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Chitosan beads as the adsorbent for glyphosate removal from an aqueous solution

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Abstract

Chitosan beads were prepared to remove glyphosate from an aqueous solution via a batch adsorption system. The optimum conditions, including initial glyphosate concentration, adsorbent dose, and contact time, were investigated. Increasing the initial glyphosate concentration increased the equilibrium adsorption capacity onto the chitosan beads. The rapid sorption of glyphosate was found at an initial contact time of 30 min. The maximum adsorption capacity from 35 $mg\cdot L^{-1}$ glyphosate in solution onto 0.1 g chitosan beads was 12.7 $mg\cdot g^{-1}$. Increasing amount chitosan to 0.5 g dosage could remove more than 94% of the glyphosate for all initial glyphosate concentrations (1–35 $mg\cdot L^{-1}$), pH 7, and room temperature. The pH_{PZC} value of chitosan surface was determined approximately at pH 8. The glyphosate removal by chitosan bead was favored at pH below pH_{PZC}. The effects on the adsorption capacity, adsorption isotherm, and kinetics model were evaluated. The glyphosate uptake behavior fitted with the Freundlich adsorption model, while the kinetic adsorption fitted a pseudo-second order. The adsorption of glyphosate was proposed to be by electrostatic interaction between the negatively charged $–PO(OH)^-$ and $–COO^-$ groups, and the positively charged $–NH_3^+$ groups of chitosan.

1. Introduction

The organophosphate herbicide glyphosate, *N*-(phosphonomethyl) glycine ($C_3H_8NO_5P$; CAS registry number 1071-83-6), which contains phosphonic and amino acid groups [1], is a broad spectrum, non-selective, post-emergence herbicide that is extensively used in the control of many annual and perennial weeds [2]. Hence, these pollutants were contaminated to environment. Glyphosate is implicated in the biochemical alternation of various processes in plants and microorganisms [3]. Its main effect is to inhibit the enzymatic conversion that plants need to synthesize amino acids and proteins [4]. Although glyphosate adsorbs onto clay and organic matter, slowing its degradation by soil microorganisms and leading to its accumulation in soil over time [5], its strongly polar, water soluble (solubility in water is 12 $g\cdot L^{-1}$ at 25°C), and low volatility lead to a significant amount of glyphosate reaching the surface water, groundwater, and soil [6-8] after crop application. The health based value for glyphosate in drinking water is currently set at 0.9 $mg\cdot L^{-1}$ [9]. However, an enforceable regulation for glyphosate contamination of water of a maximum contaminant level at 0.7 $mg\cdot L^{-1}$ was permitted by the United States Environmental Protection Agency (USEPA) [10,11]. The maximum residual level of glyphosate in most crops is set at 0.1 $\mu g\cdot g^{-1}$ by the European Union [12]. Thus, monitoring the level of glyphosate in water is important for environmental control [13,14].

The development of efficient and cost effectiveness materials that could be used for drinking water treatment has attracted especially in rural communities. The use of various low-cost adsorbents for the removal of pesticides from water and wastewater applications has been reviewed [15-19]. Chitosan, poly[β-(1→)-2-deoxy-D-glucopyronose], is a linear polysaccharide composed of randomly distributed β-(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). Chitosan, has become increasingly attractive compared to other adsorbents due to its abundance, biodegradability, low toxicity, effectiveness, and environmentally friendly. Chitosan is derived from the deacetylation of chitin, which is obtained from renewable sources, such as the major component of crustacean shells. Adsorption with a modified adsorbent is a well-known method to eliminate herbicides because of its effectiveness and powerful adsorptive capacity. For example, a chitosan membrane could adsorb 10.88 μg glyphosate/g membrane [18]. Functional groups on chitosan chain has a high level of positively charged amino ($-NH_3^+$) groups (at a pH of less than 7) and hydroxyl (-OH). The $-NH_2$ and -OH functional groups are highly reactive giving the strong adsorptive capacity between chitosan and pollutants [20,21]. These binding sites are responsible for the removal of negatively charged herbicides like glyphosate. The adsorption of glyphosate has been investigated using pseudo-first and pseudo-second order kinetic models, as well as Langmuir and Freundlich isotherm models [19].

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The simple analytical method for glyphosate determination is based on the spectrophotometric absorption using colored reagents and chromophore groups [18,22-24]. The application of chitosan materials in form of beads were chosen due to an ease of operation and handle.

In this study, the potential of chitosan beads in the adsorption of glyphosate as the model herbicide was focused. Chitosan bead characterization, in terms of morphology, size distribution, and swelling capacity, was studied. The amount of glyphosate after adsorption was determined by spectrophotometry. The adsorption in terms of the adsorption capacity, adsorption isotherm model, and adsorption kinetics model was investigated.

2. Experimental

2.1 Materials

Chitosan (commercial grade; ; $\overline{M_w}$ 250,000 Dalton from shrimp shell, degree of deacetylation of 85%, moisture 13.0±0.01%, ash 1.1±0.08%, protein 3.2±0.08%, solubility 92.7±0.26%) was purchased from A.N. Lab, Thailand. Sodium hydroxide (analytical grade) was purchased from Carlo Erba, Italy. Acetic acid at 1% (v/v) was prepared for chitosan solvation. Ethanol and acetone (analytical grade) from QRëc, New Zealand were used as received without further purification. A syringe pump (New Era Pump Systems, Inc., USA) was used for bead preparation. Glyphosate solution (commercial grade, Esteem Intertrade Co. Ltd., Thailand) was used for preparing the stock solution of model herbicide. Ninhydrin (analytical grade, Fisher Scientific, USA) and sodium molybdate (analytical grade, Univar, Australia) were each prepared as a 5%w/v solution, the latter as 1 mL final.

2.2 Preparation of chitosan beads

Chitosan solution was prepared by dissolving 3%w/v of chitosan in 1%v/v acetic acid and then filtered. Typically, the viscous solution was extruded drop-wise into a mixture of 10%w/v sodium hydroxide in 50%v/v ethanol using a syringe pump attached to a micropipette tip (diameter of 0.4572 mm) under a controlled flow rate of chitosan solution at 70 $\text{mL}\cdot\text{h}^{-1}$. The chitosan beads that formed were gently stirred for 30 min and then washed with deionized water until the pH was neutral. The obtained chitosan beads were further washed with 50, 75, and 100%v/v aqueous ethanol solution, followed by acetone. The chitosan beads were then dried at room temperature and kept in a desiccator prior to use.

2.3 Swelling of chitosan beads

The swelling capacity of the chitosan beads were determined in a batch experiment at 25°C using 50 mL of deionized water per 0.1 g of chitosan bead (sample no. CS3) in a beaker. At the indicated time, the swollen beads were observed and measured under an optical microscope. The weight of absorbed water was determined from Equation (1) [18];

$$\text{Swelling} = (m_f - m_i)/\, m_i \qquad (1)$$

where m_i is the weight in the dry state (g) and m_f is the weight at equilibrium (g).

2.4 Characterization of adsorbents

The morphology of the chitosan beads was observed by scanning electron microscopy (SEM; Model SU3500, Hitachi Ltd., Japan). The samples were mounted directly onto the specimen stub using double-side carbon tape and were sputter coating with gold/ palladium (Au/Pd) to prevent charging of the specimen before analysis. The SEM was performed under a high vacuum at an electron voltage of 15 kV. The morphology of the chitosan beads was also examined under optical microscopy (Model C-3040, Olympus Camedia, Japan). In both cases, the diameter of about 200 chitosan beads were measured and the average diameter and size distribution is reported. The points of zero charge (pH_{PZC}) for chitosan bead as adsorbent was determined using the pH drift method [25,26]. A batch technique was used with three replicates for each experimental set. The pH of the 0.01 M NaCl as an electrolyte solution was adjusted to an initial value in range of 3 to 10 using either 0.5 M HCl and 0.5 M NaOH an pH meter (model UltraBasic, Denver Instrument, USA). Besides, the 5.0 mg/L of glyphosate was prepared. The 0.05 g of chitosan beads was added to 20 ml of each solution at pH adjusted solution. The solution was equilibrated for 24 h under agitation. The final pH of each sample was measured. The final pH values were plotted against initial pH. The pH at the intersection of initial pH equal to final pH was taken to be the PZC.

2.5 Batch adsorption experiments

Batch experiments were carried out to obtain a preliminary assessment of the effective of chitosan as sorbent materials. The glyphosate stock solution (500 $\text{mg}\cdot\text{mL}^{-1}$) was prepared in a volumetric flask and then diluted with deionized water to 100 mL final volume to give a final concentration of 1, 5, 15, 25, and 35 $\text{mg}\cdot\text{L}^{-1}$. To 1 mL each of test solution was added 1 mL of 5%w/v ninhydrin and 1 mL of 5%w/v sodium molybdate, mixed and then immersed in a water bath at 85-95°C for 10-15 min, then cooled to room temperature and quantitatively transferred to 10 mL volumetric flasks prior to determining the level of glyphosate spectrophotometrically as reported [18,23]. The assay is based upon the reaction of the secondary-amine (-NH) moiety of glyphosate with the ninhydrin in the presence of sodium molybdate as a catalyst to eliminate a H_2O molecule and produce a purple colored product that is then detected using a UV-visible spectrophotometer (model 20 Genesys, Spectronic Instruments, USA) at an absorbance wavelength of

570 nm [23,24]. The calibration curve was then derived from these five concentrations of glyphosate.

The effect of the initial glyphosate concentration on the adsorption time was investigated. The dosage of 0.1 g of chitosan beads were placed into a 250 mL Erlenmeyer flask containing 50 mL of different initial glyphosate concentrations (1, 5, 15, 25, and 35 mg·L^{-1}). The effect of the initial glyphosate concentration onto adsorption on its uptake by 0.1 g and 0.5 g of chitosan beads was investigated. The constant glyphosate volume (50 mL) and agitation (150 rpm) was used. The pH of the glyphosate solution is adjusted to pH 7.0. Batch experiments were carried out by using a mechanical shaker at a speed of 150 rpm and 27°C for 4 h. the mean of three independent measurements was calculated. The content of glyphosate adsorbed by the chitosan beads was determined as outlined above.

2.6 Adsorption isotherms of glyphosate onto chitosan beads

To evaluate herbicide adsorption, Langmuir and Freundlich isotherms were used as adsorption models. The Langmuir model describes adsorption by a surface with a finite number of identical sites, where each adsorbate molecule occupies a single site, and so forms a monolayer of adsorbate on the surface of the adsorbent. The Langmuir adsorption is described in Eq. (2) [15];

$$Q_e = \frac{Q_m K_L C_e}{(1+K_L C_e)} \tag{2}$$

where Q_e is the amount of glyphosate per chitosan weight at equilibrium (mg·g^{-1}), Q_m is the maximum amount of glyphosate adsorbed as a complete monolayer (mg·g^{-1}), C_e is the concentration of glyphosate solution at equilibrium (mgL^{-1}), and K_L is the Langmuir adsorption constant. Equation (2) could be linearized, as shown in Equation (3) and (4) [15];

$$\frac{1}{Q_e} = \left(\frac{1}{C_e}\right)\left(\frac{1}{Q_m{*}K_L}\right) + \frac{1}{Q_m} \tag{3}$$

$$\frac{C_e}{Q_e} = \frac{1}{(Q_m{*}K_L)} + \frac{C_e}{Q_m} \tag{4}$$

The Langmuir isotherm model can explain the adsorption characteristic in terms of the Langmuir adsorption constant separation factor (R_L), as shown in Equation (5);

$$R_L = \frac{1}{1+K_L C_0} \tag{5}$$

where $R_L > 1$ is a bad adsorption, $R_L = 1$ is a constant adsorption, $0 < R_L < 1$ is a good adsorption, and $R_L = 0$ is a reversible reaction [21].

The Freundlich model considers a multilayer coverage of the solute on the adsorbent, and is used to describe highly heterogeneous surfaces [18], and is described by Equation (6) [15],

$$Q_e = K_F C_e^{1/n} \tag{6}$$

However, Equation (6) could be linearized, as shown in Equation (7) [8];

$$\ln Q_e = \ln K_F + \frac{1}{n}\ln C_e \tag{7}$$

where Q_e is the amount of glyphosate per chitosan weight at equilibrium (mg·g^{-1}), C_e is the concentration of glyphosate solution at equilibrium (mg·L^{-1}), K_F is a Freundlich adsorption constant, and n is a Freundlich constant in terms of the concentration of adsorption.

For all of the chitosan bead adsorbents, the removal efficiency (R) of glyphosate was calculated using Equation (8)[27]:

$$R = \frac{C_0 - C_e}{C_0} \times 100\% \tag{8}$$

where C_0 is the initial concentration of glyphosate solution at equilibrium (mg/L), and C_e is the concentration of glyphosate solution at equilibrium (mg·L^{-1}).

2.7 Adsorption kinetics

In order to investigate the rate of adsorption and mechanism of adsorption by mass transferring between adsorbate and adsorbent, rate equations were applied to the data. The two models for the adsorption process explanations are the pseudo-first and second-order reactions. The pseudo-first order equation is shown in Equation (9) [28];

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \tag{9}$$

where q_t and q_e represent the amount of adsorbed glyphosate at time t and equilibrium (mg·g^{-1}), respectively, and k_1 is the first-order rate constant (min^{-1}). When $t = 0$; $t = t$, and $q_e = q_t$.

The pseudo-second order kinetic adsorption was proposed, where a plot of t/q_t against t gives a linear relationship, and is shown in Eq. (10) [29];

$$\frac{t}{q_t} = \frac{1}{k_2 q2_e} + \frac{1}{q_e} \tag{10}$$

where k_2 is the so-called pseudo-second order constant (mg·min^{-1}). The constant k_2, q_e, and the correlation coefficient (R^2) were obtained from a graph between t/q_e and t.

3. Results and discussion

3.1 Characterization of the chitosan beads

3.1.1 SEM analysis

The histogram of the beads size distribution revealed a narrow size distribution (Figure 1(a)) with an average diameter (from 200 beads) of 0.95±0.004 mm. The optical micrograph of the chitosan beads revealed they were spherical-shaped with a smooth surface (Figure 1(b)), along with irregular water droplet-like beads (Figure 1(c)). SEM was used to observe the surface morphology of the chitosan beads. The SEM micrograph revealed a quite smooth chitosan bead surface was covered with adhered substances outside the beads (Figure 1(d)).

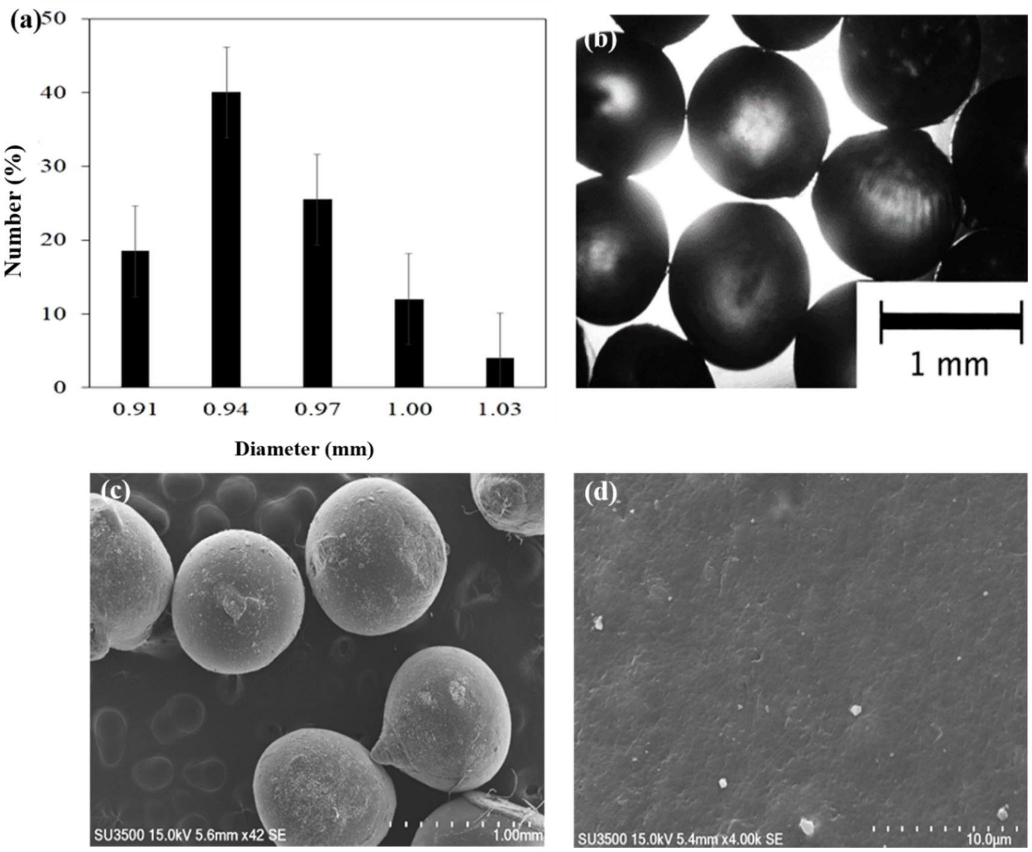

Figure 1. Characteristic of the chitosan beads showing (a) a histogram of their size distribution, and representative (b), optical micrograph (×40 magnification), and (c, d) SEM micrographs of the beads at a (c) low magnification (× 45), and (d) high magnification (× 4000) showing the beads surface.

3.1.2 Determination of pH_{PZC}

Point of zero charge (PZC) indicates the ability to adsorb the ions of pollutants on the adsorption surface of an adsorptive materials. The pH_{PZC} was described as the pH at which the net charge of total surface charge of adsorbent is equal to zero. The pH_{PZC} of chitosan is the pH when the nonspecific surface adsorption of anions and cation is equivalent. The pH_{PZC} of chitosan beads were evaluated by measurement of Na^+ and Cl^- as a function of pH (Figure 2(a)). The PZC for chitosan was determined to be approximately at pH 8, due to surface heterogeneity of chitosan. The existence of charge balance occurring in the basic region where the surface of chitosan is negatively charged. At the pH values lower than $pH_{PZC,}$ the chitosan showed the positively charges surface. Then, the pH values below pH_{PZC}, the positively charged on chitosan ($-NH_3^+$), and anions ($-PO(OH)^-$ and $-COO^-$) groups on glyphosate was enhanced. The similar experiment was set for glyphosate solution at different pH adjusted. The glyphosate solution at initial pH 3, the final pH is lower than pH_{PZC}. The high amount of H^+ ions in acidic region may inhibits the pH induction by chitosan. Besides, the initial pH in range of 4 to 10, the final pH at around pH_{PZC} value was determined. Glyphosate is a zwitterion with pKa values of for first phosphonic $pKa_2 = 2.2$; for second phosphonic $pKa_3 = 5.4$ and for amine $pKa_4 = 10.2$ [30]. The pH-dependent of glyphosate was found decreasing when increasing pH. However, this experiment was investigated the use of the pesticide by taking the environmental considerations into the account. For an adsorption study, the pH 7 was used as the pH_{PZC} of chitosan affect to the adsorptive strength of glyphosate. There is an increase in glyphosate adsorption when the solution pH is lower than pH_{PZC} [25].

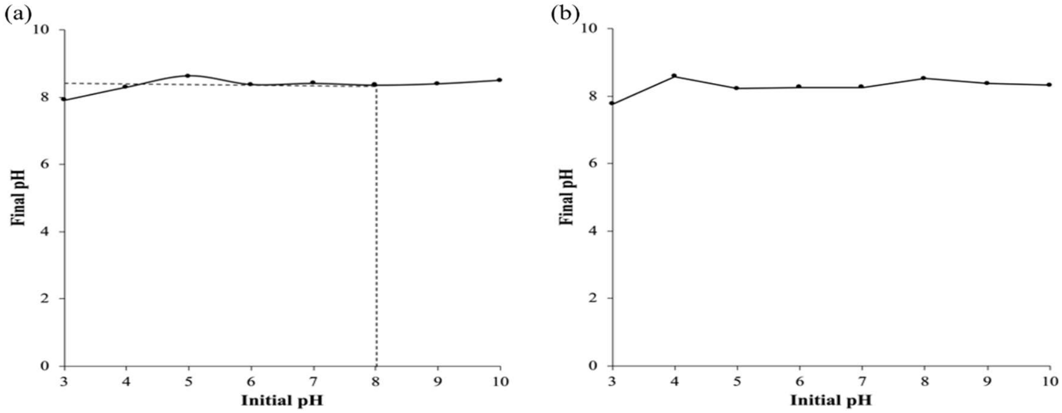

Figure 2. a) PZC of chitosan beads using 0.01 M NaCl solutions by pH drift method, and b) change of pH in the 5.0 mg·L^{-1} glyphosate; conditions: chitosan 0.05 g, 20 mL each solution volume, and contact time 22 h, room temperature.

3.2 Swelling behavior

Figure 3 shows the swelling data of the chitosan beads in deionized water over 120 h. The swelling capacity rapidly increased during the first couple of hours, then continued for several hours at a much slower rate until a maximum swelling of 66.7% was reached at 72 h. The swelling capacity then gradually decreased to 50% at 96 h and remained stable thereafter.The reduced swelling capacity after the equilibrium point indicates that the diffusion of water through the chitosan beads surface passed through the surface from the external solution outside of the beads until the maximum water holding capacity inside the beads was achieved. Subsequently, some of the water inside the beads was released in equilibrium by osmosis.

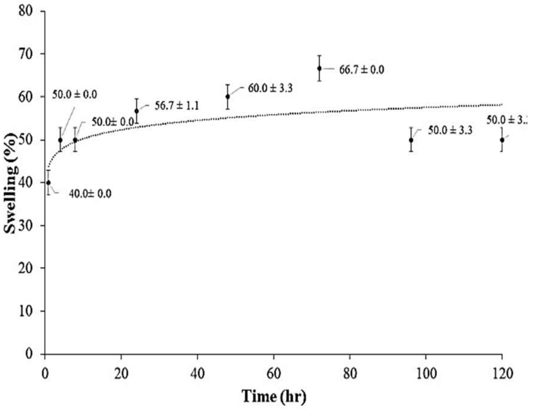

Figure 3. Swelling capacity curve for water adsorption by the chitosan beads. Data are shown as the mean ± SD, derived from 3 replicates.

3.3 Adsorption of glyphosate

The effect of initial concentration of glyphosate solution over a range 1-35 mg·L^{-1} by chitosan beads were investigated. The experimental data were fitted to the Langmuir and Freundlich isotherm models in order to predict the adsorption characteristic. Adsorption isotherms describe the distribution of adsorbate molecules between the liquid and solid phases. The glyphosate molecules are adsorbed on the surface of chitosan beads. The capacity of the adsorbent was described. Figure 4 demonstrates the fit of the data for the adsorption of glyphosate by these two adsorption isotherms. The relationship between the glyphosate adsorbed onto the chitosan beads (C_e/q_e) and glyphosate in the solution (C_e), based upon a monolayer adsorption onto a homogeneous surface without any interaction between molecules follows the Langmuir isotherm [29]. The linearized Freundlich isotherm, expresses the relationship between the adsorption capacity (ln q_e) and the intensity of glyphosate adsorption (ln C_e), respectively, in terms of a heterogeneous surface and for multilayer adsorption behavior [31], where q_e is the amount of glyphosate adsorbed at equilibrium (mg·g^{-1}).

Comparison of the coefficient of determination (R^2) for chitosan beads (sample no. CS3GP) with various concentrations of glyphosate were calculated. The equations for the linear regression ($y = ax + b$) matched reasonably well with the Freundlich equation ($R^2 = 0.8711$), but not with the Langmuir isotherm ($R^2 = 0.0851$). The calculated Freundlich adsorption constant K_F(mg·g^{-1})/(L·mg^{-1}) (1.5209) and n (1.4879) were obtained assuming a multilayer coverage of the glyphosate on the chitosan beads as a highly heterogeneous surface [18]. Therefore, a similar explanation could be offered as chitosan surfaces had available functional groups for glyphosate adsorption [32]. The Freundlich isotherm, an empirical isotherm for non-ideal adsorption on heterogeneous surfaces as well as multilayer adsorption of chitosan beads surfaces, had an n value more than 1, which indicated that the adsorption intensity was favor at higher concentrations. The adsorption steps could be explained as follows; (1) the diffusion of glyphosate through the liquid layer to the outer surface of chitosan, (2) the diffusion of glyphosate to internal pores of chitosan, and (3) the finally adsorption of glyphosate occurred inside the pores of chitosan.

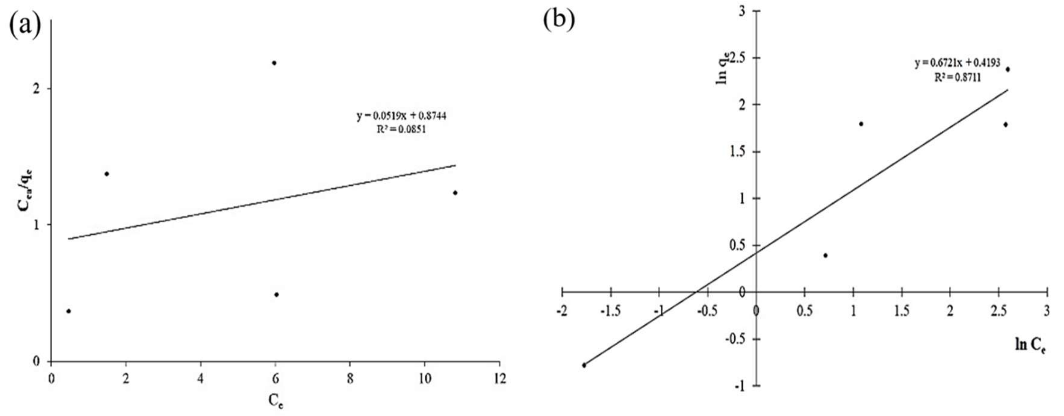

Figure 4. Adsorption isotherms of glyphosate solution on chitosan beads. (a) Langmuir isotherm and (b) Freundlich isotherm. Data are shown as the mean of triplicate trials at room temperature and pH 7.0

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3.4 Effect of the initial glyphosate concentration on adsorption glyphosate onto chitosan bead

Based on the assumption that the equilibrium state of a liquid/solid adsorption system is determined by four mutually related components: adsorbate in liquid phase, adsorbate in solid phase, uncovered adsorption site and covered adsorption site. Effect of the various initial glyphosate concentration against the chitosan dosage were determined. As shown in Figure 5, all the samples showed a rapid adsorption (at initial up to 30 min), which is due to the availability of vacant sites for adsorption. The adsorption subsequently slowed down until the maximum adsorption capacity for each glyphosate concentration was reached. The adsorption capacity increased with an increasing initial glyphosate concentration (Figure 5(a)), which was due to the different concentrations of glyphosate between the two phases; liquid/solid adsorption system. The glyphosate concentration at the surface of the chitosan beads form the driving force, causing an increased a mass transfer of glyphosate molecules and resulting in the glyphosate moving into the surface of chitosan beads. Increasing the initial concentration of glyphosate solution increased the liquid phase glyphosate, and so an increased electrostatic interaction between glyphosate- chitosan beads. The highest adsorption capacity uptake by 0.1 g chitosan was 12.7 mg·g^{-1} when using an initial glyphosate concentration of 35 mg·L^{-1}.

Increasing the adsorbent dose from 0.1 g to 0.5 g chitosan beads increased the maximum glyphosate adsorption in the initial contact time (Figure 5(b)). A plot of the initial glyphosate concentration against the removal efficiency shows that increasing the absorbent dose from 0.1 g to 0.5 g gave a higher removal efficiency for all the initial glyphosate concentrations. Chitosan has a specific number of adsorption sites available per fixed amount of adsorbate. Thus, the extent of adsorption by chitosan is governed by their surface properties, or in other words, surface charge on the sample [33], where the amino groups on the chitosan surface provide suitable adsorption sites to facilitate the adsorption of the negatively charged glyphosate.

3.5 Effect of contact time on the adsorption capacity of glyphosate

The influence of the contact time on the adsorption capacity of glyphosate over a range of 1-35 mg·L^{-1}was determined over a time range of 15-3240 min in separate runs. After the specific time, the supernatant was taken for analysis of glyphosate concentration (section 2.5). The adsorption capacity of chitosan beads for glyphosate showed slow kinetics. The adsorption capacity was increased by increasing of contacting time (Figure 5(a) and 5(b). The maximum glyphosate adsorption was reached within 240 min at 52-83% and 94-99% removal for 0.1 g and 0.5 g chitosan (Figure 5(c)). The rapid adsorption at 15 min with a high adsorption rate was observed suggesting the initial abundant surface area and availability of adsorption sites. The position of active sites on the chitosan beads surface was available, while the number of adsorbate molecules was constant [34]. The adsorption rate then gradually slowed due to the proportion of occupied active sites increased leading to the limited number of available binding sites until it reached equilibrium point. The slow absorption kinetics was observed after 75 min (for 0.1 g chitosan beads). In contrast, the adsorption capacity of glyphosate was found rather high (for 0.5 g chitosan beads) suggesting a large number of sites available for glyphosate adsorption. The adsorption pattern did not change with the contact time. The sorption and the removal efficiency was rapidly since the initial contact time. The sorption equilibrium for glyphosate was reached after 75 min (55-96% of 1-35 mg·L^{-1}), while the removal efficiency did not change afterwards.

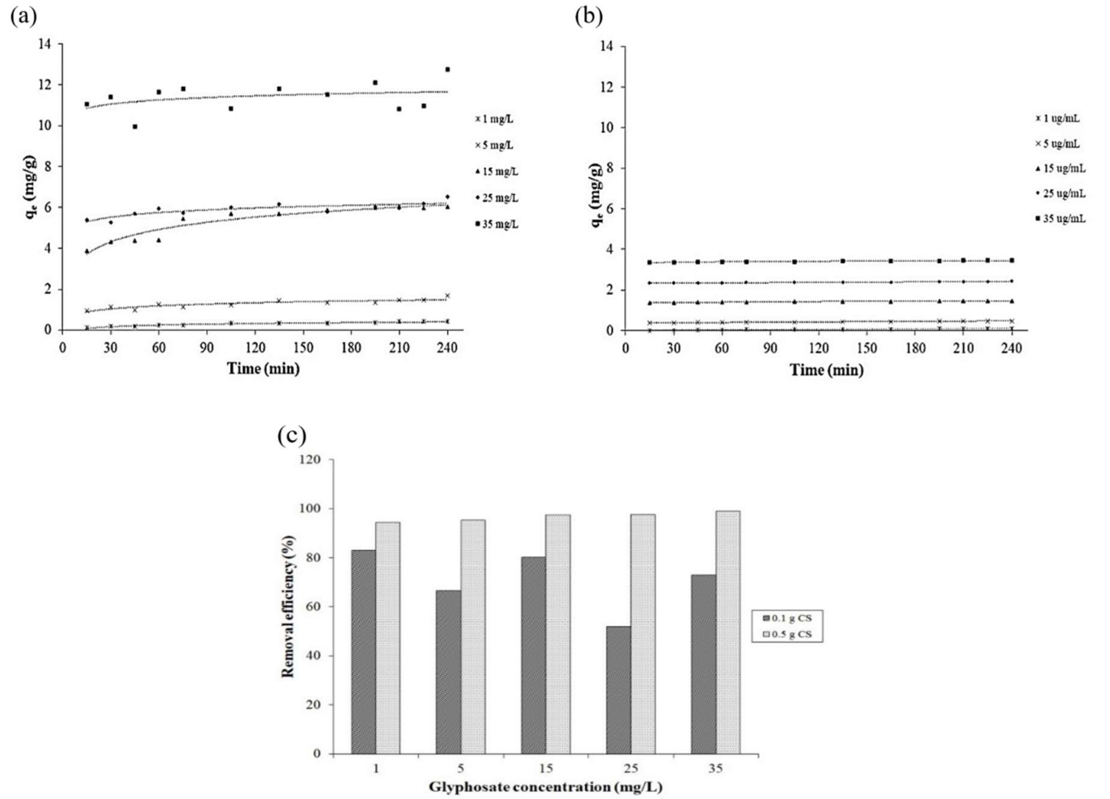

Figure 5. Adsorption capacity and glyphosate removal at different chitosan bead doses of: (a) 0.1 g and (b) 0.5 g. (c) removal efficiency. Data are shown as the mean derived from triplicate trials at room temperature and pH 7.0.

3.6 Adsorption kinetics

The adsorption kinetics of glyphosate on the chitosan beads was examined in a batch mode of operation under various conditions. Fitting of the experimental adsorption kinetics to the pseudo-first and -second order Equations was described (Table 1). The obtained kinetic data for the adsorption of different initial glyphosate concentrations by the chitosan beads (0.1 g) as shown in Figure 6. The results are indicated that the glyphosate adsorption capacity better fit to the pseudo-second order (R^2 close to 1) than that of the pseudo-first order. The adsorption of glyphosate onto chitosan beads increased with increasing initial glyphosate concentrations to a maximum adsorption of 12.7 $mg \cdot g^{-1}$when using an initial glyphosate concentration of 35 $mg \cdot L^{-1}$. Thus, the overall rate-limiting step for the adsorption of glyphosate was controlled by electrostatic interaction between the positive charges of the $–NH_3^+$ groups of chitosan and the negative charges of the phosphate ($–PO(OH)^-$) and carboxyl ($–COO^-$) groups of glyphosate in media at pH 2-7. The proposed adsorption interaction between chitosan and glyphosate is shown in Figure 7. In order to compare the glyphosate adsorption on chitosan beads with other studies previously published in literature. Table 2 shown the adsorption capacity of glyphosate with several materials and their conditions.

Table 1. Kinetic parameters of the glyphosate adsorption on chitosan fitted to pseudo-first and -second order kinetic models.

Sample	Initial concentration of glyphosate (mg/L)	$q_{e\,(exp)}$ (mg/g)	Pseudo-first-order			Pseudo-second-order		
			$q_{e\,(cal)}$ (mg/g)	k_1 (min^{-1})	R^2	$q_{e\,(cal)}$ (mg/g)	k_2 (g/mg·min)	R^2
CS3GP1	1	0.4583	0.3010	0.0140	0.8975	0.5133	0.0626	0.9885
CS3GP5	5	1.6669	0.7396	0.0058	0.8290	1.6393	0.0256	0.9740
CS3GP15	15	6.0264	3.4634	0.0203	0.9355	6.4599	0.0092	0.9969
CS3GP25	25	6.5106	1.0230	0.0044	0.5919	6.3211	0.0278	0.9955
CS3GP35	35	12.7625	1.5467	0.0009	0.0315	11.8064	0.0266	0.9854

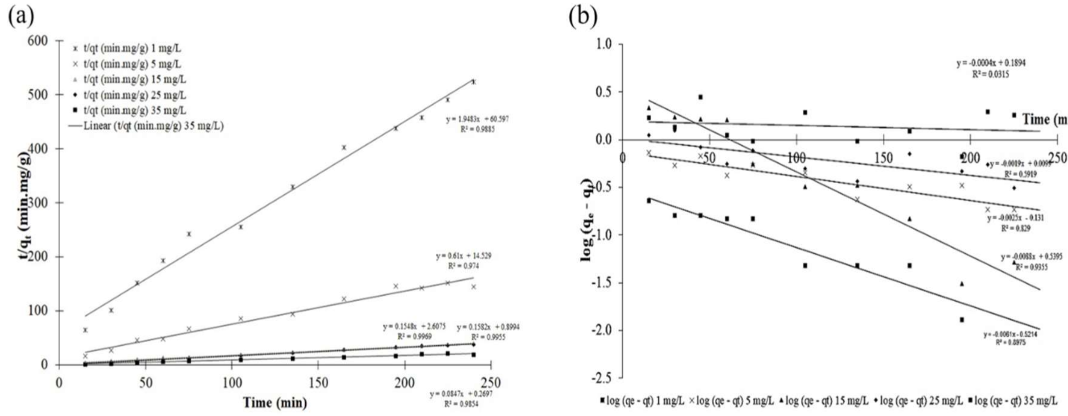

Figure 6. Adsorption kinetic curves of glyphosate on chitosan and its fit to (a) pseudo-first order and (b) pseudo-second order kinetic models. The initial glyphosate concentration was varied at 1, 5, 15, 25, and 35 mg/L against 0.1 g chitosan. Data are shown as the mean of triplicate trials at room temperature and pH 7.0.

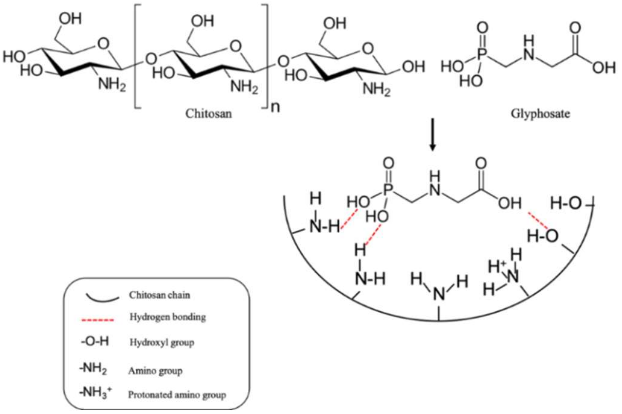

Figure 7. Schematic representation of the probable ways of glyphosate bonding onto the chitosan surface.

Table 2 Glyphosate adsorption capacity by several sorbents.

Adsorbent types	Description	Adsorption capacity	References
Chitosan and alginate	polymer membrane	10.88 mg·g^{-1} for chitosan membrane Glyphosate adsorption fits to Pseudo-second order model	[18]
Chitin and chitosan	powder	Glyphosate adsorption likely fitted by Langmuir model	[35]
Woody biochar	carbonaceous material with highly aromatic, porous structure	Maximum adsorption at 44 mg·g^{-1} glyphosate adsorption fitted by Freundlich and Temkin models	[36]
Rice husk derived biochar	carbon-rich product	82% maximum removal of glyphosate at pH 4	[37]
Ferrihydrite	mineral forms of iron oxide	84% of adsorbed glyphosate interacted to ferrihydrite, as function of pH	[38]
Alum sludge (AS)	Dewater form (DAS) and liquid form (LAS)	The maximum glyphosate adsorption capacity computed by Langmuir isotherm is 85.875 mg·g^{-1} for DAS and 113.636 mg·g^{-1} or LAS. Glyphosate adsorption kinetics onto alum sludge can be described by the pseudo second-order model.	[39]
Chitosan	beads	Maximum adsorbed at 12.7 mg·g^{-1} as a function of glyphosate concentration (35 mg·L^{-1}) 94% of the glyphosate removal with 0.5 g of chitosan dosage	Our study

4. Conclusions

To remove glyphosate from aqueous solution, the chitosan beads as adsorbent was used. The pH_{PZC} of chitosan was evaluated approximately at pH ≅ 8. The adsorption rates from five initial glyphosate concentrations were rapid. The adsorption of glyphosate onto chitosan moderately increased with increasing glyphosate concentrations, with a maximum adsorption on 0.1 g of chitosan of 12.7 $mg\cdot g^{-1}$ when using an initial glyphosate concentration of 35 $mg\cdot L^{-1}$. Overall, the adsorption equilibrium was reached before 75 min in a batch experiment. The glyphosate adsorption data fitted the Freundlich isotherm model better than the Langmuir isotherm, reflecting that the adsorption occurred on a heterogeneous surface where many functional groups as active sites were available. Furthermore, the adsorption followed pseudo-second order kinetics, with equilibrium being reached in 210 min. The adsorption of glyphosate-chitosan mainly involving electrostatic interaction between $-NH_3^+$ groups on chitosan and $-PO(OH)^-$ and $-COO^-$ groups on glyphosate. The possible mechanism of glyphosate adsorption were double steps of adsorption, providing by diffusion inside the pore, and equilibrium of adsorption. The chitosan beads could be a promising eco-friendly adsorbent for the economical and effective glyphosate removal from wastewater treatment.

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References

[1] V. K. Nandula, *Glyphosate resistance in crops and weeds: History, Development, and Management*. New Jersey: John Wiley & Sons, 2010.

[2] A. V. Sviridov, T. V. Shushkova, I. T. Ermakova, E.V. Ivanova, D.O. Epiktetov, and A.A, Leontievsky, "Microbial degradation of glyphosate herbicides (review)," *Applied Biochemistry and Microbiology,* vol. 51, pp. 188-195, 2015.

[3] C. V. Waiman, M. J. Avena, M. Garrido, B. F. Band, and G. P. Zanini, "A simple and rapid spectrophotometric method to quantify the herbicide glyphosate in aqueous media. Application to adsorption isotherms on soils and goethite," *Geoderma,* vol. 770, pp. 154-158, 2012.

[4] M. Mörtl, G. Németh, J. Juracsek, B. Darvas, L. Kamp, F. Rubio, and A. Szekacs, "Determination of glyphosate residues in Hungarian water samples by immunoassay," *Microchemical Journal,* vol. 107, pp. 143-151, 2013.

[5] C. Zhou, D. Jia, M. Liu, X. Liu, and C. Li, "Removal of glyphosate from aqueous solution using nanosized copper hydroxide modified resin: Equilibrium isotherms and kinetics," *Journal of Chemical & Engineering Data*, vol. 62(10), pp. 3585-3592, 2017.

[6] S.O. Duke, J. Lydon, W.C. Koskinen, T.B. Moorman, R.L. Chaney, R. and R. Hammerschmidt, "Glyphosate effects on plant mineral nutrition, crop rhizosphere microbiota, and plant diseases in glyphosate-resistant crops," *Journal of Agricultural and Food Chemistry*, vol. 60, no. 42, pp. 10375-10397, 2012.

[7] M.P. Gomes, E. Smedbol, A. Chalifour, L. Henault-Ethier, M. Labrecque, L. Lepage, M. Lucotte, P. Juneau, "Alteration of plant physiology by glyphosate and its by-product aminomethylphosphonic acid: an overview," *Journal of Experimental Botany*, vol. 65, no. 17, pp. 4691-4703, 2014.

[8] E. Schonbrunn, S. Eschenburg, W.A. Shuttleworth, J.V., Schloss, N. Amrhein, J.N.S. Evans, and W. Kabsch, "Interaction of the herbicide glyphosate with its target enzyme 5-enolpyruvylshikimate 3-phosphate synthase in atomic detail," *Proceedings of the National Academy of Sciences of the United States of America,* vol. 98(4), pp. 1376-1380, 2001.

[9] Glyphosate and AMPA in drinking-water, background document for development of WHO Guidelines for drinking-water quality, WHO/SDE/WSH/03.04/97. [Online]. Available at http://www.who.int/water_sanitation_health/dwq/chemicals/glyphosateampa290605.pdf [Accessed Jun, 2005].

[10] Drinking Water Standards and Health Advisories, United States Environmental Protection Agency (USEPA), Washington, DC. Available at http://water.epa.ov/action/advisories/drinking/upload/dwstandards2012.pdf. (accessed Jun 2019)

[11] J. Guo, Y. Zhang, Y, Luo, F. Shen, and C. Sun, "Efficient fluorescence resonance energy transfer between oppositely charged CdTe quantum dots and gold nanoparticles for turn-on fluorescence detection of glyphosate," *Talanta*, vol.125, pp. 385-392, 2014.

[12] The EU-MRLs set in Regulation (EC) No 396/2005 from the European Union pesticide database. [Online]. Available at http://ec.europa.eu/sanco_pesticides/public/index.cfm. [Accessed Jun, 2019).

[13] S.A. Briggs, *Basic Guide to Pesticides: Their Characteristics and Hazards*. Washington, DC: Taylor & Francis, 1992.

[14] B. Freedman, *Environmental Ecology*. 2nd edn. San Diego: Academic Press, 1995.

[15] Y.S. Hu, Y.Q. Zhao, and B. Sorohan, "Removal of glyphosate from aqueous environment by adsorption using water industrial residual," *Desalination*, vol. 271, no. 1-3, pp. 150-156, 2011.

[16] T.K. Saha, N.C. Bhoumik, S. Karmaker, M.G. Ahmed, H. Ichikawa, and Y. Fukumori, "Adsorption characteristics of Reactive Black 5 from aqueous solution onto chitosan," *Clean*, vol. 39(10), pp. 984-989, 2011.

[17] R. Grillo, Z. Clemente, J.L. de Oliveira, E.V.R. Campos, V.C. Chalupe, C.M. Jonsson, R. de Lima, G. Sanches, C.S. Nishisaka, A.H. Rosa, K. Oehlke, R. Greiner, and L.F. Fraceto, "Chitosan nanoparticles loaded the herbicide paraquat: The influence of the aquatic humic substances on the colloidal stability and toxicity," *Journal of Hazardous Mater*ials, vol. 286, pp. 562-572, 2015.

[18] R.T.A. Carneiro, T.B. Taketa, R.J.G. Neto, J.L. Oliveira, E.V.R. Campos, M.A. de Moraes, C.M.G. da Silva, M.M. Beppu, and L.F. Fraceto, "Removal of glyphosate herbicide from water using biopolymer membranes," *Journal of Environmental Management,* vol. 151, pp. 353-360, 2015.

[19] M.A. Moraes, D.S. Cocenza, F.D.C. Vasconcellos, L.F. Fraceto, and M.M. Beppu, "Chitosan and alginate biopolymer membranes for remediation of contaminated water with herbicides," *Journal of Environmental Management,* vol. 131, pp. 222-227, 2013.

[20] S.M. Dehaghi, B. Rahmanifar, A.M. Moradi, and P.A. Azar, "Removal of permethrin pesticide from water by chitosan-zinc oxide nanoparticles composite as an adsorbent," *Journal of Saudi Chemical Society*, vol. 18, no. 4, pp. 348-355, 2014.

[21] M. Zhang, R. Helleur, and Y. Zhang, "Ion-imprinted chitosan gel beads for selective adsorption of Ag^+ from aqueous solution," *Carbohydrate Polym*ers, vol. 130, pp. 206-212, 2015.

[22] D.K. Sharma, A. Gupta, R. Kashyap, and N. Kumar, "Spectrophotometric method for the determination of glyphosate in relation to its environmental and toxicological analysis," *Archives of Environmental Science,* vol. 6, pp. 42-49, 2012.

[23] D.F. Tzaskos, C. Marcovicz, N.M.P. Dias, and N.D. Rosso, "Development of sampling for quantification of glyphosate in natural water," *Ciência e Agrotecnologia,* vol. 36, no. 4, pp. 399-405, 2012.

[24] B.L. Bhaskara, and P. Nagaraja, "Direct sensitive spectrophotometric determination of glyphosate by using ninhydrin as a chromogenic reagent in formulations and environmental water samples," *Helvetica Chimica Acta,* vol. 89, pp. 2686-2693, 2006.

[25] M.R. Yazdani, E. Virolainen, K. Conley, and R. Vahala, "Chitosan–zinc(II) complexes as a bio-sorbent for the adsorptive abatement of phosphate: Mechanism of complexation and assessment of adsorption performance," *Polymers (Basel),* vol.10, no. 1, p.25, 2018.

[26] M. Nasiruddin Khan, and A. Sarwar, "Determination of points of zero charge of natural and treated adsorbents," Surface Review and Letters, vol. 14, no. 3, pp. 461-469, 2007.

[27] P. Saha, S. Chowdhury, S. Gupta, and I. Kumar, "Insight into adsorption equilibrium, kinetics and thermodynamics of Malachite Green onto clayey soil of Indian origin," *Chemical Engineering Journal*, vol. 165, no. 3, 874-882, 2010.

[28] R. L. Tseng, F. C. Wu, and R. S. Juang, "Characteristics and applications of the Lagergren's first-order equation for adsorption kinetics," *Journal of the Taiwan Institute of Chemical Engineers,* vol. 41, no. 6, pp. 661-669, 2010.

[29] Y.S. Ho, and G. McKay, "Pseudo-second order model for sorption processes," *Process Biochemistry*, vol. 34, pp. 451-465, 1999.

[30] L.O.B. Benetoli, H. Santana, and C.E.A. Carneiro e Dimas A.M. Zaia, "Adsorption of glyphosate in a forest soil: A study using Mössbauer and FT-IR spectroscopy" *Química Nova*, vol. 33, no. 4, pp. 855-859, 2010.

[31] M. Jain, V.K. Garg, and K. Kadirvelu, "Chromium (VI) removal from aqueous system using *Heleanthus annuus* (Sunflower stem waste)," *Journal of Hazardous Material*s, vol. 162, no. 1, pp. 365-372, 2009.

[32] W.S.W. Ngah, and S. Fatinathan, "Adsorption of Cu(II) ions in aqueous solution using chitosan beads, chitosan–GLA beads and chitosan–alginate beads," *Chemical Engineering Journal*, vol. 143, pp. 62-72, 2008.

[33] P. Pal, and A. Pal, "Dye removal using waste beads: Efficient utilization of surface-modified chitosan beads generated after lead adsorption process," *Journal of Water Process Engineering*, vol. 31, p. 100882, 2019.

[34] V.K. Gupta, B. Gupta, A. Rastogi, S. Agarwal, and A. Nayak, "Pesticides removal from wastewater by activated carbon prepared from waste rubber tire," *Water Research*, vol. 45(13), pp. 4047-4055, 2011.

[35] L. Rissouli, M. Benicha, T. Chafik, and M. Chabbi, "Decontamination of water polluted with pesticide using biopolymers: Adsorption of glyphosate by chitin and chitosan,". *Journal of Materials and Environmental Science*, vol. 8(12), pp. 4544-4549, 2017.

[36] S.S. Mayakaduwa, P. Kumarathilaka, I. Herath, M. Ahmad, M. Al-Wabel, Y.S. Ok, A. Usman, A. Abduljabbar, and M. Vithanage, "Equilibrium and kinetics mechanism of woody biochar on aqueous glyphosate removal," *Chemosphere*, vol. 144, pp. 2516-2521, 2016.

[37] I. Herath, P. Kumarathilaka, M. Al-Wabel, A. Abduljabbar, M. Ahmad, A.R.A. Usman, and M. Vithanage, "Mechanistic modeling of glyphosate interaction with rice husk derived engineered biochar," *Microporous Mesoporous Materials*, 225(1), pp. 280-288, 2016.

[38] R.C. Pereira, P.R. Anizelli, E. Mauro, D.F. Valezi, A.C.S. Costa, C.T.B.V. Zaia, and D. A. M Zaia, "The effect of pH and ionic strength on the adsorption of glyphosate onto ferrihydrite," *Geochemical Transactions*," vol. 20, no. 3, pp. 1-14, 2019.

[39] Y.S. Hu, Y.Q. Zhao, and B. Sorohan, "Removal of glyphosate from aqueous environmental by adsorption using water industrial residual," *Desalination*, vol. 271, no. 1-3, pp. 150-156, 2011.