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Equilibrium and kinetic mechanisms of woody biochar on aqueous glyphosate removal

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HIGHLIGHTS

- A waste byproduct of a bioenergy industry was used for glyphosate remediation.
- Maximum glyphosate removal at pH 5–6 due to electron donor–acceptor interactions.
- Rate limiting step may be chemisorption through sharing or exchange of electrons.
- Phenolic, amine, and carboxylic functional groups were involved in adsorption.

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ABSTRACT

We investigated the removal of aqueous glyphosate using woody (dendro) biochar obtained as a waste by product from bioenergy industry. Equilibrium isotherms and kinetics data were obtained by adsorption experiments. Glyphosate adsorption was strongly pH dependent occurring maximum in the pH range of 5–6. The protonated amino moiety of the glyphosate molecule at this pH may interact with π electron rich biochar surface via π – π electron donor–acceptor interactions. Isotherm data were best fitted to the Freundlich and Temkin models indicating multilayer sorption of glyphosate. The maximum adsorption capacity of dendro biochar for glyphosate was determined by the isotherm modeling to be as 44 mg/g. Adsorption seemed to be quite fast, reaching the equilibrium <1 h. Pseudo-second order model was found to be the most effective in describing kinetics whereas the rate limiting step possibly be chemical adsorption involving valence forces through sharing or exchanging electrons between the adsorbent and sorbate. The FTIR spectral analysis indicated the involvement of functional groups such as phenolic, amine, carboxylic and phosphate in adsorption. Hence, a heterogeneous chemisorption process between adsorbate molecules and functional groups on biochar surface can be suggested as the mechanisms involved in glyphosate removal.

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1. Introduction

Increasing use of pesticides and herbicides has led to ubiquitous contamination of water resources. Leaching, run-offs from agricultural lands, deposition from aerial applications and indiscriminate discharge from industrial wastewater are responsible for

water contamination by pesticides and herbicides (Arias-Estévez et al., 2008). Glyphosate [N-(phosphonomethyl)-glycine] is a broad-spectrum, non-selective, post emergence type of organophosphorus herbicide, widely used to control annual and perennial weeds (Waiman et al., 2012). According to the recent findings, around 650,000 tons of glyphosate has been used worldwide (Ke, 2013). In addition, glyphosate is highly water soluble and could be mobile in aquatic systems (Veiga et al., 2001). Water contamination with glyphosate has recently been reported. For example, glyphosate was detected in maximum concentration of

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0.476 mg L⁻¹ in natural water of United States (Battaglin et al., 2014). Similarly, 1.26–1.48 mg L⁻¹ concentration range of glyphosate was reported in natural waters of Brazil (Tzaskos et al., 2012). Although there is no specific guideline value for glyphosate, the European Union limits 0.1 µg L⁻¹ for any herbicide in drinking water (Hu et al., 2011). While glyphosate is generally believed to be an environmentally safe herbicide due to microbial degradation and short half-life, recently its biosafety is questioned (Hagner et al., 2013). Depending on soil structure and environmental conditions such as rainfall, glyphosate is prone to leaching and contaminating groundwater thereafter (Borggaard and Gimsing, 2008). Glyphosate is responsible for cardiac and respiratory problems, allergic reactions and many other acute toxic effects (Hu et al., 2011). Glyphosate is considered as an endocrine disruptor in human cell lines (Richard et al., 2005). Therefore, it is an urgent subject to treat glyphosate from water. Adsorption is a kind of potential and effective method for the remediation of such pollutants, in terms of low cost, flexibility and simplicity of design, and ease of operation (Salman and Abid, 2013). Glyphosate contains functional groups that are positively (secondary amino group) or negatively (phosphonic and carboxylic group) charged in aqueous phase (Cáceres-Jensen et al., 2009) and the adsorption mechanisms of glyphosate have been suggested to be as ligand exchange (Piccolo et al., 1992), surface complexation (Morillo et al., 1997), precipitation reactions (Cáceres-Jensen et al., 2009), and coordination bonding (Cáceres-Jensen et al., 2009). Compared to conventional wastewater treatment protocol adsorption is applicable for large-scale biochemical and purification applications which benefit from unique properties such as simple design, using non toxic and low cost adsorbents and high efficiency (Ghaedi et al., 2014).

Several studies have reviewed on using different materials, such as activated carbon (Speth, 1993), water industrial residues (Hu et al., 2011), clay substances (Gimsing and Borggaard, 2007) for glyphosate adsorptive removal. Recently, biochar is being widely focused as a universal sorbent similar to activated carbon, nevertheless biochar has drawn more attention due to its low cost and high removal capacity. However, residue remains after removal again to be disposed safely. In this case, a sorbent with high capacity would be an added advantage to the process. It is a carbonaceous material produced by thermal conversion of biomass under partial exclusion of oxygen using pyrolysis or gasification systems. The highly aromatic and porous structure, high negative surface charge and charge density is suggested to contribute high adsorption capacities of biochar (Zhang et al., 2013). Moreover, though biochar has demonstrated outstanding capabilities for the removal of organic pollutants from water (Zheng et al., 2010; Sun et al., 2012), little attention has been given to the adsorption of glyphosate onto biochar (Hagner et al., 2013). Biochar can be produced from any type of organic residue such as agricultural byproducts (Rehrah et al., 2014), plant residues (Zheng et al., 2010), animal manure (Zhang et al., 2013) and even from municipal solid waste (Jin et al., 2014). Hence, biochar has a high versatility of feedstocks. Not only that, biochar can be obtained as a waste byproduct from bioenergy industry. Very few studies reported the use of byproduct biochar on water contaminant remediation (Mohan et al., 2007). In our earlier study (Herath et al., 2015), waste woody biochar (dendro biochar) from a bioenergy production plant has been characterized and successfully used for immobilization of heavy metals. Nevertheless dendro biochar has not been explored for organic pollutant removal. The potential to combine bioenergy production, environmental remediation and waste management into one approach, using biochar may offer sustainable outcomes for our economy and environment. Thus, our aim was to examine the adsorption of glyphosate onto dendro biochar. The adaptability of different

adsorption isotherm and kinetic models to describe the experimental equilibrium data was also investigated.

2. Materials and methods

2.1. Biochar production and characterization

Biochar was obtained as a waste byproduct from a bioenergy industry (Dendro) at Thirappane, Anuradhapura District, Sri Lanka, where biomass of *Gliricidia sepium* was gasified at 700–1000 °C in order to generate electricity. The collected dendro biochar was air dried and ground to less than 1 mm prior to use. Physico-chemical characterization of biochar was done in our earlier study using standard procedures (Herath et al., 2015). Accordingly parameters as moisture, mobile matter, ash content, resident matter, pH, elemental composition and BET surface area were determined.

2.2. Sorption experiments

Glyphosate (98% purity) was purchased from Sigma Aldrich, USA. The working solution concentration was selected based on glyphosate concentrations reported in environmental water samples and especially in the wastewater produced in glyphosate manufacturing. The pH of the mixtures was adjusted using 0.1 M HNO₃ and 0.1 M NaOH. Distilled deionized water (resistivity: 18.2 MΩcm⁻¹) was used to prepare all the solutions throughout the experiment. A 1 g L⁻¹ dose of biochar was added followed by shaking at 100 rpm for an equilibrium period of 4 h selected based on preliminary experiments. Solutions were then filtered and aqueous glyphosate concentrations were determined using the procedure given in elsewhere (Bhaskara and Nagaraja, 2006) with a few modifications. Briefly, 0.5 mL each of 1% ninhydrin and 1% sodium molybdate was added to 0.2 mL of filtered sample and kept in a water bath at 85–95 °C for 12 min. Then the samples were cooled to room temperature, quantitatively transferred to 5 mL volumetric flasks and the volume was made up with distilled deionized water. The absorbance of the resulted purple color complex was measured at 530 nm using UV-Vis spectrophotometer (model UV-160 A, Shimadzu, Japan) and the remaining glyphosate concentrations were obtained from the calibration curve plotted by using 4 appropriate standards 4, 6, 10, 15 mg L⁻¹.

Adsorption edge experiments were conducted at 20 mg L⁻¹ glyphosate at different pHs from 3 to 8 using different acetate and phosphate buffers for a biochar dosage of 1 g L⁻¹. Batch isotherm studies were carried out in the glyphosate concentration range of 5–100 mg L⁻¹. Both isotherm and kinetic experiments were conducted at pH 5 with a biochar dosage of 1 g L⁻¹, buffered to pH 5 using 0.1 M acetic acid and 0.1 M sodium acetate (tri-hydrate) and shaken at 100 rpm (Hinotek THZ-100). A 20 mg L⁻¹ glyphosate was used for kinetics experiments. Samples were taken at pre-determined time intervals, filtered and analyzed for remaining glyphosate amount following the procedure mentioned above. The amount of glyphosate retained in the adsorbent phase was calculated using following equation (Mohan et al., 2011):

$$q_e = [C_0 - C_e]VM^{-1}$$

where q_e is the glyphosate amount adsorbed on biochar (mg g⁻¹); C_0 and C_e are the initial and equilibrium glyphosate aqueous phase concentrations (mg L⁻¹); V is the solution volume (L) and M is the biochar mass (g). In both isotherm and kinetic modeling, the non-linear regression analysis was conducted using Microcal Origin (Version 6).

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