.J., Gao, B., Zong, R., Zhang, S., Chen, J., 2016. Synthesis, characterization and adsorption capacity of magnetic carbon composites activated by CO₂: Implication for the catalytic mechanisms of iron salts. *J. Mater. Chem. A* 4, 18942–18951. <https://doi.org/10.1039/c6ta06614c>
 37. Rocha, L.S., Pereira, D., Sousa, É., Otero, M., Esteves, V.I., Calisto, V., 2020. Recent advances on the development and application of magnetic activated carbon and char for the removal of pharmaceutical compounds from waters: A review. *Sci. Total Environ.* 718. <https://doi.org/10.1016/j.scitotenv.2020.137272>
 38. Sapsford, D., Santonastaso, M., Thorn, P., Kershaw, S., 2015. Conversion of coal

- mine drainage ochre to water treatment reagent: Production, characterisation and application for P and Zn removal. *J. Environ. Manage.* 160, 7–15.
<https://doi.org/10.1016/j.jenvman.2015.06.004>
39. Shepherd, J.G., Sohi, S.P., Heal, K. V., 2016. Optimising the recovery and re-use of phosphorus from wastewater effluent for sustainable fertiliser development. *Water Res.* 94, 155–165. <https://doi.org/10.1016/j.watres.2016.02.038>
40. Sophia A., C., Lima, E.C., 2018. Removal of emerging contaminants from the environment by adsorption. *Ecotoxicol. Environ. Saf.* 150, 1–17.
<https://doi.org/10.1016/j.ecoenv.2017.12.026>
41. Thommes, M., Kaneko, K., Neimark, A. V., Olivier, J.P., Rodriguez-Reinoso, F., Rouquerol, J., Sing, K.S.W., 2015. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure Appl. Chem.* 87, 1051–1069. <https://doi.org/10.1515/pac-2014-1117>
42. 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, 11253–11262.
<https://doi.org/10.1021/acs.est.6b03239>
43. Wang, L., Ok, Y.S., Tsang, D.C.W., Alessi, D.S., Rinklebe, J., Wang, H., Mašek, O., Hou, R., O'Connor, D., Hou, D., 2020. New Trends in Biochar Pyrolysis and Modification Strategies: Feedstock, Pyrolysis Conditions, Sustainability Concerns and Implications for Soil Amendment. *Soil Use Manag.* 1–29.
<https://doi.org/10.1111/sum.12592>
44. Wang, S., Gao, B., Zimmerman, A.R., Li, Y., Ma, L., Harris, W.G., Migliaccio,

- K.W., Gao, B., Migliaccio, K.W., Wang, S., Li, Y., Gao, B., Zimmerman, A.R., Li, Y., Ma, L., Harris, W.G., Migliaccio, K.W., Gao, B., Migliaccio, K.W., Wang, S., Li, Y., 2015. Removal of arsenic by magnetic biochar prepared from pinewood and natural hematite. *Bioresour. Technol.* 175, 391–395.
<https://doi.org/10.1016/j.biortech.2014.10.104>
45. Xia, S., Li, K., Xiao, H., Cai, N., Dong, Z., xu, C., Chen, Y., Yang, H., Tu, X., Chen, H., 2019. Pyrolysis of Chinese chestnut shells: Effects of temperature and Fe presence on product composition. *Bioresour. Technol.* 287.
<https://doi.org/10.1016/j.biortech.2019.121444>
46. Yan, L., Kong, L., Qu, Z., Li, L., Shen, G., 2015. Magnetic Biochar Decorated with ZnS Nanocrytals for Pb (II) Removal. *ACS Sustain. Chem. Eng.* 3, 125–132.
<https://doi.org/10.1021/sc500619r>
47. Yang, Y.Y., Liu, W.R., Liu, Y.S., Zhao, J.L., Zhang, Q.Q., Zhang, M., Zhang, J.N., Jiang, Y.X., Zhang, L.J., Ying, G.G., 2017. Suitability of pharmaceuticals and personal care products (PPCPs) and artificial sweeteners (ASs) as wastewater indicators in the Pearl River Delta, South China. *Sci. Total Environ.* 590–591, 611–619. <https://doi.org/10.1016/j.scitotenv.2017.03.001>
48. Zhou, Z.J., Hu, Q.J., Liu, X., Yu, G.S., Wang, F.C., 2012. Effect of iron species and calcium hydroxide on high-sulfur petroleum coke CO₂ gasification. *Energy and Fuels* 26, 1489–1495. <https://doi.org/10.1021/ef201442t>

Figure captions

Figure 1. Pyrolysis gas emission patterns ($\text{mmol g}^{-1} \text{ s}^{-1}$ feedstock).

Figure 2. Pyrolysis gas yields (mmol g^{-1} feedstock d.b.) and gas energy content (MJ kg^{-1} feedstock d.b.).

Figure 3. Activation gas emission patterns ($\text{mmol g}^{-1} \text{ s}^{-1}$ feedstock).

Figure 4. Pore size distribution 1 nm to 14 nm (QSDFT) of a) softwood biochars, and b) wheat straw biochars.

Table captions

Table 1. Product yield distribution (wt. % d.b.).

Table 2. Physico-chemical properties of activated biochars.