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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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## 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.
- Grass fibre char removed 92.96% Zn from groundwater after pyrolysis for 2 h at 300 °C.

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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 *L. perenne* and its extracted fibre displayed the greatest zinc adsorption performance and removed 83.27–92.96% respectively. Optimum process conditions in terms of both char yield and zinc adsorption performance were achieved from slow-pyrolysis at 300 °C for 2 h using a feedstock with a particle size of less than 1 mm.



## 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 and 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

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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., 2014, 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 viminalis*) 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 and 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 and 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 and 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 $O_2$ and/or provide an entrained flow is typical. However most commercial slow-pyrolysis reactor systems $O_2$ concentration within the reactor is reduced principally by $CO_2$ 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 $CO_2$ 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 rigour. Several studies have identified effects on char yield and surface properties under fast-pyrolysis conditions at temperatures between 550 and 850 °C (Guizani et al., 2014; Zhang et al., 2011) however the effects of $CO_2$ 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

*F. excelsior* (*Fraxinus*) and *P. sitchensis* (*Picea*) feedstocks were obtained as chip from a commercial saw mill. *L. 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 *S. viminalis* (*Salix*) samples were also taken from research plots at Aberystwyth University. *S. viminalis* was obtained from 2 year. growth from a short-rotation coppice bed and 1 year. growth senesced *M. x giganteus*; both plots have

**Table 1**
Factors and levels included in Taguchi experimental design.

| Factor | Level 1 | Level 2 | Level 3 |
|---|---|---|---|
| Temperature (°C) | 300 | 450 | 600 |
| Residence time ($min^{-1}$) | 120 | 240 | 360 |
| Particle size (micron) | <500 | 500–1000 | 1000–2000 |
| Gas atmosphere | $N_2$ | $CO_2$ | – |

**Table 2**
$L_9$ orthogonal array used in the study.

| Treatment no. | Temperature | Residence time | Particle size | Gas 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 | 2 | 3 | 1 | 2 |
| 7 | 3 | 1 | 3 | 2 |
| 8 | 3 | 2 | 1 | 1 |
| 9 | 3 | 3 | 2 | 1 |