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Mechanistic modeling of glyphosate interaction with rice husk derived engineered biochar

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ABSTRACT

Biochar (BC), a carbon-rich solid product of biomass, and its surface activation via steam have been recognized as alternative economically viable strategy to decontaminate wastewaters. Existence of glyphosate, the most extensively used non-selective herbicide, in waters at elevated concentrations has received worldwide attention due to its ill consequences. The main objective of the present study was to investigate the potential of steam activated BC produced from rice husk (RHBC) via slow pyrolysis at 700 °C to remove glyphosate from aqueous solution. Batch adsorption experiments were carried out to evaluate the effects of pH, reaction time and glyphosate loading on the RHBC adsorption process. Results showed that a maximum removal of glyphosate (82.0%) occurred at pH 4, and the adsorption capacity decreased significantly with increasing pH. Both the Freundlich and Langmuir models fitted best to the equilibrium isotherm data suggesting physisorption as well as chemisorption mechanisms governing the glyphosate adsorption. The Langmuir maximum adsorption capacity was 123.03 mg/g. The kinetics of the adsorption process was well described by the pseudo-first order indicating that the glyphosate adsorption onto RHBC would be more inclined towards physisorption depending on the initial glyphosate concentration. Pore diffusion, π–π electron donor–acceptor interaction and H-bonding were postulated to be involved in physisorption, whereas electrophilic interactions led to chemisorption type of adsorption. Overall, steam activated RHBC could be a promising remedy of glyphosate removal from aqueous solution.

1. Introduction

Contamination of water by pesticides at elevated concentrations has manifested the whole world due to its adverse effects on human health as well as the surrounding environment. Glyphosate ($C_3H_8NO_5P$) is a type of organophosphorous herbicide that is widely used in controlling unnecessary growth of some grasses, sedges, weeds and plants [1]. Glyphosate was introduced into the market in 1974, and it now accounts approximately 60% of the global herbicide sales with the total worldwide consumption of over 70,0000 tons per year [2]. Several surveys conducted in some countries documented that glyphosate is the most predominant herbicide used in UK arable crop production. In Denmark, the consumption of glyphosate accounts for 35% of all pesticides used in agricultural production and also Germany applies glyphosate on 4.3 million hectares (39%) of agricultural land per year [3].

Glyphosate can contaminate water systems via agricultural runoff by rain or water irrigation, and leakage to the groundwater from infected crop residues [4]. The fate of glyphosate is mainly associated with the soil, since it can easily drain off into surrounding water reservoirs. Consequently, humans have been subjected to numerous health consequences of glyphosate exposure, such as eye and skin irritation, contact dermatitis, eczema, cardiac and respiratory problems and allergic reactions [4]. The negative impacts of glyphosate in the environment mainly depend on its chemical formulation and speciation rather than on the concentration [5]. The use of glyphosate as a herbicide has been recently banned in Sri Lanka and El-Salvador due to the hypothesized

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involvement in chronic kidney disease of uncertain etiology (CKDu). However, its high demand and excessive usage have posed widespread contamination of water bodies due to remaining glyphosate residues [6].

Adsorption is an efficient and widely used phenomenon of decontaminating water. Because of various types of pesticides and their residues can exist in contaminated water systems, choosing a non-selective adsorbent is of particular concern. Carbon-rich solid materials such as activated carbon and biochar (BC) have been recently used as an alternative and economically viable adsorbent to remove or immobilize inorganic as well as organic pollutants, such as heavy metals, nutrients and veterinary drugs found in soil and water systems [1,7–10]. The high adsorption of pollutants onto BC is supposed to be due to the high surface area, micro-, meso- and macro-pores of BC and pH of the medium [8]. Many studies have focused on the production of BCs, their characterization and application in the remediation of antibiotics and heavy metals contaminated in water and soil systems [9,11,12]. However, only few studies have recently been found to be focusing on the use of engineered BC for the removal of some contaminants including heavy metals, pharmaceuticals, and nutrients (phosphates and nitrates) present in the environment [10,13–16].

It is presumed that steam activation of BC is capable of escalating its adsorption capacity. Steam can act as an effective oxidizing agent that may increase the surface area and pore volume of the BC. The functional groups attached on the BC surface are also capable of enhancing the adsorption process, which is directly influenced by the production conditions such as pyrolysis temperature, gas purging and steam activation. 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 a sorption capacity of 33.81 mg/g [8]. Activated carbon derived from waste newspapers has been successfully used as an adsorbent to remove glyphosate from aqueous solution [17], and this study estimated that the maximum adsorption capacity of activated carbon for glyphosate adsorption is 48.4 mg/g. More recently, it has been reported that birch wood BC is capable of controlling the fate of glyphosate in the soil by decreasing its leaching capability [18]. However, to our knowledge, the adsorption behavior of glyphosate on engineered BCs has not previously been evaluated, although it has been reported as one of the most widely used pesticide in the world. Hence, this is the first time reporting of engineered BC on the removal or immobilization of herbicide glyphosate along with postulated mechanisms.

In the present study, the adsorbent was produced by pyrolyzing rice husk biomass at 700 °C and produced rice husk biochar (RHBC) was further activated by purging steam in order to improve its capacity for glyphosate adsorption. The adaptability of different adsorption isotherm models to describe the experimental equilibrium data and different kinetic models to study the dynamic behavior of glyphosate adsorption process are investigated. Potential mechanism(s) of glyphosate adsorption onto the steam activated RHBC also are discussed at the end the paper.

2. Experimental

2.1. Biochar production and characterization

The RHBC samples were 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. The pH of the steam activated RHBC was measured in a suspension of 1:5 (w/v) BC/de-ionized water, using a digital pH meter (Orion, Thermo Electron Corp., Waltham, MA, USA). Moisture was determined by calculating the weight loss after heating the BC at 105 °C for 24 h to a constant weight. Mobile matter (analogous to volatile matter), which reflects the non-carbonized portion in BC, was determined as the weight loss after heating in a covered crucible at 450 °C for 30 min [12]. Ash content was also measured as the residue remaining after heating at 700 °C in an open-top crucible. The portion of the BC not ashed, referred to as resident matter (analogous to fixed matter), was calculated by the difference in moisture, ash, and mobile matter. Each sample was analyzed in triplicate.

Exchangeable Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} present in steam activated RHBC were extracted via the ammonium acetate procedure [19] and concentrations of metals were determined using an atomic absorption spectrophotometer (AAS, GBC933, Australia). The organic matter content was determined following the Walkley–-Black method [20]. The surface functional groups of steam activated RHBC were characterized by Fourier-transform infrared spectroscopy (FTIR) (Bio-Rad Excalibur 3000MX spectrophotometer, Hercules, CA, USA). The specific surface area, total pore volume, and pore diameter were determined using a gas sorption analyzer (NOVA-1200; Quantachrome Corp., Boynton Beach, FL, USA). Surface functional groups present on the steam activated RHBC were determined by the method Boehm titration. Surface titration was carried out to determine the point of zero charge of the steam activated RHBC.

2.2. Materials and measurements 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. [21]. 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, 8, 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 tubes were then sealed and the mixtures were heated in a water bath at a temperature of 85–95 °C for 12 min. The samples were cooled to room temperature and transferred to 5 mL volumetric flasks and the volume was made up to the mark with distilled water for the quantification. The color intensity of samples was measured at 570 nm ($\lambda_{\max}$) using a UV–visible spectrophotometer (UV-160A, Shimadzu, Japan). Finally, the concentration of glyphosate in each sample was determined by using the calibration curve in the range from 4 to 14 mg/L ($R^2 = 0.9963$). The blank solution was prepared with 0.5 mL of ninhydrin and sodium molybdate solutions to a total volume of 5 mL for the base line correction of the instrument.

2.3. Effect of initial pH

The effect of pH on glyphosate adsorption onto steam activated RHBC was studied by adjusting the pH of glyphosate solutions with 1 M HNO_3 or NaOH solution in the range of 3.0–9.0 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 conducted to study the adsorption kinetic of glyphosate onto steam activated RHBC with respect to time. In this study, 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 of 4.0 was chosen based on the optimum pH value obtained from the edge experiment. Firstly, 0.005 g of BC was weighed using a microbalance (Sartorius CPA2P Microbalance, 500 mg × 1 μg) into 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 (*G*-force = 1831, with 181.6 mm rotor radius; Beckman, GP Benchtop Centrifuge) for 15 min. The supernatants were then filtered through Whatman No. 1 filter paper for glyphosate analysis. The remaining concentration of glyphosate in the supernatants was analyzed by UV–visible spectrophotometer following the method described in Section 2.2.

2.5. Adsorption isotherm

Batch isotherm studies were carried out in the concentration range of 0–100 mg/L at pH 4.0 at room temperature. An adsorbent dose of 0.5 g/L was used for all adsorption experiments. An equilibrium time of 3 h was chosen based on preliminary kinetic experiments. The supernatants were then filtered using Whatman No. 1 filter papers for glyphosate analysis as described in Section 2.2.

2.6. Experimental data modeling

The chemical kinetics describes possible reaction pathways as a function of reaction time to reach the equilibrium. Kinetics of adsorption processes usually depends on the physical and/or chemical characteristics of the adsorbent, which may further influence the adsorption mechanism. In this study, non-linear isotherm and kinetic models were particularly applied to the experimental data due to discrepancies of linear models as reported in recent studies [22–24]. It is reported that in some circumstances, where the experimental data are well fitted to particular linearized kinetic model, it is statistically erroneous to compare the goodness of fit based on R^2 values [23]. Hence in such cases, applying non-linear models is supposed to be producing accurate and efficient estimates of the experimental data [23]. 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 [25]. Adsorption equilibria generally provide fundamental physio-chemical mechanisms for predicting the applicability and stability of adsorption processes as a unit operation. The isotherm experimental data were therefore analyzed using four non-linear isotherm models including, the Langmuir, Freundlich, Redlich–Peterson and Dubinin-Radushkevish [26].

3. Results and discussion

3.1. Biochar characterization

Proximate and surface characterization data of steam activated and non-activated RHBC are summarized in Table 1. The activation of BC surface by steam was attributed to increase the specific surface area and pore volume in significant extent. In this study, the steam activation increased the surface area of RHBC by over 4-fold compared to the non-activated RHBC. Similarly, pore volume and pore size of steam activated RHBC were observed to be a 2- and 3-fold increase respectively, compared to the non-activated RHBC (Table 1). The activation of RHBC purging steam to the pyrolysis leads to liberate excessive syngas, mainly in the form of hydrogen and thereby resulting increased values of pore volume and surface area of the steam activated RHBC. In a similar study, the specific surface area of a steam activated BC derived from tea waste recorded to be approximately 576 m^2/g which was nearly 1.5-fold higher than that of non-activated BC [8].

Fig. 1 shows the SEM micrographs of steam activated and non-activated RHBCs. The SEM images showed morphological changes in steam activated and non-activated RHBC produced at the same temperature. The structures of both RHBCs clearly showed that the steam activated RHBC has a macroporous surface texture. It is obvious that the surface of steam activated RHBC is smoother than that of non-activated RHBC, suggesting that the activation with steam at 700 °C could create more pores and lead to a considerable removal of volatile matter preset in BC.

The point of zero charge (pHpzc) is the pH at which the net charge on the surface becomes zero. This was found to be 6.65 for the steam activated RHBC tested in this study (Fig. 2). When pHpzc < pH of the solution, the surface of a BC will be negatively charged whereas, when the pHpzc > pH of the solution, the BC surface tends to be positively charged [27]. The surface functional groups were characterized by the FTIR spectroscopy and quantified by using the Boehm titration method. The concentration of total acidic groups present on the surface of steam activated RHBC was 898.2 ± 8.57 μmol/g bearing phenolic, lactonic and carboxylic groups at concentrations of 430.8 ± 9.3, 439.0 ± 11.5 and 28.4 ± 2.8 μmol/g, respectively (Table 3). The exchangeable Ca^{2+}, Mg^{2+}, Na^+, and K^+ in steam activated RHBC were 0.095 ± 0.074, 0.089 ± 0.026, 0.024 ± 0.051 and 0.449 ± 0.083 cmol/kg, respectively and the cation exchangeable capacity (CEC) was 1.857 ± 0.234 cmol/kg. The total organic carbon (TOC) of steam activated RHBC was found to be 261.9 ± 1.8 mg/g.

The FTIR spectra of the steam activated RHBC before and after the adsorption of glyphosate are shown in Fig. 3. All peak assignments were based on previous studies [7,28,29]. The entire spectra showed that some peak shifting, increase in intensity as well as appearance of new peaks due to glyphosate interaction. The broad peak observed at 3425 cm^{-1} in RHBC corresponded to the stretching vibration of –OH groups which is likely from either alcoholic or phenolic or carboxylic functional groups present on the BC surface. The phenolic O–H stretching is further proved by strong absorption peak exhibited at 1097 cm^{-1} in the fingerprint region of the FTIR spectrum. The absence of a sharp peak appeared near 1642 cm^{-1} confirms that there was no physically sorbed water on the adsorbent. The peak at 2919 cm^{-1} in untreated RHBC is assigned mainly to C–H stretching vibration. Both spectra exhibit peaks at the wave numbers lower than 900 cm^{-1} (465 and 765 cm^{-1}), which represent C–H out-of-plane deformation condensing smaller aromatic units into larger sheets. The peak at 1578 cm^{-1} in untreated RHBC corresponded to the C=C ring stretching vibration that can be attributed to the aromatic C–C bonds and has shifted to 1632 cm^{-1} in glyphosate adsorbed RHBC spectrum which may be due to creating different types of interactions with aromatic derivatives present in the activated RHBC and glyphosate molecule. The prominent peak exhibited at 1384 cm^{-1} in glyphosate treated activated RHBC could be due to C–N stretching vibration of a newly formed bond. The other new peak arisen at 1744 cm^{-1} can be assigned to either free COOH or C=O stretching from adsorbed glyphosate molecules.

Table 1
Kinetic model parameters of glyphosate adsorption onto steam activated RHBC at 25 °C.

Model	Non-linear equation	Description	Isotherm parameters	Value	R^2
Pseudo-first order	$q_t = q_e(1 - e^{-k_1 t})$	k_1 – the rate constant (min^{-1}) q_e, q_t – sorption capacity at equilibrium and at time t, respectively (mg g^{-1})	k_1 q_e	0.0318 31.5551	0.9723
Pseudo-second order	$q_t = \frac{q_e^2 k_2 t}{1 + k_2 t q_e}$	k_2 – the rate constant ($\text{g mg}^{-1}\ \text{min}^{-1}$) q_e, q_t – sorption capacity at equilibrium and at time t, respectively (mg g^{-1})	k_2 q_e	0.0013 35.7057	0.8984
Elovich	$q_t = b\ln(ab) + \ln(t)$	q_t – sorption capacity at time t (mg g^{-1}) a – initial sorption rate ($\text{mg g}^{-1}\ \text{min}^{-1}$) b – desorption constant (g mg^{-1})	a b	7.9974 0.1732	0.7922
Power function	$q_t = a + k_p\sqrt{t}$	q_t – sorption capacity at time t (mg g^{-1}) b – power function constant k_p – power function rate constant	b k_p	11.4132 0.1964	0.7436
Parabolic	$q_t = b(t^{k_f})$	k_f – parabolic rate constant ($\text{cm}^2\ \text{sec}^{-1}$) q_t – sorption capacity at time t (mg g^{-1}) a – parabolic constant	k_f a	1.0930 16.8548	0.6679

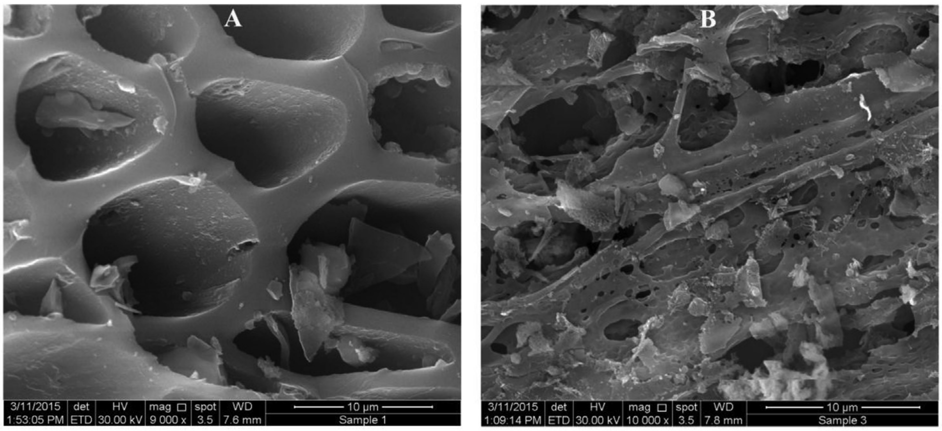

Fig. 1. SEM images of (A) steam activated RHBC and (B) non-activated RHBC.

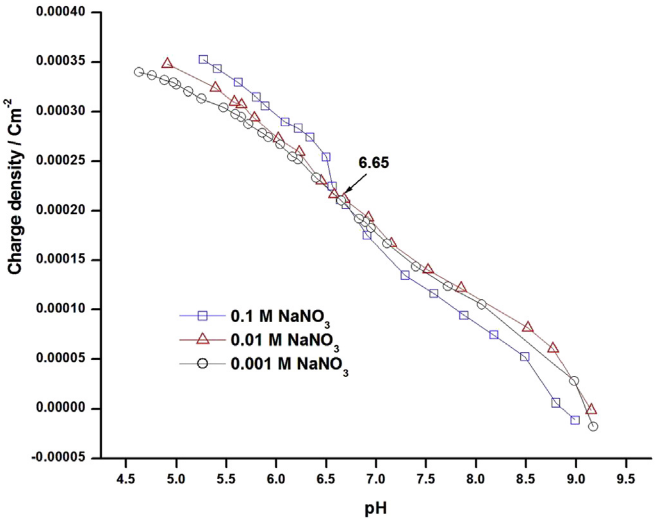

Fig. 2. Proton titration curves of steam activated RHBC as a function of ionic strength. The workable titration window is defined between pH 4.5 and 9.5.

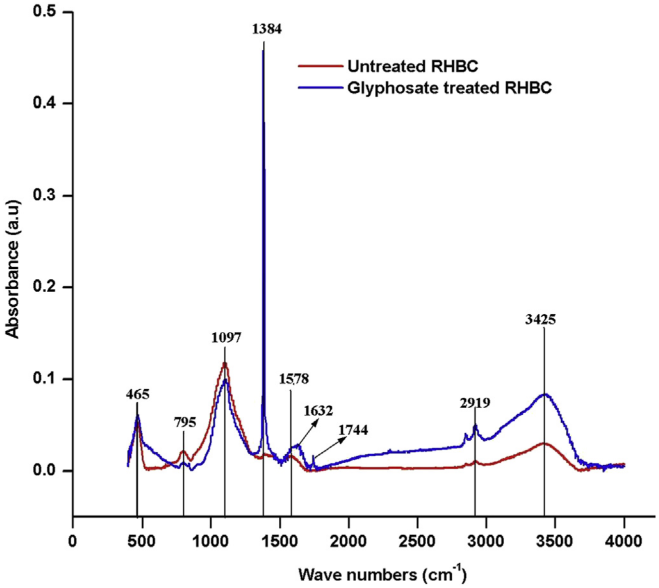

Fig. 3. FTIR spectra of untreated steam activated RHBC and glyphosate-adsorbed steam activated RHBC.

3.2. *Effect of initial pH*

The pH of solution is one of the key indices which have an impact on the adsorption process [1]. Fig. 4 shows the variation in the adsorbed amount of glyphosate by the steam activated RHBC with initial pH of the solution. The optimum pH for maximum adsorption of glyphosate (16.4 mg/g) was observed at 4.0. The adsorption capacity decreased significantly with increasing solution pH, resulting relatively a poor percentage adsorption of 56%

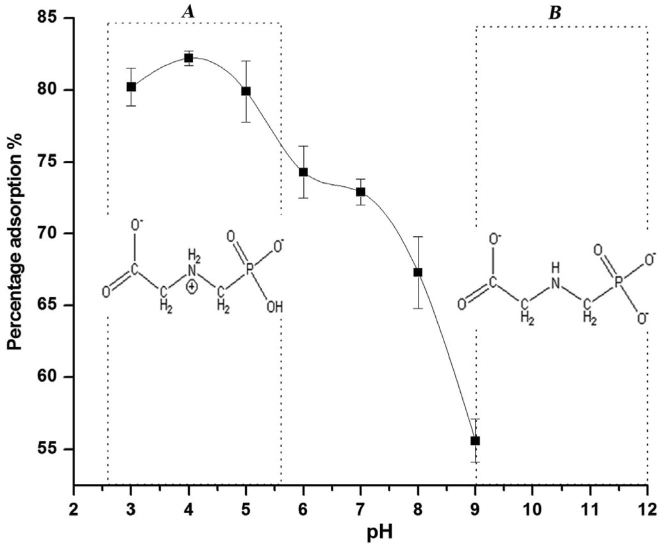

Fig. 4. Effects of pH on the adsorption of glyphosate onto steam activated RHBC and dissociation species of glyphosate (A) at 2.6 < pH < 5.6, (B) pH > 9. Error bars represent the standard deviation of three replicates ($N = 3$).

(11.1 mg/g) at pH 10.0. It is therefore clear that the adsorption of glyphosate onto the steam activated RHBC is highly dependent on pH of the solution, since it affects the surface charge of the adsorbent, as well as the degree of ionization and speciation of the adsorbate [1]. Moreover, the interaction of the ionic and functional surface group charge can be influenced on the adsorption process.

The pHpzc can be used to explain the effect of pH on the adsorption process (Fig. 2). 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. In this study, the maximum adsorption occurred at 4.0 pH at which glyphosate dissociates into its ionic form as shown in Fig. 4 [1]. Since the pH value of the solution is below the pHpzc (pH < 6.65), the surface of the BC becomes positively charged, exhibiting predominantly the strong electrostatic interactions with negatively charged groups of glyphosate molecules. Hence, when pH of the solution is decreased, the adsorption of glyphosate onto activated RHBC surface increases significantly due to the fact that increase in positive surface charge 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 the activated RHBC 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 activated RHBC 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. The same observation was reported in a recent study carried out on adsorption of glyphosate onto activated carbon derived from waste newspaper [1]. Moreover, phenolic and carboxylic derivatives present on the surface of steam activated RHBC can act as H-donor and acceptor groups, forming strong H-bonding with the glyphosate molecule, so that high amount of glyphosate adsorbed onto the BC at 4.0 pH.

3.3. Adsorption kinetics

Fig. 5(A) shows the effects of shaking time on the adsorption of glyphosate onto steam activated RHBC. 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. A similar trend was also observed for the adsorption of carbofuran from aqueous solution onto orange peel [29]. The two-phase adsorption is a commonly possible phenomenon, predominated by a rapid phase and a relatively slow phase [30]. This could be attributed to the fact that available active sites on the RHBC tend to get progressively saturated with time and hence 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 steam activated RHBC for glyphosate interaction and decrease in sorption with time is perhaps due to the electrostatic hindrance between the adsorbed negatively charged adsorbate species and the surface.

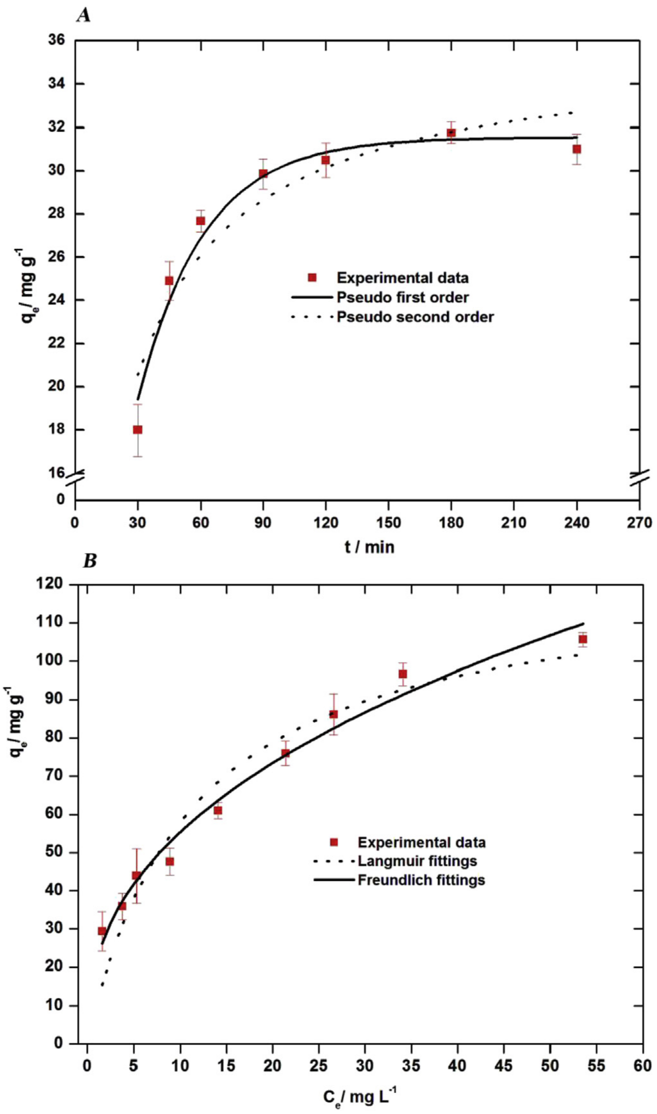

Fig. 5. (A) Non-linear kinetic model fittings of pseudo-first order and pseudo-second order models. (B) Non-linear isotherm model fittings of Freundlich and Langmuir models. Error bars represent the standard deviation of three replicates ($N = 3$).

The estimated values of kinetic model parameters together with the correlation coefficient (R^2) values are summarized in Table 2. It can be noted that kinetics of glyphosate adsorption process is

Table 2
Values of isotherm parameters for glyphosate adsorption onto steam activated RHBC at 4.0 pH. All parameters were calculated by non-linear regression.

Model	Non-linear equation	Description	Isotherm parameters	Value	R^2
Freundlich	$q_{ads} = K_F C_e^n$	K_F ((mg g^{-1})/(mg $L^{-1})^n$) − the Freundlich affinity − capacity parameter n − the Freundlich exponent	K_F ((mg g^{-1})/(mg $L^{-1})^n$) n	21.66 2.45	0.9827
Langmuir	$q_{ads} = \frac{q_{max} K_L C_e}{1+K_L C_e}$	q_{ads} (mg g^{-1}) − the amount of adsorbate adsorbed per unit weight of adsorbent q_{max} (mg g^{-1}) − the maximum adsorption capacity K_L (L mg^{-1}) − the Langmuir affinity parameter C_e (mg L^{-1}) − the equilibrium adsorbate aqueous phase concentration	q_{max} (mg g^{-1}) K_L (L g^{-1})	123.03 0.0892	0.9349
Redlich–Peterson	$q_e = \frac{K_R C_e}{1+a_R C_e^{b_R}}$	K_R (L mg^{-1}) − Redlich–Peterson isotherm constant, C_e − equilibrium adsorbate concentration (mg L^{-1}), a_R −Redlich–Peterson isotherm constant, b_R − Redlich–Peterson isotherm exponent	K_R (L mg^{-1}) A (dm^3 $mmol^{-1}$) b	0.1468 −1.0011 −0.0161	0.8062
Dubinin-Radushkevish	$q_{ads} = q_D \exp(-B_D[RT\ln(1+1/C_e)]^2)$	q_D − monolayer adsorption capacity B_D − mean free energy of sorption (mol^2 kJ^{-1})	q_D (mg g^{-1}) B_D (mol^2 kJ^{-1})	87.1737 3.93E-06	0.6418

described well by the pseudo-first order non-linear model than other kinetic models applied in this study [Fig. 5(A)]. The goodness of the fitting of experimental data to the pseudo-first order non-linear model is further proven by the value of adsorption capacity evaluated by the pseudo-first order model (31.6 mg/g), as it is very much close to the experimental value (29.5 ± 0.7 mg/g). Pseudo first order model can particularly be used to distinguish the concentration of glyphosate and adsorption capacity of the steam activated RHBC. Fitting experimental data best to the pseudo-first order model suggests that the adsorption of glyphosate onto the steam activated RHBC would be more inclined towards physisorption mechanism, and also the adsorption process depends on the initial concentration of glyphosate.

3.4. Adsorption isotherm and distribution coefficient

Adsorption isotherm models generally 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. The adsorption isotherms of Freundlich and Langmuir models for the adsorption of glyphosate onto the steam activated RHBC is shown in Fig. 5(B), and the isotherm parameters are given in Table 3. The adsorption data best fitted to both Freundlich and Langmuir isotherm models with high regression coefficients (R^2 > 0.93) compared to other isotherm models. Freundlich isotherm model suggests that glyphosate adsorption is a multilayer physical type of adsorption onto heterogeneous surfaces of the activated RHBC having different adsorption energies [26,31]. The Freundlich parameter, n, was always less than 1 (Table 3), further suggesting that the adsorption sites on the activated RHBC were not homogeneously distributed. In physical adsorption processes, the adsorption capacity is often a function more of the adsorbate rather than the adsorbent and interestingly, the adsorption mechanism does not lead to a change in the physical properties of adsorbent. Glyphosate adsorption data were also well described by the Langmuir model, proposing that the glyphosate adsorption is also governed by chemisorption mechanism. The maximum adsorption capacity calculated from the Langmuir model was 123.03 mg/g. With regard to the maximum adsorption capacities of both pseudo-first order and Langmuir isotherm models, it seems judicious to assume that at 4.0 pH, glyphosate is adsorbed onto the steam activated RHBC via both physical and chemical interactions.

The separation factor (R_L), which is based on Langmuir parameters can be used to determine the favorability of the glyphosate–RHBC adsorption system. The relationship between the calculated R_L and initial concentration of glyphosate is shown in Fig. 6(A). The R_L values were <1 for all concentrations of glyphosate, indicating that the adsorption of glyphosate onto the steam activated RHBC is a favorable and feasible process. Moreover, the affinity of glyphosate adsorption process can also be explained by the adsorption distribution coefficient (K_D) and it was calculated at different pH values following the lowest equilibrium concentration (20.0 mg/L). Fig. 6(B) shows the dependence of K_D values on pH for glyphosate adsorption. Within the tested concentration, K_D lay in the order of 10^3 for all pH values and the highest KD value (4.6 × 10^3 L/kg) was observed at pH 4.0 at which the maximum glyphosate sorption occurred. However, the K_D values decreased sharply with increasing pH, which would be the case for the reduction of glyphosate adsorption with increasing solution pH. The calculated K_D values were significantly larger than those reported in recent studies for natural geo-sorbents such as soils (K_D < 10 L/kg), humic substances and clay minerals (K_D < 100 L/kg) [32] and less than those recorded for steam and N_2 activated tea waste BC produced at 700 °C (10^4 L/kg) [8] and black carbon (K_D < 10^6 L/kg) [9].

Table 3
Proximate and surface characterization data of steam activated and non-activated RHBC.

Proximate parameters					
RHBC	pH	Moisture (%)	Mobile matter (%)	Ash (%)	Resident matter (%)
Non-activated	9.87 ± 0.14	3.42 ± 0.62	26.13 ± 0.95	39.24 ± 1.73	31.21 ± 0.98
Steam activated	9.53 ± 0.58	3.03 ± 0.37	15.96 ± 1.40	45.62 ± 0.84	35.39 ± 1.69
Surface characterization					
RHBC	BET surface area/m^2 g^{-1}	Pore volume/cm^3 g^{-1}	Pore size/nm	Total carboxylic groups/μmol g^{-1}	Total phenolic groups/μmol g^{-1}
Non-activated	51.92 ± 0.01	0.04 ± 0.006	4.79 ± 0.08	–	–
Steam activated	229.94 ± 0.07	0.08 ± 0.003	14.91 ± 0.05	28.4 ± 2.8	430.8 ± 9.3

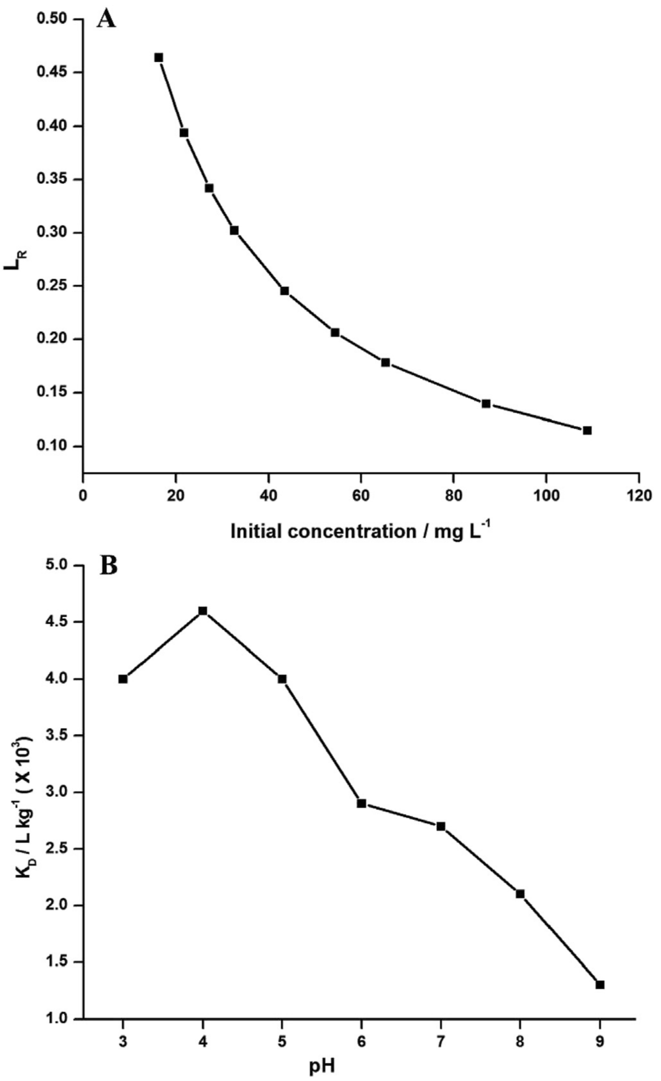

Fig. 6. (A) Separation factor (R_L) obtained from the Langmuir isotherm model at 4.0 pH. (B) The dependence of K_D values on solution pH for glyphosate adsorption.

3.5. Possible mechanisms for glyphosate adsorption

In this study, isotherm and kinetics modeling data suggested that both physisorption and chemisorption mechanisms trigger the adsorption of glyphosate onto the steam activated RHBC. Physical adsorption is mainly caused by the forces of molecular interactions including permanent dipole/induced dipole and quadrapole interactions, van der Waals dispersion forces, π^+–π electron donor–acceptor interactions as well as hydrogen bonding via H-donor–acceptor interactions [27]. These forces are particularly formed by the physical changes such as surface area, pore volume and surface functional groups occurred in steam activated RHBC, thereby facilitating the glyphosate adsorption onto the steam activated RHBC surface. A graphical representation of possible mechanisms for glyphosate adsorption onto steam activated RHBC at 4.0 pH is illustrated in Fig. 7.

The diffusion of glyphosate through the pores of activated RHBC would likely to be the primary mechanism involved in the increased glyphosate adsorption by the steam activated RHBC. As shown in the SEM image, steam activated RHBC consisted of a large number of micro-, meso- and macro-pores with high pore volumes, nevertheless the majority was observed to be mesopores (2–50 nm). The glyphosate molecule may easily diffuse into such micro-, meso-, and macro-pores in the steam activated RHBC. High surface area of the steam activated RHBC greatly influenced the glyphosate adsorption.

The π^+–π electron donor–acceptor interaction is considered as another possible mechanism for glyphosate adsorption on the RHBC at low pHs. At pH 4.0, the glyphosate molecule can exhibit strong cation–π bonding as indicated by the highest K_D value (Fig. 7). Electron rich graphene surface of the activated RHBC can be bonded with protonated amino group of the glyphosate molecule forming strong π^+–π electron donor–acceptor interactions. This newly formed C–N bond stretching frequency corresponds to the prominent peak appeared at 1384 cm^{-1} in the FTIR spectrum of glyphosate treated activated RHBC (Fig. 3).

Moreover, at acidic pHs (pH < 5), the phosphate group of glyphosate residue 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 steam activated RHBC surface and thereby leading chemisorption mechanism via strong chemical bonding between glyphosate molecule and the RHBC surface. With regard to the FTIR spectra, the peak at 1578 cm^{-1} in untreated RHBC corresponds to the C=C ring stretching vibration that can be attributed to the aromatic C–C bonds and this band clearly shifted to 1632 cm^{-1} in glyphosate treated RHBC. This could possibly due to different types of such interactions including electrostatic, electrophilic and π–π electron donor–acceptor interactions with the glyphosate molecule, shielding the aromatic core of the activated RHBC surface.

The pH dependence of the equilibrium of the adsorbate and that of protonation/deprotonation equilibria of carboxylic acid and phenolic groups usually changes with pH. These changes can cause H-bonding between RHBC's surface carboxylic and phenolic groups and glyphosate molecule [8,27]. In acidic pHs, surface phenolic and carboxylic groups of the steam activated RHBC show a great tendency to act as H-donor and acceptor, thus resulting in strong H-bonding with glyphosate molecule. The formation of such strong intermolecular H-bonding is evident with appearing significantly increased O–H stretching frequencies at 3425 cm^{-1}, while dropping the stretching vibration of phenolic O–H at 1097 cm^{-1} in the FTIR spectrum of glyphosate adsorbed RHBC (Fig. 3).

Under alkaline conditions (9 < pH), glyphosate predominately prevails as an anionic species as shown in Fig. 4 (B), thereby decreasing the glyphosate adsorption. This is mainly due to the electrostatic repulsion between negatively charged glyphosate molecule and the RHBC surface. At high pHs (9 < pH), electrostatic repulsion between the negatively charged glyphosate and RHBC surface is mainly due to existence of conjugate bases of carboxylic and phenolic derivatives such as carboxylate and phenolate anions on the RHBC surface. Nevertheless, the formation of H-bonding is possible between surface carboxylate/phenolate anions with the donor H atom of the amine group of glyphosate molecule. Apart from that, the amine group of ionized glyphosate molecule in the alkali region (Fig. 4) can react with carboxylic groups present on the RHBC surface forming strong amide bonding, which may capable of withstanding the repulsive forces between the RHBC surface and glyphosate molecules at high pH values. Consequently, together with H-bonding and amide bonding resulted in a considerable glyphosate adsorption of 11.1 mg/g (55%) onto the steam activated RHBC even at 9.0 pH. Hence, the steam activated RHBC tested in this study can be used for the removal of glyphosate over a wide range of pH which

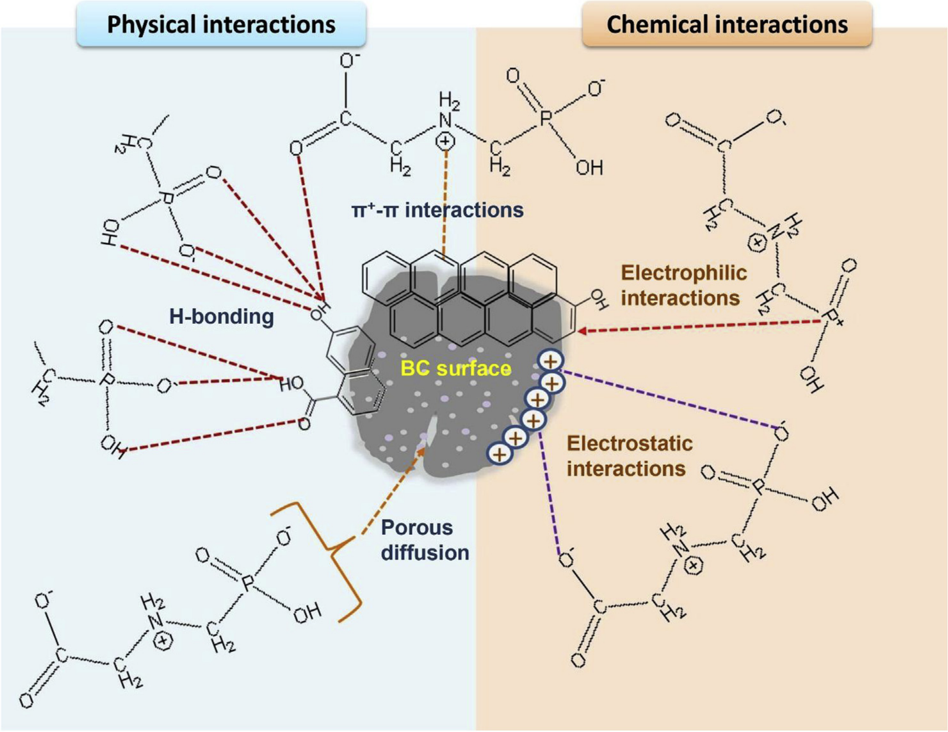

Fig. 7. Graphical representation of possible mechanisms for glyphosate adsorption onto steam activated RHBC.

would provide an efficacious benefit in the remediation of wastewater.

4. Conclusion

The present study was conducted for the first time to investigate the potential of a steam activated RHBC produced at 700 °C as an adsorbent to remove glyphosate from aqueous solution. The steam activated RHBC showed a significant adsorption capacity towards glyphosate adsorption due to its high surface area and pore volume. The adsorption of glyphosate onto steam activated RHBC was highly pH dependent and the maximum adsorption was recorded under low pH conditions ($pH < 4$), while significantly decreasing the adsorption capacity with increasing pH. Both Freundlich and Langmuir models fitted best the equilibrium isotherm data suggesting physisorption as well as chemisorption mechanisms governing the glyphosate adsorption. The kinetics of the adsorption process was explained well by the pseudo-first order model, indicating that the glyphosate adsorption onto steam activated RHBC would be more inclined towards physisorption mechanism depending on the initial concentration of glyphosate. Overall results concluded that the steam activated RHBC is highly effective in removing glyphosate in aqueous solution over a quite broad range of pH and thereby, providing a distinct advantage in the remediation of glyphosate contaminated wastewaters. Therefore, it is critical that this green technology is transferred from the laboratory phase to the field in order to remediate glyphosate contaminated wastewater reservoirs.

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