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Kinetics, thermodynamics and mechanistic studies of carbofuran removal using biochars from tea waste and rice husks

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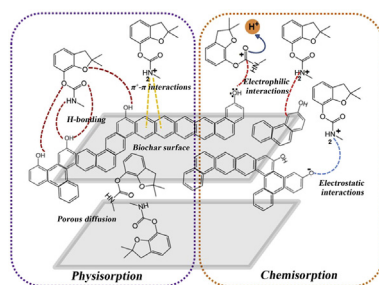
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HIGHLIGHTS

- RHBC 700 showed the highest equilibrium adsorption capacity for carbofuran.
- Negative ΔG values indicated the feasibility of carbofuran adsorption process.
- Physisorption was evident with enthalpy values and pseudo first order kinetics.
- Pore diffusion, $\pi^*-\pi$ interactions and H-bonding were physisorption interactions.
- Chemisorption mechanisms led via chemical bonding with phenolic and amine groups.

GRAPHICAL ABSTRACT



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ABSTRACT

This study reports the thermodynamic application and non-linear kinetic models in order to postulate the mechanisms and compare the carbofuran adsorption behavior onto rice husk and tea waste derived biochars. Locally available rice husk and infused tea waste biochars were produced at 700 °C. Biochars were characterized by using proximate, ultimate and surface characterization methods. Batch experiments were conducted at 25, 35, and 45 °C for a series of carbofuran solutions ranging from 5 to 100 mg L⁻¹ with a biochar dose of 1 g L⁻¹ at pH 5.0 with acetate buffer. Molar O/C ratios indicated that rice husk biochar (RHBC700) is more hydrophilic than tea waste biochar (TWBC700). Negative ΔG (Gibbs free energy change) values indicated the feasibility of carbofuran adsorption on biochar. Increasing ΔG values with the rise in temperature indicated high favorability at higher temperatures for both RHBC and TWBC. Enthalpy values suggested the involvement of physisorption type interactions. Kinetic data modeling exhibited contribution of both physisorption, via pore diffusion, $\pi^*-\pi$ electron donor-acceptor interaction, H-bonding, and van der Waals dispersion forces and chemisorption via chemical bonding with phenolic, and amine groups. Equilibrium adsorption capacities of RHBC and TWBC determined by pseudo second order kinetic model were 25.2 and 10.2 mg g⁻¹, respectively.

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1. Introduction

Biochar (BC) is emerging as a cost-effective alternative for activated carbon to remove various different pollutants from aqueous media as it can be produced by many feed stocks in the aid of different pyrolysis processes (Ahmad et al., 2014). Biochar preparation requires less energy versus activated carbon (Lehmann et al., 2011). However, type of feedstocks, process and pyrolysis temperature are the crucial factors which determines the quality and economic feasibility of biochars (Lehmann et al., 2011; Manyà et al., 2014). Biochars have been extensively used to remediate heavy metal, metalloids, antibiotics, pesticides from contaminated soils and waters (Ahmad et al., 2014). Pesticides are intensively used for preventing, destroying, repelling any pest in agricultural practice and their worldwide use has increased dramatically during the last two decades (Diez, 2010).

Due to widespread use of pesticides, their residues are frequently found in the water environment. Carbamate is one of the most frequently used pesticide. Carbofuran is a type of broad spectrum systemic carbamate used to control of soil dwelling and foliar feeding insects in many crop cultivations such as potatoes, corn, rice and grapes. Furthermore, carbofuran is known to be more persistent than other carbamate or organophosphate insecticides and thus often detected in water (Salman and Hameed, 2010). Low concentrations of carbofuran and its metabolites have been recorded in water samples from Kenya (0.005–0.495 mg L⁻¹) in the farmlands (Otieno et al., 2010) whereas highest concentrations reported from Bangladesh paddy land water were 0.198 mg L⁻¹ (Chowdhury et al., 2012). The World Health Organization specified the permissible limit of 0.007 mg L⁻¹ for carbofuran (Stewart et al., 2002) in drinking water. Generally, carbofuran has a half-life of 30–117 days depending on environmental conditions such as soil organic matter, pH and moisture content (Bermúdez-Couso et al., 2011). Due to high mobility of carbofuran in soils, it has high potential to runoff from treated sites, thereby contaminating groundwater in aquifers at elevated concentrations (Bermúdez-Couso et al., 2011).

In the recent decades, carbofuran is considered as one of the most hazardous pesticides widely used whole over the world including Sri Lanka, due to its toxicity, carcinogenicity, and mutagenicity (Bermúdez-Couso et al., 2011; Chen et al., 2012; Chowdhury et al., 2012; Makehelwala et al., 2012). Adverse effects of carbofuran contamination in soil and water systems may impact on humans, wildlife, animals as well as microorganisms. Presence of carbofuran in drinking water may directly cause irreversible neurological damages in living organisms causing attention deficit hyperactivity disorder, and developmental disorder in fetuses and children (Chowdhury et al., 2012). Carbofuran is currently encountered in malicious poisoning and hence, it can be considered as an emerging pollutant in the environment (Bermúdez-Couso et al., 2011; Chen et al., 2012). So that, experiment upon cost effective and environmental friendly strategies to remediate carbofuran contaminated waters is an urgent necessity.

Up to date, several treatment methods including ozonation, membrane filtration, chemical oxidation with ozone, photocatalytic method, combined ozone, UV radiation and adsorption have been applied for removal of pesticides from water (Makehelwala et al., 2012; Salman, 2012). The OH radical is being recognized as the best treatment strategy to destroy contumacious macro pollutants present in water (Makehelwala et al., 2012). However, aforementioned methods are highly expensive, destructive to the environment and required skill training (Makehelwala et al., 2012). Adsorption is effective and promising method of decontaminating wastewaters (Foo and Hameed, 2010; Chang et al., 2011; Salman, 2012). Carbon rich materials including biochars (BC) have been

recently applied as an economically and environmentally feasible adsorbent to immobilize organic as well as inorganic pollutants, such as pesticides, pharmaceuticals, heavy metals and nutrients present in soil and water systems (Ahmad et al., 2014; Vithanage et al., 2014; Herath et al., 2015). The adsorption characteristics of carbofuran on different types of adsorbents including, commercially activated carbon (Salman et al., 2011a), woody biochar (Yu et al., 2009), rice straw derived activated carbon (Chang et al., 2011) and walnut shells (Memon et al., 2014) have been investigated. Application of BC for the removal of pesticides from waters is of particular concern, since choosing a non-selective type of adsorbent has still become quite a difficult task. In a previous study, newspaper derived activated carbon has proved useful in removing glyphosate from aqueous solution with an adsorption capacity of 48.4 mg g⁻¹. More recently, it has been reported that birch wood derived BC can significantly reduce the mobility of glyphosate in the soil (Hagner et al., 2013).

The most important physicochemical aspects for the evaluation of adsorption batch process are the adsorption equilibria and the adsorption kinetics (Ho and Ofomaja, 2005). Mechanistic modeling of kinetic parameters plays a crucial role in describing the adsorption behavior of liquid–solid phase sorption systems. For practical applications such as designing a wastewater treatment plant for pesticides, it is essential to model the rate of adsorption and equilibrium time under different process conditions (El-Khaiary et al., 2010; Malarvizhi and Ho, 2010). Since adsorption/desorption of pesticides including carbofuran in soils is not an instantaneous processes, evaluation of their kinetics would provide an accurate prediction of the potential of carbofuran to be leached in the soil. In a recent study, adsorption–desorption kinetics of carbofuran have been tested by using three different methods such as, batch, soil column and stirred flow chamber to distinguish their performances (Bermúdez-Couso et al., 2012). Moreover, adsorption/desorption kinetics of carbofuran in acid soils have suggested that the desorption kinetic constant for carbofuran is generally higher than its adsorption kinetic constant and hence it is capable of rapidly leaching out than it is adsorbed in this soil system (Bermúdez-Couso et al., 2011). Walnut shell has been applied as an adsorbent to remove carbofuran from aqueous solution and this adsorption was first order process controlled by film diffusion (Memon et al., 2014). Hence, it is clear that adsorption kinetics is of great significance to evaluate the performance of a given adsorbent for particular contaminants and to gain insight into the underlying mechanisms. Kinetic performance of a given adsorbent is also important for the pilot application in order to design field scale remediation systems (Ho and Ofomaja, 2005).

Thermodynamics is important in terms of assessing the feasibility of adsorption reactions as well as the stability of solid–liquid phase system. Effects of temperature on the adsorption of carbofuran onto certain type of adsorbent can particularly be examined by thermodynamic parameters. The nature of carbofuran adsorption process onto walnut shells have further been described by thermodynamic parameters including, enthalpy change (ΔH) and gift free energy change (ΔG) in which, values of (ΔG) and (ΔH) indicated that carbofuran adsorption onto walnut shells is naturally feasible through an exothermic reaction (Memon et al., 2014).

However, to our knowledge, limited studies are available on using kinetics and thermodynamics data to assess the potential of biochar–carbofuran interactions in aqueous media (Mahmoud et al., 2012; Van Vinh et al., 2015; Yakout and Elsherif, 2015). The equilibrium of different pollutants in adsorption on biochars is still in its immaturity due to variable surface characteristics depending on pyrolysis temperature, production mechanisms and feedstocks, complexity of operating mechanisms of pollutants binding to biochar with ion exchange, complexation, electron donor–acceptor

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