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Optimisation of slow-pyrolysis process conditions to maximise char yield and

heavy metal adsorption of biochar produced from different feedstocks

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Abstract

The objective of this work was to identify biomass feedstocks and optimum pyrolysis process conditions to produce a biochar capable of adsorbing metals from polluted groundwater. Taguchi experimental design was used to determine the effects of slow-pyrolysis process conditions on char yield and zinc adsorption. Treatments were repeated using six candidate feedstocks (*Lolium perenne, Lolium perenne* fibre, *Miscanthus x giganteus, salix viminalis, fraxinus excelsior and picea sitchensis*) and the resultant chars were tested for metal adsorption performance. Chars produced from *Lolium Perenne* and its extracted fibre displayed the greatest zinc adsorption performance and removed 83.27 to 92.96 % respectively. Optimum process conditions in terms of both char yield and zinc adsorption performance were achieved from slow-pyrolysis at 300°C for 2 hours using a feedstock with a particle size of less than 1 mm.

Keywords: Remediation, Zinc, Taguchi-method, Bio-refinery, Grasses

1. Introduction

Metal-polluted groundwater leaching from abandoned mine-sites poses an environmental and public health hazard for many places around the world. In the UK it is estimated that 170 tonnes of zinc per annum is discharged into the environment from mines in England and Wales each year (EA national picture SC030136/R2) and is associated with 9% of rivers failing European Water Framework Directive standards (2000/60/EC). There are very few treatment systems in place to treat this contaminated mine water. Slow-pyrolysis for char production has received renewed interest in recent years since the rise in popularity of 'biochar' as a soil conditioner, filtration medium, pollution remediate and also as potential method of mitigating carbon dioxide emissions (Ahmad et al., 2014). In this study we investigate the zinc adsorption of biochars produced from a range of abundant feedstocks and assess their potential for pyrolysis optimisation and practical application as adsorbents.

Biochar is a type of porous carbon which has similarities with activated carbon, which is widely used in wastewater treatment for the removal of both organic and inorganic pollutants (Goher et al., 2015; Qiu & Huang, 2015). The removal of metal cations from dilute solutions has mainly been attributed to electrostatic exchange, co-precipitation, inner surface reactions and π -orbital metal bonding onto the electron-rich surface (Kołodyńska et al., 2012; Li et al., 2014). Activated carbons are produced at very high temperatures (typically 700 – 900 °C) which result in a highly ordered and graphitic type carbon structure. The carbon surface is then modified through mechanical, chemical and electrochemical processes (Shen, 2008). Porous carbons are good absorbers due to the large surface area, pore volume and a high surface reactivity but

their widespread use is restricted due to high production costs. Lessons can however be learned from the extensive research into activated carbon for the production and characterisation of biochar.

Utilisation of design of experiment (DOE) methodologies such as the Taguchi method have been widely and successfully applied to engineering problems as a tool for identifying critical process parameters and optimising processes which are affected by multiple inter-related factors (Rao et al., 2008). The method comprises a simple statistical tool which creates an integrated multifactorial experimental design through a system of tabulated orthogonal arrays. Application of these matrices in experimental design maximises the number of main effects which can be estimated and minimises the total number of individual experiments required. The usefulness of this method for optimising pyrolysis processes has already been demonstrated on several specific conversion processes but to-date has not been applied to optimise slow-pyrolysis for multiple feedstocks (Chan et al., 2014; Chen et al., 2014a; Chen et al., 2011; Dang et al., 2013). In this study the Taguchi method was used to determine the effects of four basic factors on char yield and quality. Particular emphasis was placed on determination of how these effects varied between feedstocks. Six feedstocks were selected for pyrolysis trials: two grasses (Lolium perenne and Miscanthus x giganteus), two broadleaf tree species (Fraxinus excelsior and Salix viminialis) and one coniferous species *Picea sitchensis*. These species were selected as all are commercially available, proximally abundant and represented several different taxonomic groups. Treatment temperature, residence time, particle size, and pyrolysis gas atmosphere were the key factors included in the design. Treatment temperature range was selected to be within

the practical operational limits of most slow-pyrolysis reactors which are commercially available. Temperature levels of 300, 450, and 600 °C were selected, as points at which degradation of main cell wall polymers will have occurred (Müller-Hagedorn & Bockhorn, 2007; Yang et al., 2007; Zhou et al., 2013).

Feedstock parameters which affect slow-pyrolysis for char production include the relative proportion and composition of cell wall polymers, moisture content, the severity of pyrolysis conditions employed and the presence of inorganic/organic constituents which can catalyse certain reactions (Fahmi et al., 2007). The biochemical variations also relate to taxonomic division, for example differences between eudicots and monocots such as the poales (e.g. grasses/straws) have been observed to effect thermal degradation characteristics and pyrolysis products in previous research (Greenhalf et al., 2013; Müller-Hagedorn & Bockhorn, 2007).

Biomass materials fractionate differently during biomass pre-processing which makes particle size an important factor to include in experimental design (Bridgeman et al., 2007; Demirbas, 2004), both to ensure that any observed differences are not simply the result of fractional differences but also to ensure this inherent variation is accounted for and included in the data.

In terms of pyrolysis process parameters: temperature, heating rate and residence time in the reactor are regarded as the key factors (Williams & Besler, 1996). Another factor which is often not given as much attention, is the gaseous atmosphere under which pyrolysis is performed. In most experimental pyrolysis rigs utilisation of N_2 gas to

exclude O₂ and/or provide an entrained flow is typical. However most commercial slow-pyrolysis reactor systems O₂ concentration within the reactor is reduced principally by CO₂ derived from either combustion of the priming fuel, used to introduce the initial heat load to the system, or from degradation of the feedstock itself depending on the system used. The influence of CO₂ in high-temperature gasification of coal and in production of activated carbons has been extensively researched, but its influence on the physiochemical properties of biomass chars has not received similar rigor. Several studies have identified effects on char yield and surface properties under fast-pyrolysis conditions at temperatures between 550-850°C (Guizani et al., 2014; Zhang et al., 2011) however the effects of CO₂ atmosphere have not yet been investigated for slow-pyrolysis conditions, this is critical to interpreting results with respect to informing production at greater scale and ensuring analytical experimentation and monitoring is representative and applicable to commercial situations.

Experiments reported in the literature often are divided by either a production or utilisation focus. In order to gain a comprehensive overview, both sets of factors need to be accounted for in experiments to ensure the origin of the observed variation can be accurately discerned as a feedstock effect, process effect, or combination of both. This knowledge is essential to process development and optimisation particularly in terms of production at greater scales. This work has attempted to include as many of the critical factors as possible to allow investigation of factor interactions and the potential to optimise pyrolysis processes for both product yield and quality.

2. Methods

2.1 Design of experiment and analysis

The study was developed using the Taguchi approach and Qualitek 4 DOE software (Nutek, USA). Selected process parameters and levels (Table 1) were incorporated into an L9 orthogonal array which identified nine separate treatment regimens which gave representative account of all process factor combinations (Table 2). These nine treatments were subsequently applied to each of the feedstocks. Subsequent data handling and analysis was performed using Microsoft Excel (Microsoft, USA) and SPSS (IBM, USA).

2.2 Biomass feedstocks selected and preparation

Fraxinus Excelsior (*Fraxinus*) and *Picea sitchensis* (*Picea*) feedstocks were obtained as chip from a commercial saw mill. *Lolium perenne* (*Lolium*) was mown and harvested from IBERS research plots, a sub sample was processed through a 10" screw-press to extract water and soluble carbohydrates, and the resultant fibre was dried and stored. *Miscanthus x. giganteus* and *Salix viminalis* (*Salix*) samples were also taken from research plots at Aberystwyth University. *S. viminalis* was obtained from 2 yr. growth from a short-rotation coppice bed and 1 yr. growth senesced *M. x giganteus*; both plots have been established for over 10 years. All biomass feedstocks were oven dried at 80 °C for 16 hrs and milled to <2mm. Milled material was subsequently fractionated using graded sieves to size ranges of <0.5 mm, 0.5-1 mm, and 1-2 mm. Ash content of samples was determined by 'loss on ignition' after incineration in a muffle furnace at 550 °C for 5 h.

2.3 Char production

Pyrolysis of samples was performed using a Carbolite vertical single-zone split-tube furnace (Verder International B.V). A custom-made pyrolysis reactor chamber was used to pyrolyse samples in batches. The reactor comprised of a 316 stainless steel cylinder 110mm in diameter and 900mm in length with gas-tight plates fitted at each end. The primary end-plate included a gas inlet for cylinder/line connection and a sealed thermocouple insert for accurate measurement of internal reactor temperature. The secondary end plate included a pressure relief valve and gas outlet. The outlet pipe was connected to a separate condensation unit which was used to collect pyrolysis gas condensates prior to venting into a fume cabinet. A bubble trap was also fitted to the outlet pipe to provide a small amount of back-pressure, monitor gas flow exiting the reactor and also to prevent influx of air in the event of failure in the gas flow. This reactor chamber was inserted inside the tube furnace and sample trays were inserted and removed before/after each run. Samples were pyrolysed in the tube furnace using custom designed 316 stainless steel trays (80 x 180 x 1 mm) which were designed to give a uniform sample surface area to volume ratio of 1:1. Samples were loaded into pre-weighed trays so the feedstock material filled the full volume and was level with the top of the container tray. This was performed with each sample to ensure equal surface area to volume ratio for each sample pyrolysed. Sample trays were subsequently reweighed and inserted into the reactor chamber and contained 10 ± 1.7 g feedstock on a DM basis. The reactor was then sealed and the chamber purged with N₂ or CO₂ for a minimum of 5 minutes prior to initiation of the temperature program. During all experimental runs a continuous gas flow of 5L min-1 was maintained using a gas flow meter. Entrained gases were injected into the reactor chamber via the inlet valve on the

primary end-plate to provide a constant gas flow over the samples and to purge the chamber of residual air and pyrolysis product gases. Temperature parameters during experimental runs were controlled and regulated by a Eurotherm 301 standard and 3216 programmable control unit. All samples were heated to the target temperature at a heating rate of 25 C min⁻¹ held at the target temperature for the required treatment duration then allowed to cool-back to ambient before being removed from the furnace.

2.4 Thermogravimetric analysis (TGA)

Experiments were carried out on untreated and pyrolysed material using a Perkin-Elmer Pyris-1 thermogravimetric analyser (Hodgson et al., 2011).

2.5 Minewater used in adsorption experiments

The effluent used in this investigation is collected from the former Bwlch mine at Cwmerfyn, 19 km east of Aberystwyth (British National Grid Reference SN 701 825). The drainage was collected at 4 intervals during the course of the experiment and stored in 50 litre potable water containers for subsequent use. Small variation was observed in the concentration of zinc in Bwlch mine-water used over the duration of the experiment mean zinc concentration was $18.5 \pm 2.1 \,\mu$ g/mL. Results used in subsequent analyses were expressed in terms of percentage removal to account for this variation.

2.6 Elemental analysis

The major element concentration was determined by atomic absorption spectroscopy (AAS) using a Perkin-Elmer AAnalyst 400; trace element analysis was performed via ICP-MS using an Agilent 7700x. The concentration change between the untreated mine

water and post-experiment water was used to calculate the influence of each char material. A char mass of 1 gram (+/-0.01g) was introduced to 500mL conical flasks and 500mL of Bwlch mine water was added to the flasks, these were shaken and left for 24 hrs at room temperature. The resulting water was filtered through Whatman No.1 paper and a 60mL subsample was removed and stabilised with 3 drops of 50% HNO₃. The removal percentage and capacity were calculated from difference between initial and final concentrations.

3. Results and discussion

3.1 Characterisation of feedstocks

Thermogravimetric analysis (TGA) was performed on each of the raw feedstocks and particle size-fractions and the mass loss and derivative curves are presented together for ease of comparison (Fig 1). The mass loss curves at 600 °C show a great degree of similarity in terms of resultant char yield, but the derivative curves highlight distinct differences between the thermal degradation of different feedstocks. Features and transitions evident from the derivative curve of biomass feedstocks are known to equate to compositional differences, principally the main cell wall polymers, hemicellulose, cellulose and lignin (Zhou et al., 2013). Derivative profiles of these feedstocks identify differences in pyrolytic degradation behaviour (Fig 1.). Distinct differences in ash content were identified between feedstocks: *Lolium* feedstocks contained significantly greater concentrations of ash in the dry matter (7-10%) than the other feedstocks tested. The extracted Lolium fibre contained less ash than untreated Lolium biomass but was still found to be significantly higher than all other feedstocks (Table 3). This difference in ash content was observed to inversely correlate with the temperature at which the maximum rate of volatilisation occurred (Tmax) during the TG analysis: where a higher feedstock ash content correlated linearly with reduced Tmax temperature (Fig 1) which suggests inorganic species present in the high-ash biomass is having a catalytic effect during pyrolysis and may also result in compositional differences in the resultant chars.

Another noticeable difference was a transition peak that occurred at approximately 230 °C during the degradation of the *Lolium* and to lesser extent, the *Miscanthus* chars which is absent from the DG profiles of other feedstocks (Fig 1), this mass-loss feature

is likely to relate to volatilisation of protein present within the biomass. It should be noted that the high-ash content of the grass biomass is related to the greater proportion of leaf to stem material which is the opposite with other feedstocks. Leaf material contains a greater quantity of protein and inorganic constituents due to requirements of photosynthetic function; however these constituents are reduced in the above-ground biomass during translocation of nutrients and leaf loss during senescence (Purdy et al., 2015). Lolium biomass was harvested during the growing season whereas Miscanthus grass was harvested at the end of the growing season once senescence had taken place which meant less leaf material was present in the harvested biomass and therefore reduced levels of protein and inorganic constituents. During the *Lolium* fibre extraction process a proportion of the protein and inorganic species are removed along with the water soluble fraction of the biomass (Corton et al., 2014). These results highlight additional influences of feedstock species and composition which are independent of the treatment factors included in the Taguchi experimental design. As a consequence of the observed differences the relative effects of process parameters on char yield and zinc adsorption quality will be examined on a feedstock by feedstock basis.

3.2 Char product characteristics

On the basis of the overall means, there was little difference in total char yield and fixed carbon content of the resultant chars (Table 3). Increased treatment temperature and residence time resulted in reduction in total char yield but increase in fixed carbon content; this was consistent for all feedstocks tested. Treatment temperature had the greatest overall influence on char yield and explained 71.3-94.9% of the total variation (Table 4). Retention time had less influence on total char yield but its effect varied

between feedstocks by 0.44-19.58%. CO_2 had little overall influence on char yield, but a small positive contribution was identified in pyrolysis of *Picea* and *Fraxinus* at 450-600 °C. Clear differences were observed in response to the treatments applied both within and between feedstocks as indicated by the standard deviations of the feedstock means (Table 3). This was particularly evident from the within-feedstock variation in fixed-carbon content of the woody feedstocks (Table 3). The smaller particle size fractions (<1 mm) correlated with a lower total char yield and greater adsorption of zinc due to increased surface area. However, in the case of both char yield and zinc adsorption, little difference was evident between the 0.5-1.0 mm and 1.0-2.0 mm fractions (Levels 2 and 3 respectively).

The effects of treatment factors on the char yield and zinc adsorption performance of the chars produced from each feedstock were examined separately and assessed by ANOVA to determine the significance and relative contribution of included factors. Tables 4 and 5 present the char yield and zinc adsorption data for each feedstock and the positive or negative influence of treatment conditions. The relative contributions of factors are also included and are expressed in percentage terms based on the total observed variation for all factors². Optimum factor levels¹ predicted to result in the char with the maximum calculated char yield or Zn adsorption capacities are also given (Tables 4-5).

Zinc adsorption performance

Following slow pyrolysis trials the zinc adsorption performance of the resultant chars was assessed and compared in terms of percentage removed from the mine-water

samples. The *Lolium* and *Lolium* fibre chars displayed significantly greater zinc adsorption than all other feedstocks by a considerable margin: 41-51% more than the *Miscanthus* chars and 54-64% more than *Picea* chars which had the poorest zinc adsorption of all the feedstocks tested (Table 3). Particle size had the greatest overall contribution to adsorption performance but no difference was observed between the particle size fractions below 1 mm. Chars produced from untreated *Lolium* biomass adsorbed 30–80% of the zinc from the Bwlch minewater. Greatest adsorption performance was achieved from pyrolysis at 300 °C for 4 hours with an initial particle size of less than 1 mm. Pyrolysis performed at temperatures above 300 °C had a negative effect on the adsorption performance of the *Lolium* char and residence time had a small positive contribution when held at temperature for over 4 hrs.

Lolium fibre chars had the greatest performance overall and adsorbed 58.7 - 93.0 % of the zinc present in the mine-water which equated to a maximum zinc capacity of 9210 μ g Zn/g char. Chars with greatest adsorption were produced from the smallest size fraction (<0.5 mm) at 450 °C with a retention time of 6 hours. These results also suggest a relationship between the ash content and/or ash composition of the feedstock and its zinc adsorption performance which is independent of pyrolysis treatment.

Miscanthus and *Salix* chars adsorbed zero to 35.7 and 30.7 % zinc respectively. Best performance was observed by chars produced at 600 °C for 6 hours using the smallest particle size fraction. *Fraxinus* and *Picea* chars adsorbed from zero to 54.8 and 16.1 % respectively, in both cases the best performance resulted from chars pyrolysed at 600 °C for 2-4 hours with a particle size below 1 mm. Little or no adsorption was observed

from these chars when pyrolysed below 600 °C. In the case of *Fraxinus* CO₂ was identified as having a small but significant ($P \le 0.05$) negative effect on adsorption of the resultant char, but this was the only time CO₂ was identified as having any impact on adsorption quality and its effect was negligible.

These results highlight the potential of *Lolium* and its processed fibre residue for adsorption applications. Furthermore, there is considerable scope to optimise slow-pyrolysis process conditions to improve char adsorption properties without causing major detrimental effects to the total char yield.

Optimisation of char yield and zinc adsorption to specific feedstock types

Unlike the case with char yield, temperature was not consistent as the main contributing factor to the zinc adsorption capacity of the resulting chars, relative contribution of process factors differed distinctly between feedstocks (Table 5). The zinc adsorption capacity of the *Fraxinus* and *Picea* chars were most influenced by temperature and chars displayed very low zinc adsorption when produced at temperatures less than 600 °C, particularly in the case of *Fraxinus*. Retention time had much less of an overall effect on zinc adsorption of the produced chars, however an increase in residence time had different effects depending on feedstock: improved adsorption of *Fraxinus* chars but reduced adsorption of *Picea*.

Particle size had little overall effect but the intermediate 1-2 mm particle size fraction gave the best adsorption for both *Picea* and *Fraxinus* as opposed to the <0.5 mm fraction which gave consistently better adsorption for all other feedstocks. *Picea* and

Fraxinus also displayed the greatest response to pyrolysis in CO_2 rather than N_2 which in both cases significantly reduced the zinc adsorption but resulted in a modest increase in total char yield.

Miscanthus and *Salix* chars displayed better zinc adsorption when pyrolysed over 450 °C, however the residence time in the reactor had the greatest overall effect on their zinc adsorption; longer residence times and smaller particle sizes (<0.5 mm) resulted in the greatest adsorption. *Salix* chars did however display a modest increase in zinc adsorption in response to CO₂, which had the opposite effect on *Picea* and *Salix* chars.

Despite being derived from the same biomass origin, the untreated *Lolium* and its extracted fibre displayed very different responses to process factors. Zinc adsorption of *Lolium* chars decreased as pyrolysis temperatures increased and were little affected by residence time. Particle size had a significant overall contribution to zinc adsorption, however the difference was only really observed between <1 mm and 1-2 mm size fractions. The *Lolium* fibre was less affected by pyrolysis temperature, but adsorption increased with residence time duration. Particle size below <0.5 mm resulted in the greatest zinc adsorption although for particle size fractions between <0.5-1 mm there was not much difference between the raw *Lolium* and its extracted fibre.

Implications for practical application

The result show that feedstock is the most significant variable influencing low temperature pyrolysis of biomass and, although significant influences from production conditions are evident, these differ within individual feedstocks. These results highlight

the potential of Lolium and its processed fibre residue for adsorption applications.

Associated with the zinc adsorption was a release of potassium into the mine water. This suggests that a proportion of the metals (especially alkali and alkaline earth) present in the biomass are, with partial degradation to the cell wall structure, liberated into a more liable and water-soluble fraction. It has been suggested that the inorganic ash constituents associated with biochar can facilitate metal removal due to the formation of insoluble phosphates and carbonates (Xu et al., 2014). To further investigate this, a bulk sample of lolium fibre biochar was produced and subjected to pre-washing with distilled water (data not presented). This reduced the amount of potassium released into the minewater by 51%, however a negligible influence on zinc adsorption was observed. The remaining potassium was liberated into the minewater and was assumed to be subject to exchange processes, which is supported by a balance in the equivalent concentrations. This shows that the water-soluble inorganic fraction, associated with the biochar does not play a role in metal adsorption. Although this inorganic fraction may not directly influence metal adsorption, its presence in the feedstock during pyrolysis may influence the biochar properties. The role of alkali and alkali-earth metals as a pyrolysis catalyst has long been understood in the production of activated carbon, where the metal ion becomes inserted into the graphene structure during pyrolysis. This influence has been shown to increase the carbons surface area, lowering Tmax temperature (enabling volatilisation of hemicelluloses and cellulose at lower temperatures) and increase the oxidation of the carbon surface (Bhat et al., 2010; Fahmi et al., 2007; Lukaszewicz, 1999). Further to this, the condensed liquid products such as volatile organic acids, alcohols, saturated fatty acids which are abundant in the

lolium feedstock may further catalyse the pyrolysis (Ross et al., 2010). These influences are evident from the TGA programs which show a distinct negative correlation between the ash content of the feedstocks and the temperature at which Tmax is reached and an additional transition peak that occurred at approximately 230 °C (Fig 1). This is further supported by differences observed between the untreated *Lolium* biomass and the extracted fibre: In the extracted fibre a great proportion of water-soluble carbohydrate and inorganics present in the raw biomass at harvest, are removed during processing. This pre-processing has resulted in the difference between the ash content of the raw biomass and the extracted fibre (Table 3) and consequently the difference between the two feedstocks during pyrolysis and the suggested optimum process parameters which were higher for the extracted fibre than for untreated *Lolium* biomass (Table 5).

Selection of feedstocks such as *Lolium* and potentially other grassy feedstocks, such as cereal straws, which contain high concentrations of alkali or alkaline metals within the harvested biomass, may also be suitable feedstocks for adsorption applications. Alternatively, more conventional pyrolysis process parameters and feedstock types may be used to produce porous char which at high temperatures behaves more similar to a typical activated-carbon product. This was particularly the case with the mature hardwood species (*Fraxinus*) and also the softwood (*Picea*).

In terms of practical production and use as an adsorbent *Lolium* would appear to be a good choice of feedstock both in terms of feedstock availability and also pyrolysis process requirements. Optimum conditions were among the lowest levels of all parameters tested which as a consequence resulted in the highest yield and lowest

energy input during the pyrolysis process (Table 6). One issue with practical utilisation of *Lolium* as a feedstock for this process is the moisture content of the harvested material which may be in excess of 60% immediately following harvest. Drying in the field can reduce this water content to be more comparable with that of harvested timber however the influence of these factors on economic feasibility and sustainability of biochar production from these feedstocks needs to be further investigated. Alternatives are presented by the grass bio-refinery concept where the grass fibre is obtained as a byproduct following extraction of valuable carbohydrates and proteins from the freshly harvested biomass (Charlton *et al.* 2009). In this case, subsequent pyrolysis and utilisation as an adsorbent material could present a viable addition to the material cascade of a grass-based bio-refinery.

Conclusions

Scope to optimise for adsorption quality without detrimental effect on product yield was identified. Temperature was the significant factor in determining char yield but not char quality: feedstocks responded differently to process conditions due to physiochemical differences in composition. Results suggested both inorganic and organic constituents of the biomass feedstocks act as catalysts with ability to both reduce process energy requirement and improve biochar quality. *L. perenne* char gave better performance at lower temperatures and retention times than all other feedstocks and adsorbed three times more zinc. Extracted fibre from biorefinery process further improved the process efficacy and product quality.

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- Figure 1. Comparison of percentage mass loss and derivative curves of feedstocks used in slow pyrolysis experiments as determined by thermogravimetric analyses.
- Table 1. Factors and levels included in Taguchi experimental design
- Table 2. L₉ orthogonal array used in the study
- Table 3. Effect of source feedstock on char yield, composition and zinc adsorption
- Table 4. Effect of slow-pyrolysis process parameters on char product yield of resultant

 chars produced from selected feedstocks including optimum factor levels
- Table 5. Effect of slow-pyrolysis process parameters on zinc adsorption performance of resultant chars produced from selected feedstocks including optimum factor levels.
- Table 6. Summary of optimum conditions and predicted char yield and zinc adsorption

performance.

Treatment					
	Temperature	Residence	Particle	Gas	
No.		time	size	atmosphere	
1	1	1	1	1	
2	1	2	2	2	
3	1	3	3	1	
4	2	1	2	1	
5	2	2	3	1	
6	$\frac{1}{2}$	3	1	2	
7	3	1	3	$\frac{-}{2}$	
8	3	2	1	-	
9	3	3	2	1	
,	5	5	-	1	
			MP		
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50					

Table 2. L₉ orthogonal array used in the study

Feedstock	Char Yield		Volatiles		Fixed Ca	Ash		Zn removed			
	%DM	+/-	%DMAF	+/-	%DMAF	+/-	%DM	+/-	%	+/-	
Lolium	23.54	2.78	28.18	7.15	71.82	7.15	11.91	4.66	59.83	14.98	
Lolium fibre	24.57	3.72	28.25	7.44	71.75	7.44	8.45	3.26	69.20	11.95	
Miscanthus	23.85	2.93	24.78	13.77	74.41	14.98	1.55	0.20	18.24	12.47	7
Salix	26.30	6.36	21.37	8.13	78.63	8.13	1.12	1.21	9.68	9.81	
Fraxinus	29.60	7.81	20.68	13.62	75.22	13.77	0.70	0.17	13.76	22.94	
Picea	24.97	5.76	25.59	14.98	79.38	13.48	0.32	0.20	5.40	6.23	
Total	25.47	5.40	24.81	10.85	75.20	10.83	4.01	1.62	29.35	13.06	

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Table 3	Effect	of source	teedstock	on char	vield	composition s	and zinc	adsorption
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Data reported are mean values which include all treatment factors, within feedstock

variation is represented by standard deviations.

Feedstock	Factor	Mean	Level 1	Level 2	Level 3	Opt^1	% Cont ²
Lolium	Temperature	23.54	3.17	-1.23	-1.94	1	74.60
	Retention time	23.54	-0.24	0.08	0.16	3	0.44
	Particle size	23.54	-1.84	1.03	0.82	2	24.92
	Pyrolysis in CO ₂	23.52	0.06	-0.06		1	0.03
Lolium fibre	Temperature	24.57	4.32	-1.55	-2.77	1	78.13
	Retention time	24.57	0.16	0.34	-0.50	2	1.07
	Particle size	24.57	-2.24	1.24	1.00	2	20.64
	Pyrolysis in CO ₂	24.63	-0.17	0.17		2	0.17
Miscanthus	Temperature	26.30	6.95	-2.16	-4.79	1	73.23
	Retention time	26.30	-0.58	3.43	-2.85	2	19.49
	Particle size	26.30	-0.33	1.90	-1.57	2	5.99
	Pyrolysis in CO ₂	26.57	-0.82	0.82		2	1.29
Salix	Temperature	23.85	3.68	-1.05	-2.63	1	94.86
	Retention time	23.85	0.32	-0.14	-0.17	1	0.67
	Particle size	23.85	-0.60	-0.18	0.78	3	4.40
	Pyrolysis in CO ₂	23.88	-0.09	0.09		2	0.07
Fraxinus	Temperature	24.97	6.20	-2.32	-3.88	1	68.83
	Retention time	24.97	-1.14	2.33	-1.19	2	9.49
	Particle size	24.97	-0.45	2.38	-1.93	2	11.20
	Pyrolysis in CO ₂	25.67	-2.12	2.12		2	10.48
Picea	Temperature	29.60	8.74	-2.76	-5.97	1	76.55
	Retention time	29.60	-0.80	2.68	-1.89	2	7.28
	Particle size	29.60	-1.42	2.95	-1.53	2	8.35
	Pyrolysis in CO ₂	30.42	-2.47	2.47		2	7.83
Mean	Temperature	25.47	5.51	-1.85	-3.66	1	83.91
	Retention time	25.47	-0.38	1.45	-1.07	2	6.06
	Particle size	25.47	-1.15	1.55	-0.41	2	6.92
	Pyrolysis in CO ₂	25.78	-0.94	0.94		2	3.11

Table 4. Effect of slow-pyrolysis process parameters on char product yield of resultant

chars produced from selected feedstocks including optimum factor levels.

Relative effects of pyrolysis process parameters are given for each feedstock tested. Variance from the mean in response to treatment levels is presented in the same units for each factor. Optimum conditions¹ from the ANOVA are given along with the relative contribution of factors² in percentage terms.

Feedstock	Factor	Mean	Level 1	Level 2	Level 3	Opt ¹	% Cont ²
Lolium	Temperature	59.83	11.11	-2.34	-8.77	1	37.12
	Retention time	59.83	-5.69	4.22	1.47	2	9.45
	Particle size	59.83	7.19	6.77	-13.97	1	52.75
	Pyrolysis in CO ₂	59.37	1.38	-1.38		1	0.68
Lolium fibre	Temperature	69.20	-3.15	2.00	1.15	2	4.15
	Retention time	69.20	-6.70	0.02	6.67	3	24.34
	Particle size	69.20	13.10	-7.26	-5.84	1	70.31
	Pyrolysis in CO ₂	69.70	-1.49	1.49	<u> </u>	2	1.21
Miscanthus	Temperature	18.24	-5.88	2.18	3.70	3	12.86
	Retention time	18.24	-10.58	2.19	8.39	3	45.40
	Particle size	18.24	9.19	-0.16	-9.03	1	40.27
	Pyrolysis in CO ₂	17.66	1.74	-1.74		1	1.47
Salix	Temperature	9.68	-4.51	1.97	2.54	3	13.44
	Retention time	9.68	-6.20	-2.38	8.58	3	51.61
	Particle size	9.68	6.41	-3.37	-3.04	1	26.99
	Pyrolysis in CO ₂	10.68	-3.01	3.01		2	7.95
Fraxinus	Temperature	13.76	-13.48	-12.19	25.67	3	72.44
	Retention time	13.76	-9.68	5.19	4.49	2	10.31
	Particle size	13.76	3.82	5.28	-9.10	2	9.19
	Pyrolysis in CO ₂	11.29	7.42	-7.42		1	8.07
Picea	Temperature	5.40	-3.89	-0.74	4.63	3	64.41
	Retention time	5.40	1.59	-0.04	-1.55	1	8.53
	Particle size	5.40	-0.04	1.60	-1.56	2	8.69
	Pyrolysis in CO ₂	4.63	2.30	-2.30		1	18.38
Mean	Temperature	29.35	-3.30	-1.52	4.82	3	18.46
	Retention time	29.35	-6.21	1.53	4.68	3	31.83
	Particle size	29.35	6.61	0.48	-7.09	1	47.75
	Pyrolysis in CO ₂	28.89	1.39	-1.39		1	1.96

Table 5. Effect of slow-pyrolysis process parameters on zinc adsorption performance of

resultant chars produced from selected feedstocks including optimum factor levels.

Relative effects of pyrolysis process parameters are given for each feedstock tested. Variance from the mean in response to treatment levels is presented in the same units for each factor. Optimum conditions¹ from the ANOVA are given along with the relative contribution of factors² in percentage terms.

Feedstock	Temp.	Residence Time	Particle size	Energy Used	Char yield	Zn removed	Calculated Zn capacity
	°C	Hr ⁻¹	mm ⁻¹	kW	%	%	$\mu g/g_{char}$
Lolium	300	2	< 0.5	1.015	27.74	83.27	7380
Lolium fibre	450	6	< 0.5	3.510	20.51	92.96	9210
Miscanthus	600	6	< 0.5	5.348	21.39	40.69	3530
Salix	600	6	< 0.5	5.348	20.64	31.21	3040
Fraxinus	600	4	0.5-1	4.000	22.18	54.83	5390
Picea	600	2	0.5-1	2.707	20.85	14.76	530

Table 6. Summary of optimum conditions and predicted char yield and zinc adsorption performance.



Highlights

Taguchi design was used to optimise pyrolysis process conditions for multiple feedstocks

Temperature had greatest influence on char yield but not adsorption performance Catalytic effect of feedstock components reduced energy input and improved adsorption s fr. Grass fibre char removed 92.96 % Zn from groundwater after pyrolysis for 2 hours at