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G.L. Sullivan, P.J. Holliman



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Thermal treatment of Himalayan balsam: tar and biochar analysis

G. L. Sullivan^{a,*}, P.J. Holliman^b.

^a SPECIFIC, Engineering East Swansea University, UK, SA2 8PP.

^bCEMEG, Engineering East Swansea University, UK, SA2 8PP.

*Corresponding author at:

Tel.: +44 1792 606646.

Email address: G.L.Sullivan@swansea.ac.uk

Email address: P.J.Holliman@swansea.ac.uk

Abstract.

The practicality of Himalayan balsam as an alternative biomass material was considered throughout this investigation. However, due to the materials high-water content, thermal efficiency during pyrolysis was compromised as extra energy was required to remove free and bound water. A simple solution which involved drying at ambient temperature in air, significantly lowered the moisture content, (65 % reduction) this resulted in an increase in the bulk density of the material and lowering the thermal energy input of the process. The thermal decomposition process at 300-400 ° C generated petroleum like compound; a mixture of volatile aromatic, linear and branched alkanes, and therefore a possible source for replenishment of hydrocarbon-based fuel. The solid remaining carbon generated (~ 35 % mass of dry material) termed biochar showed adsorption properties to rhodamine B dye. The level of activity was increased upon activation using phosphoric acid. The activated biochar could be a promising adsorbent used to remove aqueous organic compounds. The thermal treatment of Himalayan balsam has potential in generating useful products such as bio-fuels and biochar.

Key words

Pyrolysis

Activated Biochar

Biomass recycling

Thermal treatment

Bio-oil

Himalayan balsam

1. Introduction

Himalayan balsam (*Impatiens glandulifera*), is a relatively attractive plant with pink flowering parts and a fleshy stem, but is not native to the Northern hemisphere, and is considered an invasive species (Kelly et al., 2008). Himalayan balsam is found along river banks, woodland areas and flushes (Kelly et al., 2008) and outcompetes native plant species (Emer et al., 2015). In the Autumn months, it dies back, leaving banks scarce and bare with no winter vegetation (Kelly et al., 2008). Control of Himalayan balsam can be achieved through uprooting and cutting of the plant, but this can lead to further dispersal of seeds if not disposed carefully. Chemical treatment using glyphosate is an effective treatment method but there are concerns with its wider environmental impact on aquatic life (Kelly et al., 2008; Tarazona et al., 2017). Thermal treatment of Himalayan balsam using pyrolysis is under investigation, but may be an attractive method of disposal as intense heating destroys the seeds and flowering parts while potentially generating heat energy and value-added products. Pyrolysis involves heating carbonaceous material such as biomass in an inert (low oxygen) environment between

temperatures of 400-700° C (Al Arni, 2018; Brownsort, 2009). Himalayan balsam largely comprised of organic compounds such as cellulose, hemicellulose and lignin and therefore a potential candidate for thermal treatment processes (Brownsort, 2009; Kuglerová et al., 2017; Mohan et al., 2006). During pyrolysis of biomass, the material will change both structurally and chemically and in turn generate solids, liquids and gases. Generally, these changes happen in stages with the loss of free and bound moisture between 100-150 °C (Garcia-Perez, 2008; Ronsse et al., 2015), and the degradation of cellulosic compounds (cellulose and hemicellulose) around to 200 to 320 °C. These are primary reactions (which are highly endothermic), forming primary char or light gases or alternatively to form organic tars (Garcia-Perez, 2008; Ronsse et al., 2015). Lignin the third major structural material of biomass degrades over a wider temperature range 160-900 °C generating a wide range of phenolic compounds (Brebú and Vasile, 2010; Garcia-Perez, 2008; Kibet et al., 2012). Light aromatic compounds can evolve at low temperature charring processes between 300-400 °C (cracking secondary reactions) this is usually an exothermic process. The products generated from pyrolysis are syngas (30 %) oil (35 %) and char (35 %)(Brownsort, 2009; Marshall et al., 2014; Mohan et al., 2006). The remaining solid char, is a highly graphitised material, with many applications and has been effective in land remediation and fertility (Nartey and Zhao, 2014; Ogonnaya and Semple, 2013; Ok, 2015; Oliveira et al., 2017; Tan et al., 2015) and removal of contaminants in wastewater treatment (Han et al., 2016; Oliveira et al., 2017; Tan et al., 2015). The surface chemistry of biochar contains a number of functional groups that allows it to adsorb different pollutants. Biochar used in heavy metals removal through cation exchange (organic acids side groups), electrostatic interaction (oxygen containing functional groups), surface complexation

(cation- π) and precipitation mechanisms (Oliveira et al., 2017; Shen et al., 2018; Tan et al., 2015). The removal of organic pollutants has also been demonstrated and mechanisms include: non-polar, π - π interactions within graphene layers, hydrogen bonding with oxygen functional groups, electrostatic interaction between carboxylate and phenolic groups (Chen and Zhou, 2008; Tan et al., 2015) and pore filling mechanisms (Chen and Zhou, 2008; Oliveira et al., 2017). Activation of biochar has been shown to increase the loading capacity of adsorbates over non-activated material; the process of activation tends to increase surface area and functionalisation of the carbonaceous materials and therefore, increases its binding affinities towards adsorbates (Kawano et al., 2008; Mohammad-Khah et al., 2009)

This investigation will use of a hyphenated simultaneous thermal analysis- Fourier transform infrared- gas chromatography- mass spectrometry (STA-FTIR-GCMS), to study heat flow (differential scanning calorimetry (DSC)), mass loss (using thermogravimetric analysis (TGA)), and evolved gases (using FTIR and GCMS) generated in the heating process. The remaining biochar will be analysed using rapid solid FTIR analysis and Brunauer-Emmett-Teller (BET), to determine the chemical character and surface area of the material. Larger quantities of biochar (generated using a tube furnace) will be investigated as an adsorbent for Rhodamine B dye (simulate removal organic contaminant), from aqueous solutions. Rhodamine B is an organic dye with several functional groups which that can potentially interacted to biochar. Rhodamine B, may bind through aromatic dispersion forces, strong cation (quaternary amine group) and weak ionic exchanges (carboxylic acid) and interact through hydrogen bonding (nitrogen and oxygen groups). A comparison of non-activated and activated biochar will be investigated using this method; which in turn

will be used to estimate the of loading capacity and active sites of the material. It will be anticipated that

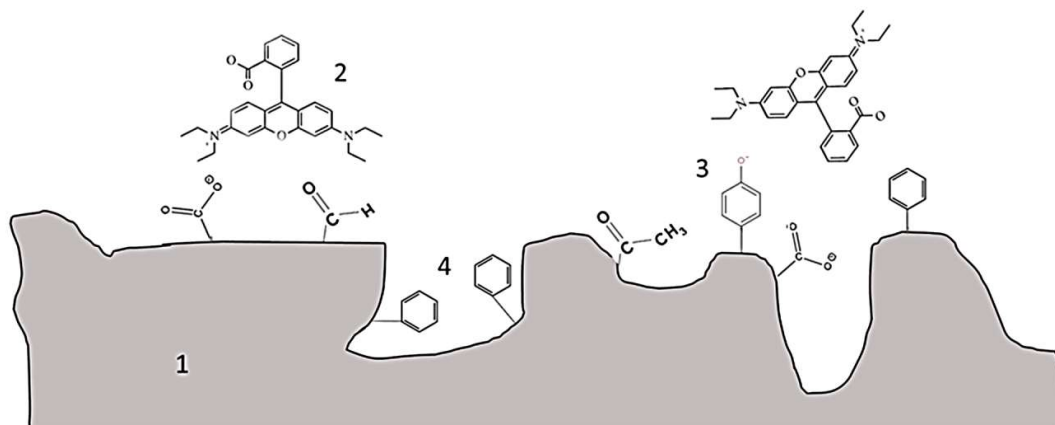


Figure 1. Illustrating the potential interactions between biochar (1) and rhodamine B (2). Interactions may include; non-polar π - π , electrostatic interaction (3), pore filling mechanisms (4) and dipole-dipole interactions (hydrogen bonding).

2 Materials and Methods

2.1 Standard reference materials

Rhodamine B, were purchased from Sigma Aldrich (Suffolk, UK). Phosphoric acid and ultrapure water were obtained from Fisher Scientific (Loughborough, UK). Ultra-pure helium gas (for GC), Nitrogen gas (pure grade) and compressed air (for the STA) was purchased from British oxygen company (BOC). Himalayan balsam (stem, flowers and leaves) were handpicked from two locations (Pontardawe 51.713663, -3.859638 and Ystalyfera 51.758435 -3.790307, South Wales UK)

2.2 Instrumentation

Thermal analysis and compound identification were undertaken using a Perkin Elmer hyphenated STA-FTIR-GCMS (STA 6000, FTIR Spectrum 1000, GC Clarus 680, MS Clarus

600 T). Surface characterisation was carried out using a Perkin Elmer FTIR Frontier for rapid solid sample analysis and a BET using a Quantachrome, NOVA 2000e instrument to characterise surface area and porosity. The vacuum manifold, pump and 3 ml empty SPE cartridges were purchased from Supelco (Sigma Aldrich corporation, Suffolk, UK) to set up the adsorption experiment.

2.3 Standard solutions

10 mg of Rhodamine B powder was dissolved in 100 mL deionised water to generate a 100 mg/L stock solution. This was then diluted by a factor of 10 to generate a 10 mg/L working solution.

2.4 Method for Hyphenated STA-FTIR-GCMS.

Thermal analysis of balsam required 50 to 100 mg of sample was placed into a ceramic STA pan, this was heated from 30 (hold 1 minute) to 500 °C (hold 5 minutes) at 10 °C per minute ramp. The purge gas was nitrogen for pyrolytic conditions (30 mL per minute) ensuring no oxygen was present. This gas could be exchanged for compressed air (30 mL per minute) to simulate oxidation conditions. Gaseous contents were drawn through to FTIR and GC-MS using a pump flow rate of 50 mL per minute. Transfer lines from STA to FTIR and FTIR to GC-MS, were maintained at 300 °C to prevent compound condensation. The gas sampling valve into GC was also kept at 300 °C, again to prevent compound condensation, in the sampling valve. The FTIR operated at a scan rate of 350- 4000 cm^{-1} , for 2 accumulations per second, over the duration of the STA run time (54 minutes). The GC was triggered using an external trigger box at different temperature events (200, 300, 400, 500 °C). The following GC method was used: GC sample loop fill of 1 minute, oven ramp 50-300 °C, using 10 °C per minute

with a hold at 300 ° C for 5 minutes. MS acquisition was in full scan from 30-450 m/z from 1 minute to 28 minutes (over duration of GC run).

2.5 Method for biochar production and characterisation

2.5.1 Biochar production and activation

20 g of dried balsam was heated in a sealed crucible at 350 ° C for 1 hour in a tube furnace. Half of the biochar material was retained for characterisation (non-activated biochar), and while the other half was treated with 3M phosphoric acid for 1 hour to chemically treat the material. The treated biochar was then filtered, and the filtrate, washed through five times with deionised water to ensure all the phosphoric acid was removed. Finally, it was oven dried for 1 hour at 100 ° C and was termed activated biochar.

2.5.1 FTIR Frontier.

Solid material placed over crystal housing and pressed down using the gauge with a force of 30 (arbitrary units). Scan was between 650-4000 cm^{-1} , with 4 accumulations per second, to get an average spectrum.

2.5.2 Brunauer-Emmett-Teller (BET) analysis.

0.03 to 0.05 g of material was degassed overnight under vacuum at 100 ° C prior analysis using multi BET. Samples were prepared in a pre-calibrated tube and immersed into a liquid nitrogen bath while the instrument commenced with adsorption and desorption tests (Brame and Griggs, 2016). This is achieved by the introduction of set amounts of nitrogen gas to calculate P/P_0 , (where p is the equilibrium pressure of nitrogen and P_0 is the saturation pressure of nitrogen

gas)(Brame and Griggs, 2016). The value of P/P_0 is plotted to generate an isotherm used to determine surface area and pore volume (Brame and Griggs, 2016).

2.6 Method for adsorption of Rhodamine B, dye simulating a treatment bed.

To analyse the adsorption of Rhodamine B by activated and non-activated biochar. 0.2 g of material was placed into an empty SPE cartridge, which only contained some glass wool (prevent loss of biochar) to simulate a treatment bed, in which contaminated water passes over the sorbent. Several washes were performed using deionised water on the biochar prior to the experiment. Once satisfied (blank biochar value $<0.050 \text{ cm}^{-1}$), 2ml of 10 mg/L rhodamine B solution (1 mL is equivalent to the addition of 10 μg of rhodamine B) was applied to the biochar and allowed to elute under gravity into a plastic cuvette. The cuvette was then analysed using the UV-VIS spectrometer at the set wavelength of 554 nm. This process was continued until absorbance plateaued, this was the saturation point.

The standard working solution was diluted accordingly to generate a series of calibration standards, 0.5, 1.0, 2.5, 4.0, 5.0 and 10 mg/L. Each standard was assessed using a UV-vis spectrophotometer set at a wavelength of 554 nm. The absorbance was then plotted versus concentration to generate a standard calibration curve and linearity assessed using regression statistics (R^2), a value greater than 0.98 was deemed acceptable. To assess the accuracy and precision of the method; a quality control standard, generated using a separate stock solution was diluted to give a concentration of 2.5 mg/L and run in 10 times against the calibration curve. Precision and accuracy were found to be 4.25 and 14.5 % below the critical value of 20 % used for ISO 17025 UKAS standards (ISO, 2006). Therefore, the method was deemed

appropriate. Some additional blanks and control samples were analysed beforehand to assess any possible losses of carryover of the experiment:

- Biochar blank- 2 mL deionised water added to biochar in SPE tube collected and analysed to attain a baseline of potential matrix.
- SPE- Blank- 2 mL deionised water past through SPE cartridge and glass wool, to ensure no contaminated that may be present that will interfere with base line.
- Recovery QC- 2 mL of stock solution was passed through SPE cartridge containing glass wool, to assess whether any losses occurred due to compound adhesion to the plastic wall and glass wool. This QC was compared to the adsorption stock solution.

3.0 Results and Discussion

3.1 Thermal treatment of Himalayan balsam.

Undried Himalayan balsam, has a high-water content 87.9 % which lowers its attractiveness for use as a biomass for thermal treatment. During heating under pyrolytic conditions (N_2 purge gas) It was observed from the DSC curve on the STA that it requires an average 1553 J/g of energy to remove the free and bound water (30-150 °C). To maximise the efficiency of thermal treatment, drying is necessary to reduce the energy input required to remove moisture and increase the bulk density of the material. Allowing the material to dry at an ambient temperature and exposed to air (air drying) for 72 hours provided a successful, energy saving means to reducing the free water of Himalayan balsam (60.8% reduction by mass). Conversely, this lowered DSC endotherm to an average of 299 J/g and therefore reducing the overall energy input required to heat the material. After air drying, the mass loss by water was

reduced to 26.58 %. Which conversely increased the remaining solid material in air dried sample (~ 30 % mass by weight) over the non-dried material (~8 % mass by weight). It was noted that an exotherm on the air-dried material around 350 °C, was believed to be a result of carbonization reactions taking place to form biochar. Carbonization reactions usually result in the loss of volatile compounds and carbon monoxide (Ronsse et al., 2015). FTIR of the evolved gases confirmed this with the generation of the CO (doublet peak around 2100 cm^{-1}) and aromatic peaks (1506 and around 3000 cm^{-1}). The GC-MS data captured at 300 and 400 °C around this time point also indicates the presence of volatile organic compounds being emitted. This same exotherm was seen when control conditions were altered to simulated combustion (Air carrier gas). The DSC curve for combustion show similar similarities to pyrolysis DSC, however, there is a second much greater exotherm at 450 °C, suggesting that oxidation of the carbon material. The net energy output from this 2032 J/g, which is more than the energy that was put into the system (417 J/g). The FTIR data of the evolved gases suggested the presence of CO_2 and no tar compounds were detected on the GC-MS at 500 °C. Therefore, oxidation of the tars (and biochar material) had occurred.

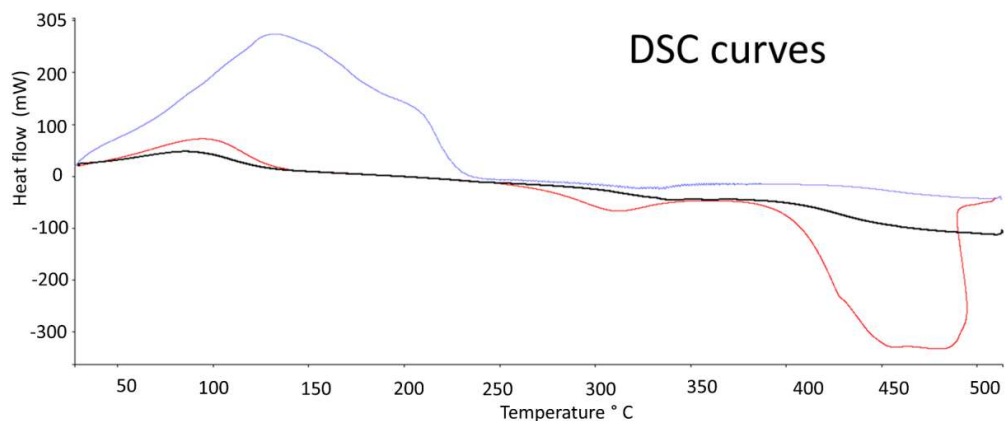


Figure 2. Shows DSC plot for non-dried balsam heated in nitrogen (blue), air dried balsam in heated nitrogen (black) and dried balsam heated in air (red). The endotherms associated with water loss (100- 150 °C) is reduced considerably by air drying and the large exotherm (450 °C) during heating in air is associated with oxidation of the material.

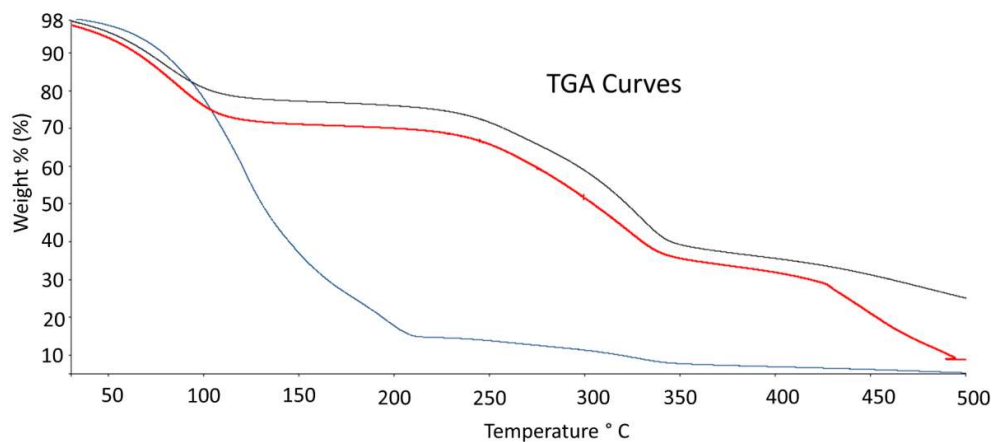


Figure 3. shows TGA plots for non-dried balsam heated in nitrogen (blue), air dried balsam heated in nitrogen (black) and dried balsam heated in air (red). 8% material is remaining after heating in air compared to whilst ~30 % of dried material heated in nitrogen. 87 % of non-dried Himalayan balsam is water.

	Non-dried balsam (N ₂)		Air dried balsam (N ₂)		Air dried balsam (Air)	
	Average	RSD	Average	RSD	Average	RSD
Endotherm 1	1553.5 J/g	2.1 %	299.1 J/g	19.5 %	455.0 J/g	17.5 %
First mass loss	86.3 %	1.7 %	21.75 %	3.12 %	28.0 %	16.2 %
Exotherm 1	-	-	-13.62 J/g	19.5 %	-36.6 J/g	19.9 %
Exotherm 2	-	-	-	-	-2249.5 J/g	9.67 %

Table 1. Summarises the typical DSC and TGA values obtained from the heating of balsam in different conditions. The precision for the replicates, are below 20 % indicating good repeatability of batches.

3.2 GC MS results.

GC-MS results detected most of tar (volatile) compounds around 300 and 400 ° C regardless if samples (air dried) are heated in nitrogen or air. The compounds identified were almost identical for the both heating conditions (air or nitrogen environments). At 300 ° C the emerging compounds contain volatile aromatics such as benzene, toluene, xylene, and ethyl benzene (BTEX) which may signify the beginning of carbonization reactions (Ronsse et al., 2015). The presence of furfural is synonymous with the breakdown product of cellulose sugars (Shen and Gu, 2009). At 400 ° C BTEX are accompanied with additional compounds; linear and branched alkanes. The presence of these larger molecules is likely linked to higher pyrolytic temperatures. At temperatures above 500 ° C only benzene and toluene are present. However, in nitrogen atmosphere toluene at 500 ° C has increased fourfold compared to 400 ° C (determined by comparison of area counts). Conversely, while in air, toluene is

significantly lower at 500 °C (tenfold decrease) than 400 °C, suggesting some oxidation of the tars.

Himalayan balsam air dried (N ₂)		
300 ° C trigger event	400 ° C trigger event	500 ° C trigger event
Compound Name	Compound Name	Compound Name
1-Methylcyclopropanemethanol	1-Methylcyclopropanemethanol	Benzene
Benzene	Benzene	Toluene
Toluene	Toluene	
Furfural	p-Xylene	
Ethylbenzene	o-Xylene	
1,3-Cyclopentendione	Decane	
1-cyano-2 methylpyrrolidine	Undecane	
Benzaldehyde	Dodecane	
	Undecane, 2,6-dimethyl	
	2,6,10 Trimethyldodecane	
	Tetradecane	
	Pentadecane	

Table 2. A summary table of the compounds identified at different temperature points during the pyrolysis of air dried Himalayan balsam using the STA-FTIR-GCMS. Compounds emerging at 400 °C comprise of volatile aromatic, linear and branched hydrocarbons, similar compounds found in petroleum distillates.

3.3 Biochar production and characterisation.

The char generated was analysed using rapid solid FTIR analysis before and after activation (using phosphoric acid). After phosphoric acid treatment the biochar shows changes to the surface chemistry. The non-activated biochar surface contains carboxylic acids functional groups (peaks at 1560, 1407 cm⁻¹) while the activated biochar presents more aromatic and phenolic compounds functionality (1611, 1317,

1195 cm^{-1}). This method of activation potentially could affect the selectivity of biochar towards different classes of compounds, the presence of more aromatic and phenolic compounds on the activated biochar will likely attract compounds that have similar functionality (those with phenyl groups) which can interact through π - π interactions and cation exchange.

The results from the BET analysis suggest that activation using phosphoric acid has an impact on the biochar structure. There appears to be an increase in surface area of the activated biochar (188.41 m^2/g) versus non-activated biochar (172.70 m^2/g).

Interestingly, the pore size and volume has also increased during activation, which activated biochar possessing average pore size radius of 33.84 Å and volume of 0.32 cc/g , whilst non-activated biochar, exhibiting a smaller average pore size radius of 28.61 Å and volume of 0.25 cc/g . The larger surface area and pore size of the activated material is likely to increase the affinity towards adsorbates through greater number of pore filling mechanisms. Pore filling mechanisms are believed to be significant contributing factor in adsorptive ability of the biochar materials and in the specificity of adsorbate of compounds, which has been investigated extensively (Azargohar, R., Dalai, 2008; Ok, 2015; Paethanom and Yoshikawa, 2012; Tan et al., 2015; Zhou et al., 2010)

3.4 Adsorption of Rhodamine B.

A comparison of adsorption of non-activated and activated biochar demonstrates the importance of the phosphoric acid treatment. Clearly, the phosphoric acid not only alters the surface chemistry (seen in FTIR results) but changes the surface area pore sizes (BET results). This allows the activated material to bind to more rhodamine B

compounds. This is illustrated by the saturation of activated biochar at 2.1 mg/g. This was considerably higher than non-activated biochar (0.6 mg/g). The breakthrough limit was determined to be 0.7 mg/g for the activated biochar again this is significantly greater than the non-activated material which appears to be below 0.05 mg/g. Therefore, activation of biochar using phosphoric acid must expose or generate more surface sites for attraction. In similar investigations using alternative biochar adsorption studies, saturation values are quoted significantly higher than values determined in this experiment (382.3 and 528 mg/g) (Ding et al., 2014; Hema and Arivoli, 2009). In experiments by Hema and Arivoli, 2009 and Ding et al. 2014, the activated carbon is immersed in a concentrated solution and adsorption is measured over a significantly longer time period (up to 6 to 12 h). It was concluded that a longer contact time had greater adsorption for Rhodamine B. It was postulated that two modes of adsorption take place, surface and intra-particle diffusive adsorption (Ding et al., 2014; Hema and Arivoli, 2009). It is highly likely that due to the short residence time (2 mL min^{-1}) of the sample in our experiment, the mechanism for adsorption is likely to be primarily surface driven, (either affinity towards the modified surface functional groups or through filling of larger surface pores) and as a result account for the difference in saturation limits to the literature. However, if this method is to simulate treatment beds whereby water flows over the carbon then retention is going to be low and therefore the predominant mechanism for adherence of compounds will be surface driven.

The total surface-active areas can be estimated from this saturation value, providing it is anticipated that one molecule binds to one site. The conversion of the mass of Rhodamine B to molecules of substrate bound gives estimated of activated areas. It was calculated that the non-activated biochar (1.5×10^{17} sites) had an order less active

sites than the activated biochar (1.45×10^{18} sites). Clearly, in this case, phosphoric acid treatment is necessary to enhance the adsorptive ability of the biochar.

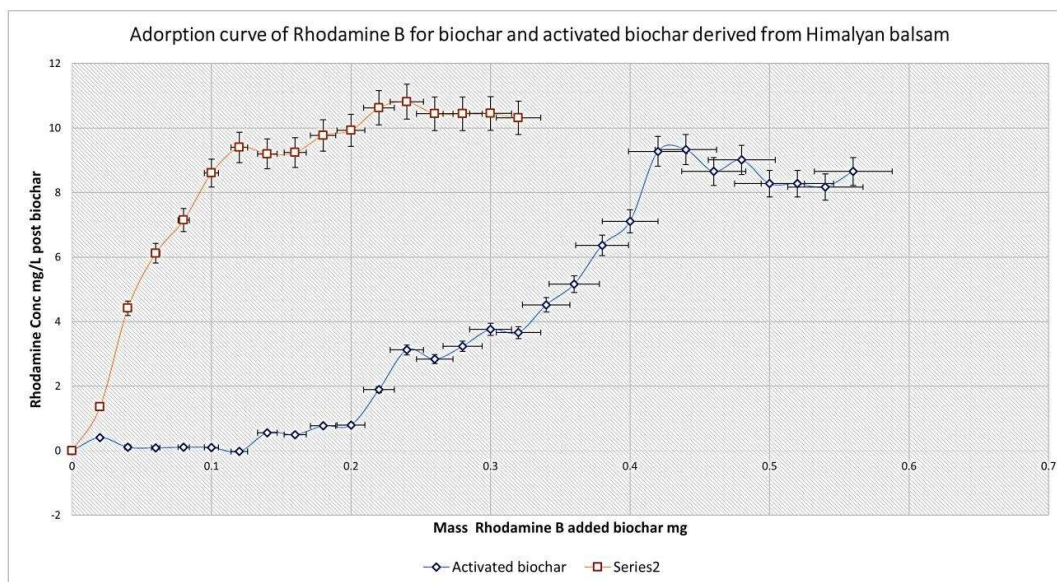


Figure 4.0. An adsorption isotherm for activated and non-activated biochar, plotted by addition of known quantity of rhodamine B to the 'sorbent' and then monitoring the eluent concentration using UV-VIS spectrophotometry. Concentration was determined using a standard calibration curve which possessed good linearity with R^2 value of 0.9986 and quality control standards passing accuracy and precision.

Conclusion

Thermal treatment of biomass can be used to manage the spread of invasive species such as Himalayan balsam. The advantage of using thermal techniques like pyrolysis or gasification, is the generation of value added products; such as calorific gas, bio-fuel and solid biochar. The degradation products (tars) generated around 300-400 ° C comprised of aromatic, linear and branched hydrocarbons, similar to compounds in petroleum distillates and if condensed can potentially be a source for replenishment for hydrocarbon-based fuels. The remaining biochar has potential to be used as an

adsorbent for aqueous organic compounds; it was shown that the biochar activity towards Rhodamine B was enhanced after activation with phosphoric acid.

Although the initial high moisture content of Himalayan balsam was potentially a problem, this was resolved with the ease, by air drying (~65 % reduction in moisture content) and significantly lowered of the initial STA endotherm (1553.5 J/g non-dried to 299.1 J/g dried) and therefore, enhancing the efficiency of the process. However, the bulk density of the non-dried material is low (13 %) compared to common feedstocks such as wood (60- 70 %) (IEA Bioenergy, 2011), which means that larger harvests are required to make this more commercially viable. Himalayan balsam however, grows in very dense areas (5000-6000 plants per m²) (Kelly et al., 2008) and ease of cutting, uprooting (no expensive logging machinery), and drying by air is actually an attractive advantage possibly boosting its feasibility. Alternatively, anaerobic digestion to generate bio-gas (IEA Bioenergy, 2011) may be much more suited treatment method for Himalayan balsam due to its high moisture content.

References

- Al Arni, S., 2018. Comparison of slow and fast pyrolysis for converting biomass into fuel. *Renew. Energy* 124, 197–201. <https://doi.org/10.1016/j.renene.2017.04.060>
- Azargohar, R., Dalai, A.K., 2008. Activated carbon from Eucalyptus camaldulensis Dehn bark using phosphoric acid activation. *Microporous Mesoporous Mater.* 110, 413–421. <https://doi.org/10.1016/j.biortech.2006.10.049>
- Brame, J., Griggs, C., 2016. Surface Area Analysis Using the Brunauer- Emmett-Teller (BET) Method Scientific Operating Procedure Series : SOP-C Environmental Laboratory. *Eng. Res. Dev. Cent.* <https://doi.org/39180-6199>
- Brebu, M., Vasile, C., 2010. Thermal degradation of lignin—a review. *Cellul. Chem. Technol.* 44, 353–363.
- Brownsort, P.A., 2009. Biomass Pyrolysis Processes: Review of Scope, Control and Variability. *Biomass* 38. <https://doi.org/10.1017/CBO9781107415324.004>
- Chen, B., Zhou, D., 2008. Transitional Adsorption and Partition of Nonpolar and Polar Aromatic Contaminants by Biochars of Pine Needles with Different Pyrolytic Temperatures 42,

5137–5143.

- Ding, L., Zou, B., Gao, W., Liu, Q., Wang, Z., Guo, Y., Wang, X., Liu, Y., 2014. Adsorption of Rhodamine-B from aqueous solution using treated rice husk-based activated carbon. *Colloids Surfaces A Physicochem. Eng. Asp.* 446, 1–7. <https://doi.org/10.1016/j.colsurfa.2014.01.030>
- Emer, C., Vaughan, I.P., Hiscock, S., Memmott, J., 2015. The impact of the invasive alien plant, *impatiens glandulifera*, on pollen transfer networks. *PLoS One* 10, 1–16. <https://doi.org/10.1371/journal.pone.0143532>
- Garcia-Perez, M., 2008. The Formation of Polyaromatic Hydrocarbons and Dioxins During Pyrolysis: A Review of the Literature with Descriptions of Biomass Composition, Fast Pyrolysis Technologies and Thermochemical Reactions. *Energy* 63.
- Han, T., Zhao, Z., Bartlam, M., Wang, Y., 2016. Combination of biochar amendment and phytoremediation for hydrocarbon removal in petroleum-contaminated soil. *Environ. Sci. Pollut. Res.* 23, 21219–21228. <https://doi.org/10.1007/s11356-016-7236-6>
- Hema, M., Arivoli, S., 2009. Rhodamine B adsorption by activated carbon: Kinetic and equilibrium studies. *Indian J. Chem. Technol.* 16, 38–45.
- IEA Bioenergy, 2011. Thermal Pre-treatment of Biomass for Large-scale Applications Summary and Conclusions from the.
- ISO, 2006. ISO 17025. General requirements for the competence of testing and calibration laboratories. Technical corrigendum 1 1–55.
- Kawano, T., Kubota, M., Onyango, M.S., Watanabe, F., Matsuda, H., 2008. Preparation of activated carbon from petroleum coke by KOH chemical activation for adsorption heat pump. *Appl. Therm. Eng.* 28, 865–871. <https://doi.org/10.1016/j.applthermaleng.2007.07.009>
- Kelly, J., Maguire, C.M., Cosgrove, P., 2008. Best Practice Management Guidelines Himalayan balsam (*Impatiens glandulifera*), Prepared for NIEA and NPWS as part of Invasive Species Ireland.
- Kibet, J., Khachatryan, L., Dellinger, B., 2012. Molecular products and radicals from pyrolysis of lignin. *Environ. Sci. Technol.* 46, 12994–13001. <https://doi.org/10.1021/es302942c>
- Kuglerová, L., García, L., Pardo, I., Mottiar, Y., Richardson, J.S., 2017. Does leaf litter from invasive plants contribute the same support of a stream ecosystem function as native vegetation? *Ecosphere* 8. <https://doi.org/10.1002/ecs2.1779>
- Marshall, A.J., Wu, P.F., Mun, S.H., Lalonde, C., 2014. Commercial application of pyrolysis technology in agriculture. *Am. Soc. Agric. Biol. Eng. Annu. Int. Meet. 2014, ASABE 2014 5*, 3868–3886.
- Mohammad-Khah, A., Ansari, R., Mohammad-Khah, A., Ansari, R., 2009. Activated charcoal: Preparation, characterization and applications: A review article. *Int. J. ChemTech Res.* 1, 859–864. <https://doi.org/ISSN 0974-4290>
- Mohan, D., Pittman, C.U., Steele, P.H., 2006. Pyrolysis of wood/biomass for bio-oil: A critical review. *Energy and Fuels* 20, 848–889. <https://doi.org/10.1021/ef0502397>
- Nartey, O.D., Zhao, B., 2014. Biochar preparation, characterization, and adsorptive capacity and its effect on bioavailability of contaminants: An overview. *Adv. Mater. Sci. Eng.* 2014. <https://doi.org/10.1155/2014/715398>

- Ogbonnaya, U., Semple, K., 2013. Impact of Biochar on Organic Contaminants in Soil: A Tool for Mitigating Risk? *Agronomy* 3, 349–375. <https://doi.org/10.3390/agronomy3020349>
- Ok, Y., 2015. *Biochar: production, characterisation and application*. CRC press.
- Oliveira, F.R., Patel, A.K., Jaisi, D.P., Adhikari, S., Lu, H., Khanal, S.K., 2017. Environmental application of biochar: Current status and perspectives. *Bioresour. Technol.* 246, 110–122. <https://doi.org/10.1016/j.biortech.2017.08.122>
- Paethanom, A., Yoshikawa, K., 2012. Influence of pyrolysis temperature on rice husk char characteristics and its tar adsorption capability. *Energies* 5, 4941–4951. <https://doi.org/10.3390/en5124941>
- Ronsse, F., Nachenius, R.W., Prins, W., 2015. *Carbonization of Biomass, Recent Advances in Thermochemical Conversion of Biomass*. Elsevier B.V. <https://doi.org/10.1016/B978-0-444-63289-0.00011-9>
- Shen, D.K., Gu, S., 2009. The mechanism for thermal decomposition of cellulose and its main products. *Bioresour. Technol.* 100, 6496–6504. <https://doi.org/10.1016/j.biortech.2009.06.095>
- Shen, Z., Zhang, Y., Jin, F., Alessi, D.S., Zhang, Y., Wang, F., McMillan, O., Al-Tabbaa, A., 2018. Comparison of nickel adsorption on biochars produced from mixed softwood and *Miscanthus* straw. *Environ. Sci. Pollut. Res.* 25, 14626–14635. <https://doi.org/10.1007/s11356-018-1674-2>
- Tan, X., Liu, Y., Zeng, G., Wang, X., Hu, X., Gu, Y., Yang, Z., 2015. Application of biochar for the removal of pollutants from aqueous solutions. *Chemosphere* 125, 70–85. <https://doi.org/10.1016/j.chemosphere.2014.12.058>
- Tarazona, J. V., Court-Marques, D., Tiramani, M., Reich, H., Pfeil, R., Istace, F., Crivellente, F., 2017. Glyphosate toxicity and carcinogenicity: a review of the scientific basis of the European Union assessment and its differences with IARC. *Arch. Toxicol.* 91, 2723–2743. <https://doi.org/10.1007/s00204-017-1962-5>
- Zhou, Z., Shi, D., Qiu, Y., Sheng, G.D., 2010. Sorptive domains of pine chars as probed by benzene and nitrobenzene. *Environ. Pollut.* 158, 201–206. <https://doi.org/10.1016/j.envpol.2009.07.020>

Conflict of interest.

This article is the result of the authors own investigations, except where otherwise stated. Other sources are acknowledged by explicit references. The authors can confirm that this work has not been published previously in whole or part, or abstract form and does not conflict with interest of any other third parties.

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Highlights

- Himalayan balsam potentially can be used as a source of biomass for pyrolysis.
- The high-water content was reduced through air drying.
- Air drying consequently increasing the Thermal efficiency of the process.
- The tar compounds revealed similarities between petroleum distillates.
- The activated biochar showed affinity towards Rhodamine B.

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