Characteristics and mechanisms of atrazine sorption to biochar for land remediation

O.W.T. McMillan

Abstract

Contaminated land is a widespread, global issue affecting millions of people. Atrazine is a commonly used herbicide which often contaminates groundwater and drinking water supplies and is associated with adverse health outcomes. Biochar is the solid product of pyrolysis and is associated with several environmental benefits. It may be an effective remediation tool when used as a soil amendment. This thesis investigates the mechanisms through which biochar can immobilise atrazine, and the implications of the mechanisms for remediating contaminated land.

Nine biochar samples were obtained from the United Kingdom Biochar Research Centre (UKBRC), which were produced from softwood pellets (SWP), wheat straw pellets (WSP), miscanthus straw pellets (MSP), rice husk (RH) and oil seed rape (OSR) each at pyrolysis temperatures of 550°C and 700°C (excluding OSR at 700°C). The sorption mechanisms controlling atrazine sorption to these biochars were determined through various characterisation methods and batch sorption experiments. The sorption tests showed that sorption to each of the standard biochars occurs via multiple simultaneously occurring mechanisms, which are each promoted under certain conditions. Studies investigating sorption kinetics, isotherms and interactions with humic acids showed that for all biochars in this study, pore filling was a significant process through which atrazine is transported to adsorption sites, although poor intraparticle diffusion for SWP and OSR biochars can prevent efficient transport. WSP and RH biochars showed effective pore diffusion, resulting in high sorption capacities. Partitioning was associated with poor remediation outcomes and was significant to SWP biochars, although adsorption dominated overall sorption for all other biochars. pH was shown to significantly influence the occurrence of various sorption mechanisms. At low pH values, most biochars showed evidence of electrostatic repulsion between positive atrazine species and the positively charged biochar surface. At intermediate pH values, all biochars showed strong hydrogen bonding between H+ groups on the surface of the biochar and atrazine. A meta-analysis of previous relevant studies provided further evidence for hydrogen bonding of atrazine to biochar and showed that hydrophobic effects likely play little role in adsorption after accounting for the effects of surface area. Varying contributions of π-π EDA interactions, hydrogen bonding involving biochar O-groups, and interactions with ash minerals resulted in different sorption profiles for each biochar at high pH values.

In order to further determine the mechanisms controlling sorption at high pH, surface compositions of SWP550, RH700 and OSR550 biochars were modified using hydrofluoric acid (HF). Modification with HF successfully removed the ash contents of RH700 and OSR550 and reduced atrazine removal at high pH values. This suggested that the ash fraction increases atrazine removal at high pH through complexation or catalytic hydrolysis. The roles of the various mechanisms are related to remediation outcomes in a novel manner allowing for the improved design of biochar for environmental remediation.