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Potential of Different Biochars for Glyphosate Removal in Water; Implications for Water Safety

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Abstract: We investigated the potential of two different types of biochars (BCs), a waste by product from a Dendro bioenergy industry (DBC) and a steam activated rice husk derived biochar (SRBC) to remove glyphosate from aqueous media. Equilibrium isotherms and kinetics experiments were conducted to study the adsorption behaviour and postulate potential mechanisms. Glyphosate adsorption on both BCs was strongly pH dependent, exhibiting maximum on DBC and SRBC at 5-6 and 2-4 pH, respectively. Isotherm data obtained for DBC adsorption was best fitted to Freundlich and Temkin models indicating a multilayer adsorption, whereas glyphosate adsorption on SRBC was well described by Freundlich and Langmuir models suggesting both physisorption and chemisorption mechanisms for the adsorption process. The Langmuir maximum adsorption capacity of DBC and SRBC was 44.00 and 123.03 mg/g, respectively. The kinetics of glyphosate adsorption on DBC were best described by pseudo-second order mode indicating that the rate limiting step can possibly be a chemical adsorption, while pseudo-first order model described kinetics of glyphosate adsorption on SRBC indicating physisorption interactions for glyphosate adsorption. Pore diffusion, $\pi^*-\pi$ electron donor-acceptor interactions and H-bonding were postulated to be involved in physisorption, whereas electrophilic interactions led to chemisorption type of adsorption for both DBC and SRBC. Overall, both DBC and SRBC could be a promising remedy of glyphosate removal from aqueous solution.

Keywords: Pesticides, physisorption, chemisorption, kinetics, Adsorption capacity.

1. Introduction

The presence of pesticides in water at elevated concentrations has become worldwide а environmental problem in the recent decades due to its serious consequences on human health as well as the surrounding ecosystems. Glyphosate $(C_3H_8NO_5P)$ is an organophosphorous herbicide that is widely applied in controlling unnecessary growth of grasses, sedges, weeds and plants in farming, forestry, play grounds, parks and roads [1]. Glyphosate was introduced into the global market in 1974 and it has currently become one of the most widely used herbicides with the total global consumption of over 70,0000 tons per year [2]. So that, its high demand and excessive usage have posed widespread environmental problems due to persistent glyphosate residues.

The fate of glyphosate is mainly associated with the soil. Due to its high water solubility (12,000 mg/L), it can easily runoff into surrounding water reservoirs leading to significant glyphosate contamination in surface as well as groundwater systems [3]. Consequently, humans may be

subjected to numerous health problems of glyphosate exposure, including eye and skin irritation, contact dermatitis, eczema, cardiac and respiratory problems and allergic reactions [4]. It has been recently hypothesized the association of glyphosate exposure for chronic kidney disease of uncertain Aetiology (CKDu) in the rice paddy farming areas in Sri Lanka [3]. Hence, the use of glyphosate as a herbicide has been recently banned in Sri Lanka.

Adsorption is an efficient and promising strategy for decontaminating wastewaters. Although glyphosate has been currently recognised as a critical pollutant in the environment, no many studies have been documented for the removal of glyphosate from aqueous solution. In a previous study, activated carbon derived from waste newspapers has been successfully used as an adsorbent to remove glyphosate from aqueous solution [1]. Nevertheless, biochar (BC), a carbonrich product of waste materials such as rice husk, tea refuse, etc. has been recently used as an alternative and economically viable adsorbent to hazardous inorganic remove and organic

contaminants [5-7]. The use of BC is therefore a good option not only for environmental remediation, but also for waste management in the environment.

Up to date, many studies have focused on the application of non-activated BC in the remediation of pollutants in water and soil systems [7]. More recently, it has been reported that birch wood BC is capable of controlling the fate of glyphosate in the soil by reducing its mobility [8]. However, the activation of BC via steam is capable of escalating its adsorption capacity [1]. Only limited studies have been found to be focusing on the use of engineered type of BC for the removal of toxic contaminant [5, 9, 10]. In a recent study, steam activated BC produced from tea waste was proposed as an assured treatment for the removal of sulfamethazine from water with an adsorption capacity of 33.81 mg/g [1]. However, to our knowledge, the adsorption behaviour of glyphosate onto engineered BC has not previously been evaluated. Similarly, the identification, characterization and application of some waste byproducts of bioenergy industries for environmental remediation aspects have also been limited [6, 11]. Hence, this is the first time reporting on a comparison of adsorption capacities of two different types of BCs; steam activated rice husk derived BC (SRBC) and a waste by product of a dendro bioenergy industry in Sri Lanka (DBC), for the removal of glyphosate from aqueous solution.

2. Materials and Methodology

2.1 Biochar Production and characterization

The DBC was obtained as a waste by-product from a bioenergy industry (Dendro) at Thirappane, Anuradhapura District, Sri Lanka, where biomass of *Gliricidia sepium* is gasified at 700-900 °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).

The SRBC was produced from rice husk collected from Sri Lankan rice mills. Rice husk was then washed several times with distilled water and air dried. The dried biomass was crushed and ground to <1.0 mm in particle size. Rice husk was pyrolyzed at 700 °C with a heating rate of 7 °C min-1 for 2 h under limited O_2 in a modified N11/H Nabertherm (Germany) furnace. Char samples were then treated with 5 mL/min of steam for an additional 45 min under the peak

temperature after the 2 h pyrolysis period had elapsed.

2.2 Analysis of glyphosate

Analytical grade herbicide glyphosate (N-(phosphonomethyl) glycine) was used for this study. All the reagents used were obtained from Sigma Aldrich and were of analytical reagent grade. Residual aqueous glyphosate concentration was measured following the method described by Tzaskos et al. 2012 [12]. This is a colorimetric method, in which a purple colored complex is developed due to the reaction of glyphosate with ninhydrin and sodium molybdate. Standard glyphosate solutions including 4, 6, 10 and 14 mg/L were prepared from a stock solution of 1000 mg/L, followed by the addition of 0.5 mL of 5% ninhydrin and sodium molybdate solutions. The colour intensity of samples was measured at 570 nm (λ_{max}) using a UV-visible spectrophotometer (UV-160A, Shimadzu, Japan).

2.3 Effect of initial Ph

The effect of pH on glyphosate adsorption on SRBC and DBC was studied by adjusting the pH of glyphosate solutions with 1 M HNO₃ or NaOH solution in the range of 2.0 to 10.0 and glyphosate concentration of 20 mg/L and BC dosage of 0.5 g/L.

2.4 Batch adsorption kinetic experiment

Batch adsorption experiments were carried out at 20 mg/L of initial concentration of glyphosate and a sorbent dose of 0.5 g/L. The initial pH was chosen based on the optimum pH value obtained from the edge experiment. Teflon centrifuge tubes containing 10 ml of 20 mg/L of glyphosate solution. The mixtures were shaken for 30, 45, 60, 90, 120, 180, 240 min of reaction time at 100 rpm of shaking speed at room temperature (25 °C). At each reaction time, three centrifuge tubes were taken out and centrifuged at 3000 rpm for 15 min.

2.5 Adsorption isotherm

Batch isotherm studies were carried out in the concentration range of 0-100 mg/L at pH 5-6 and 3-4 for DBC and SRBC, respectively for an adsorbent dose of 0.5 g/L. An equilibrium time of 3 h was chosen based on preliminary kinetic experiments.

2.6 Experimental data modelling

In this study, non-linear isotherm and kinetic models were applied to the experimental data due to discrepancies of linear models as reported in recent studies [13]. In order to investigate the mechanism of adsorption process, five different non-linear kinetic models namely, the pseudo-first order, pseudo-second order, Elovich, Parabolic diffusion and Power function were applied to the experimental data [13]. The isotherm experimental data were analysed using four non-linear isotherm models including, the Langmuir, Freundlich, Redlich-Peterson and Dubinin-Radushkevish [14].

3. Results and discussion

3.1 Characterization of biochars

Proximate and surface characterization data for SRBC and DBC are summarized in Table 1.

Table 1: Proximate and surface characterization data for SRBC and DBC.

Parameter	Values	
	SRBC	DBC
pH	9.53	10.10
Moisture (%)	3.03	6.5
Mobile matter (%)	15.96	9.9
Ash (%)	45.62	19.7
Resident matter (%)	35.39	63.8
BET Surface area $(m^2 g^{-1})$	230	774
Pore volume ($cm^3 g^{-1}$)	0.08	0.89
Pore diameter (nm)	4.79	4.08

3.2 Effect of initial pH

The pH of solution is one of the key parameters that can have an impact on the adsorption process [1]. The optimum pH for maximum adsorption of glyphosate for SRBC (16.4 mg/g) and DBC (21.6 mg/g) was observed at 3-4 and 5-6, respectively. The glyphosate adsorption on both biosorbents decreased significantly with increasing solution pH. It is clear that the adsorption of glyphosate on both SRBC and DBC is highly dependent on solution pH, since it affects the surface charge of the adsorbent, as well as the degree of ionization and speciation of the adsorbate [1].

The point of zero charge (pHpzc) can be used to explain the effect of pH on the adsorption process. It has been previously proven that when the pH of solution is below the pHpzc, the surface of the adsorbent is positively charged and it becomes negative if the pH is above the pHpzc [1]. The pHpzc values of SRBC and DBC were 6.65 and 7.30, respectively. Since the pH value of the solution is below the pHpzc of adsorbents, the surface of both SRBC and DBC becomes positively charged, exhibiting predominantly the strong electrostatic interactions with negatively

charged groups of glyphosate molecules. When pH of the solution is decreased, the adsorption of glyphosate onto BC surface increases significantly due to increase in positive surface charge of BC that would encourage the electrostatic forces between the BC surface and negatively charged glyphosate species. When the pH of solution is increased the density of positive charge sites of BC surface decreases and the adsorption of glyphosate decreases due to the repulsive force between adsorbent and negatively charged adsorbate (9<pH). Hence, strong electrostatic interactions of positively charged BC surface and anionic groups of the glyphosate molecule are believed to be the major mechanism, resulting in the highest adsorption of glyphosate at acidic pH values.

3.3 Adsorption kinetics

Figure 1 shows the effects of shaking time on the adsorption of glyphosate and non-linear kinetic model fittings for SRBC and DBC. In the adsorption process of SRBC, a rapid adsorption of glyphosate was observed within first 60 min of contact time resulting in an adsorption of 29.3 mg/g (73.0%), and it was then followed by a slow adsorption rate reaching the equilibrium after 90 min standing 29.0-30.5 mg/g (74.0-76.0%) of maximum glyphosate adsorption (Figure 1a). Whereas the adsorption of glyphosate occurred very rapidly in DBC with an apparent equilibrium reached around 50-60 min at a maximum adsorption of 18.5-20 mg/g (Figure b).

The two phase adsorption is a commonly possible phenomena, pre-dominated by a rapid phase and a relatively slow phase [4]. This could be attributed to the fact that available active sites on the SRBC and DBC tend to get progressively saturated with time, resulting in a slow adsorption of the solute ions onto the bulk of the adsorbent. The rapid adsorption at the initial contact time is due to the availability of the positively charged surface sites of biosorbents for glyphosate interaction and the decrease in adsorption with time is perhaps due to the electrostatic hindrance between the adsorbed negatively charged adsorbate species onto the surface of BCs.

It can be noted that kinetics of glyphosate adsorption on SRBC were described well by the pseudo-first order model than other kinetic models applied in this study (Figure 1a). Fitting experimental data best to the pseudo-first order model suggested that the adsorption of glyphosate onto the steam activated RHBC would be more inclined towards physisorption type interactions, and also the adsorption process depends on the initial concentration of glyphosate. In contrast to the adsorption behaviour of SRBC, the pseudo second order model described well the adsorption kinetics of DBC, suggesting that chemisorption mechanisms can trigger the glyphosate adsorption on DBC.



Figure 1: Non-linear kinetic model fittings for glyphosate adsorption on (a) SRBC (b) DBC

3.4 Adsorption isotherm

Adsorption isotherm models are generally used to describe the relationship between the amount of glyphosate adsorbed by a unit weight of adsorbent and the remaining amount of substance in the solution at equilibrium. Figure 2 shows the non-linear isotherm model fittings for the adsorption of glyphosate on SRBC and DBC at 25 °C.

The adsorption isotherm data of SRBC fitted well to both Freundlich and Langmuir isotherm models best with high regression coefficients (R2>0.93), compared to other isotherm models (Figure 2a). Freundlich isotherm model suggested that glyphosate adsorption is a multilayer physical type of adsorption onto heterogeneous surfaces of the RHBC having different adsorption energies [14]. Glyphosate adsorption on SRBC was also well described by the Langmuir model, proposing that the glyphosate adsorption can also be governed by chemisorption mechanisms. The maximum adsorption capacity of SRBC calculated from the Langmuir model was 123.03 mg/g. Hence, it seems judicious to assume that glyphosate is adsorbed on the SRBC at 4.0 pH via both physical and chemical interactions.

The adsorption isotherm data of DBC was also best fitted with Freundlich model (R2=0.96) (Figure 2b), suggesting physisorption interactions via multilayer adsorption on heterogeneous and amorphous BC surface. Moreover, fitting experimental isotherm data of DBC (R2 = 0.92) to Temkin equilibrium model indicated the involvement of chemisorption type interactions for glyphosate adsorption on DBC. Overall, isotherm modelling data was greatly evident with the association of both physisorption and chemisorption mechanisms for the adsorption of glyphosate on SRBC as well as DBC.



Figure 2: Non-linear isotherm model fittings for glyphosate adsorption on (a) SRBC (b) DBC

3.5 Glyphosate adsorption mechanisms

In this study, mechanistic modelling of isotherm and kinetics data suggested that both physisorption and chemisorption mechanisms can govern the glyphosate adsorption on SRBC and DBC. The diffusion of glyphosate through the pores of BCs would likely to be the primary physical type mechanism. The SRBC and DBC normally consist of a plenty of micro-, meso- and macro- pores with high pore volumes. So that, the glyphosate molecule may easily diffuse into micro-, meso-, and macro-pores in BCs. High surface area of BCs greatly influenced the glyphosate adsorption. The π^+ - π electron donor-acceptor interaction is considered as another possible mechanism for glyphosate adsorption on both adsorbents at low pHs. In acidic pHs, the glyphosate molecule can exhibit strong cation- π bonding. Electron rich carbonized surface of SRBC and DBC can be bonded with protonated amino group of the glyphosate molecule forming strong π^+ - π electron donor-acceptor interactions. Strong H-bonding between BC surface carboxylic and phenolic groups and glyphosate molecule can also govern the adsorption process. In acidic pHs, surface phenolic and carboxylic groups of SRBC and DBC show great tendency to act as H-donor and acceptor, thus resulting in strong H-bonding with glyphosate molecules.

Chemisorption mechanisms may occur via electrostatic and electrophilic reactions. In acidic pHs, the phosphate group of glyphosate molecule easily tends to be protonated, which is capable of acting as a strong electrophile. This protonated phosphate group has high tendency to attack on either ortho or para positions of aromatic phenolic derivatives present in the SRBC surface, thereby leading chemisorption mechanisms via strong chemical bonding between glyphosate molecule and the surface of BC. Moreover, in acidic medium, negatively charged groups of ionized glyphosate molecule can be attracted by positively charged BC surface leading strong electrostatic forces between BC surface and glyphosate molecule.

4. Conclusions

The present study was conducted to investigate the potential of two different types of BCs; SRBC and DBC to remove glyphosate from aqueous solution. The SRBC showed the highest adsorption capacity for glyphosate compared to DBC. The adsorption of glyphosate on both adsorbents was highly pH dependent and the maximum adsorption was occurred under low pH conditions. Isotherm data obtained for DBC adsorption was best fitted to Freundlich and Temkin models indicating a multilayer adsorption of glyphosate, whereas glyphosate adsorption on SRBC was well described by Freundlich and Langmuir models suggesting both physisorption and chemisorption mechanisms can govern the adsorption process. The kinetics of glyphosate adsorption onto DBC

were best described by pseudo-second order mode indicating that the rate limiting step can possibly be a chemical adsorption, while pseudo-first order model described kinetics of glyphosate adsorption on SRBC, indicating physisorption interactions for glyphosate adsorption onto SRBC. Pore diffusion, $\pi^*-\pi$ electron donor-acceptor interactions and Hbonding were postulated to be involved in physisorption, whereas electrophilic interactions led to chemisorption type of adsorption for both DBC and SRBC. Overall, results concluded that both DBC and SRBC are highly effective in removing glyphosate in aqueous solution, thereby providing a distinct advantage in the remediation of glyphosate contaminated wastewaters.

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