Investigation of Equilibrium Isotherm and Kinetic Modeling to Asses Sorption Characteristics of Nitrate onto Palm Leaf Biochar

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ABSTRACT: *Application of agriculture residue especially in biochar form seems to be effective in the removal of contaminants such as nitrate pollution. The effectiveness of biochar produced from palm leaf residues (pyrolyzed at 600 ˚C) in the removal of nitrate from aqueous solution was studied at different pH. The pH value at the point of zero charges (pH_{pzc}) and surface functional groups of biochar were also investigated. The result showed that the pH_{pzc} of palm leaf biochar was about 8 and the most adsorption of nitrate from solution (90%) was obtained at pH 2. The fit of experimental data to six adsorption isotherm and eight kinetic models showed satisfied fits to Freundlich and Langmuir 2 isotherm and pseudo-second-order, power function, Intraparticle diffusion and simplified Milovich models due to their low values of Standard Errors (SE) of estimate and high values of coefficients of determination (R^2). The result implied that the adsorption of nitrate onto palm leaf biochar was through favorable and multi-step chemisorption processes. According to the result reported herein the use of palm leaf biochar is promising for nitrate removal from aqueous solution.*

KEYWORDS: *Biochar; Equilibrium adsorption models; Kinetic models; Nitrate; Palm leaf.*

INTRODUCTION

Nitrogen (N) is a major and essential nutrient for the organism but its high amount in nitrate form leads to the deterioration of natural water results in eutrophication [1]. Over-application of fertilizers and municipal wastewaters contributed to the released of nitrate into waters and cause water pollution [2]. Excess NO_3 levels in drinking water cause adverse health effects to humans included gastrointestinal cancer and methemoglobinemia which commonly observed among children [3, 4]. Several conventional methods including biological, chemical and physical methods have been investigated for N removal from wastewaters [5] and among them, adsorption process due to its ease of use, being economical and environmentally friendly, has been widely considered for nutrient removal [6, 7]. The selection of appropriate, effective, and economical adsorbent could result in achieving significant success in this method [8]. Various adsorbents have been identified for removal of nitrate from aqueous solutions and agricultural materials have been shown high potential and capacity for ion adsorption from wastewater due to their chemical composition, rich in cellulose, being available, abundance

and low in cost [9]. Biochar is a stable and rich in carbon solid that made from low-cost sources such as agricultural waste and manure via pyrolysis under partial or complete depletion of oxygen at temperatures between 350 and 700°C [1, 10] and due of the high surface area, pore volume [11] and containing various surface functional groups [12] showed strong affinity to adsorb ions from aqueous solutions. Several studies have evaluated various agricultural waste materials in biochar forms as adsorbents for the removal of nitrate from wastewater. Some of these biochars include wheat straw biochar [10]; biochar from woody materials of the oak tree [12]; biochars from wheat-straw, corn-straw and peanut-shell [1]; biochar produced from Conocarpus waste [3]; modified sugarcane bagasse biochar [13]; activated carbon prepared from sugar beet bagasse [14] and biochars from feedstocks of corn stover, Ponderosa pine wood chips and switchgrass [8]. *Li et al.* [10] observed that using 0.6 g of wheat straw biochar in 50 mL of a solution containing 50 mg N/L removed more than 32 percent of nitrate from aqueous solution. *Hafshejani et al.* [13] found that adsorption capacity of 2 g/L of modified sugarcane bagasse biochar was 18.40 mg/g that removed more than 90 percent of 80 mg/L nitrate from aqueous solution. Also, it has been shown that application of 5 g/L of activated carbon residue from Finnish wood chips and 10 g/L of Conocarpus green biochar as adsorbents successfully removed 65 and 89.1% of 75 and 50 mg/L nitrate from solutions, respectively [3, 16].

Investigation of adsorption isotherms is an essential way of selecting the most appropriate adsorbent, determining the capacity of adsorbent and understanding the mechanisms evolved in the adsorption process [14, 15]. Some common models have been used in describing the equilibrium process and the kinetics of nitrate adsorption from wastewater. *Freundlich* and *Langmuir* have been reported by various researchers as appropriate isotherm [14, 16] and pseudo-second-order model proposed as one of the best fitted kinetic models [3, 5, 14, 17].

Iran has the second rate of date production (1 million tons per year) and the first-rate of cultivated area (240 thousand hectares) in the world. The palm tree is an evergreen plant that after 3 to 7 years the old leaves are dried up and needs to be pruned. Hence each year a considerable amount of residues are produced due to the removal of dry leaves, which requires opti management

and efficient use [18]. Some research showed that palm leaf can be used as a low-cost adsorbent for heavy metal removal [9, 18-21]. Hence due to the large abundance of palm leaf in Iran and its high ability in removing contaminants from wastewater, the present study was conducted to investigate the sorption characteristics of palm leaf biochar and its effectiveness in nitrate removal from aqueous solution.

EXPERIMENTAL SECTION
Preparation of biochar

Palm leaf residues collected from Lengeh port located in Hormozgan province, Iran (26.5628° N, 54.8887° E). The palm leaves were washed with deionized water and dried in an oven at 80 °C and then milled. Our previous study showed that the palm leaf biochar pyrolyzed at 600 °C was more suitable and effective for the removal of Zn and Cd from wastewater as compared with the biochar pyrolyzed at a lower temperature [19]. Therefore the palm leaf residues were pyrolyzed at 600 °C for 4 h. Fourier transform infrared spectroscopy (FTIR, Spectrum RXI and PerkinElmer) was used to analyze the functional groups in biochar.

Determination of pH_{pzc} of biochar

To determination of pH value at the point of zero charges (pH_{pzc}) of biochar, the same method proposed by *Hafshejani et al.* [13] were used.

Effect of solution pH

To study the effect of pH on nitrate removal by palm leaf biochar, 0.5 g of palm leaf biochar was added to 30 mL NO_3 solutions with a concentration of 50 mg/L. HCl and NaOH were used to adjust differently pH values between 2 to 11. Samples were shaken at 120 rpm for 1 h. Then solutions were centrifuged at 2500 rpm for 10 min and filtered by using Whatman filter paper and nitrate concentration in the filtered solution was measured by the phenol-di-sulfonic acid method [22]. The amount of nitrate adsorbed per unit weight of adsorbent (q_e) was calculated from Equation (1):

$$q_e = \frac{c_i - c_f}{m} V \tag{1}$$

Where C_i is initial concentrations of nitrate in solution (mg/L), C_f is equilibrium concentrations of nitrate in

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solution (mg/L), *V* is the volume of solution (L) and *m* is the weight of biochar (g).

Sorption isotherms

To investigate adsorption isotherms, 0.5 g of palm leaf biochar was added to 30 ml solutions with concentrations of 25, 50, 100 and 200 mg NO_3/L. A stock solution of NO_3, 1000 mg/L, was prepared by dissolving the adequate amount of $NaNO_3$ in deionized water) in polyethylene tubes at room temperature (25 °C). The initial pH of solutions was adjusted on 2 by using HCl. The mixture was shaken for 1 hour (according to kinetics study a period of 1 h was sufficient to achieve equilibrium) and then centrifuged at 2500 rpm for 10 min and filtered. Nitrate concentration in the filtered solution was measured by the phenol-di-sulfonic acid method [22] and the amount of nitrate adsorbed per unit weight of adsorbent (q_e) was calculated from the Equation (1). Six adsorption models were applied to describe the pattern of the adsorption process (Table 1).

Kinetics study

To study kinetic adsorption of nitrate, 30 mL of NO_3 solution with different concentrations (25, 50, 100 and 200 mg/L) was added to 0.5 g biochar in polyethylene tubes at room temperature (25 °C) and initial pH was adjusted on 2. The mixture was shaken for periods of 1, 2, 4, 8, 16, 32, 64 and 128 min and then centrifuged at 2500 rpm for 10 min and filtered by using Whatman filter paper. Nitrate concentration in the filtered solution was measured by the Phenol-di-sulfonic acid method [22] and the amount of nitrate adsorbed per unit weight of adsorbent (q_e) was calculated from Equation 1. Eight kinetic models were used to investigate the kinetics of nitrate adsorption including: zero-order (Eq. (2)) [24], first-order (Eq. (3)) [5], second-order (Eq. (4)) [5], pseudo-first-order (Eq. (5)) [14], pseudo-second-order (Eq. (6)) [14], simplified Elovich (Eq. (7)) [24], intraparticle diffusion (Eq. (8)) [5], and power function (Eq. (9)) [3] and their linear forms are given below:

$$\left[q\right]_t = \left[q\right]_e + K_0 t \tag{2}$$

$$\ln q_t = \ln q_e + q_0 k_1 t \tag{3}$$

$$\frac{1}{q_t} = \frac{1}{q_e} - k_2 t \tag{4}$$

$$\log\left(q_e - q_t\right) = \log q_e - \frac{K_3 t}{2.303} \tag{5}$$

$$\frac{t}{q_t} = \frac{1}{K_4 q_e^2} + \frac{t}{q_e} \tag{6}$$

$$q_t = q_e + \frac{1}{\beta_s} \ln t \tag{7}$$

$$q_t = q_e + k_p t^{0.5} \tag{8}$$

$$\ln q_t = \ln q_e + K_f \ln t \tag{9}$$

Where q_e and q_t are the amounts of nitrate ions adsorbed on biochar (mg/g) at equilibrium and at time *t*, respectively; K_0 is constant of zero-order (mg/g.min); K_1 is constant of first-order (min^{-1}), K_2 is constant of second-order (mg/g.min); K_3 is the rate constant of pseudo-first-order (min^{-1}), K_4 is pseudo-second-order rate constant (g/mg.min, β_s is constant of simplified Elovich (mg/g); K_p is parabolic diffusion constant [(mg/g)min$^{1/2}$] and k_f is constant of power function model (mg/g).

RESULTS AND DISCUSSION
FTIR Analysis

The FT-IR spectrum of biochar (Fig 1) and consisted of several adsorption peaks. The peak at 3297.90 cm^{-1} assigned to C–H stretching of alkynes. Two peaks at 2923.37 and 2852.05 cm^{-1} presented C–H stretching of the aliphatic groups and alkanes [25]. The peak at 1594.36 cm^{-1} may be attributed to the functional group of amides and type 1 of amines [26]. The peaks at 1413.88, 1112.41 and 803.05 cm^{-1} presented aromatic C=C stretch band, C–O stretch band of the ethers and aromatic C-H, respectively. The result from Fig. 1 demonstrated the presence of a variety of compounds in both aliphatic and aromatic forms in palm leaf biochar.

Removal of nitrate by palm leaf biochar

The percentage removal of nitrate by palm leaf biochar is shown in Fig. 2 which indicated that the initial concentration of nitrate affected its removal by palm leaf biochar. According to Fig. 2 application of 0.5 g palm leaf biochar at pH 2 for 1 hr successfully removed 93.3% of NO_3 at 25 and 50 mg/L nitrate concentrations. By increasing initial concentration to 100 and 200 mg/L the removal percentage reduced to 89 and 87, respectively.

Table 1: Adsorption isotherms models.

Isotherm	Linear form	Nomenclature
Freundlich [23]	$\text{Log } q_e{}^* = \text{Log } k_F + 1/n \text{ Log } C_e{}^{**}$	K_F: Absorption Capacity (mg/g) n: Absorption intensity
Langmuir 1 [23]	$C_e/q_e = 1/K_L.b + C_e/b$	b: maximum adsorption capacity of adsorbent (mg/g) k_L: Langmuir constant (L/mg)
Langmuir 2 [23]	$1/q_e = 1/(K_e.b.C_e) + 1/b$	b: maximum adsorption capacity of adsorbent (mg/g) k_e: Langmuir constant (L/mg)
Tempkin [23]	$q = RT/b \text{ Ln } K_T + RT/b \text{ Ln } C_e$	K_T: Tempkin constant (L/mg) b: Tempkin constant associated with absorption energy (J/mol) R: gas constant T: Temperature (K')
Redlich–Peterson [23]	$\text{Ln } C/q = \text{Ln } 1/k_{RP} + n. \; a_{RP}/k_{RP} \text{ Ln } C$	a_{RP}: Redlich–Peterson isotherm constant (L/mg) K_{RP}: Redlich–Peterson isotherm constant (L/g) n: exponent
Van huay [19]	$q = m + n(C)^{0.5}$	n: Van huay constant m: Van huay constant

* q_e: equilibrium adsorption capacity of biochar (mg/g) in each of 6 equations

** Ce: equilibrium concentration of nitrate in solution (mg/L) in each of 6 equations
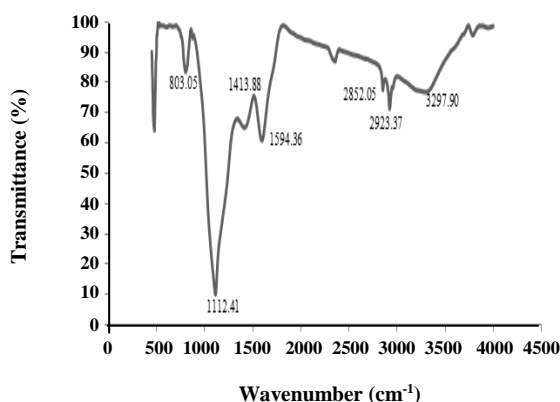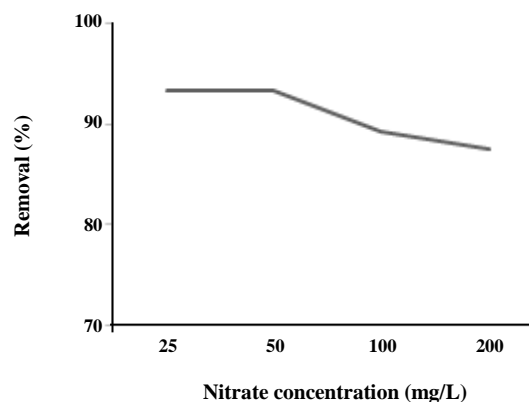

Fig. 1: FT-IR spectra of palm leaf biochar.

Fig. 2: Removal percentage (%) of nitrate by palm leaf biochar at 25, 50, 100 and 200 mg L⁻¹ initial concentrations.

In other words, percent nitrate removal decreased as the initial concentration of nitrate increased. *Kilpimaa et al.* [16] reported that a decrease in percent nitrate removal with an increase in its initial concentration was attributed to increase in a driving force that accentuated by the concentration gradient. *Usman et al.* [3] also reported that at low initial concentrations, the adsorption process was higher due to the sorption affinity between nitrate and biochar surface but at higher concentrations adsorption process was lower due to the limitation of binding sites.

Different removals of nitrate have been reported for diverse adsorbents. Percent nitrate removals were 32%

for wheat straw biochar [10], 90% for modified sugarcane bagasse biochar [13], 65% for activated carbon residue from Finnish wood chips [16] and 89% for Conocarpus green biochar [3]. A comparison of percent removals in the present study with those reported in the abovementioned researches demonstrated that palm leaf biochar is among the most efficient sorbents for nitrate removal from aqueous solutions.

Effect of solution pH

One of the most important parameters that influence the adsorption process is pH which controls adsorption
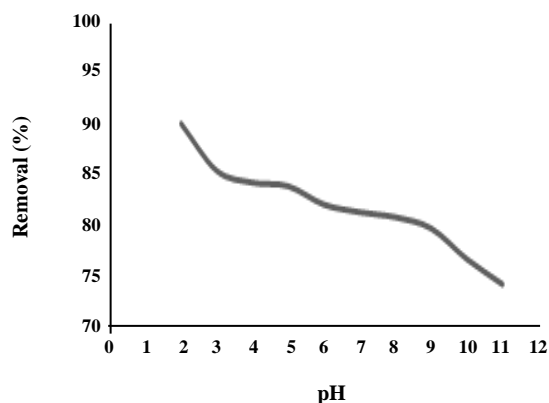
Fig. 3: Effect of pH solution on nitrate removal by palm leaf biochar.

Fig. 4: pH_{pzc} of palm leaf biochar.

the process by the electrostatic attraction between the adsorbent and ions [15]. The effect of solution pH on nitrate adsorption by palm leaf biochar is shown in Fig. 3. Under acidic conditions, due to a high amount of protons in the solution, the surface of adsorbent becomes positively charged. The positive charge on the adsorbent surface increases the electrostatic adsorption between the adsorbent and the ions. When the initial pH of the solution was 2, biochar removed 90% of nitrate and as the solution pH was raised from 3 to 11, nitrate adsorption decreased from 85 to 74 %, respectively (Fig. 3). It is mostly attributed to high competition between nitrate and hydroxide ions (OH⁻) for adsorption sites of palm leaf biochar [13, 16]. In other words, the presence of hydroxide ions may limit and hinder nitrate adsorption on biochar surface. Furthermore, as pH level increased the repulsion between negatively charged surfaces of adsorbent and anions in the solution occur due to the negative zeta potential [17]. *Öztürk & Bekta* [5] found that the most effective pH value for nitrate removal by powdered activated carbon was 2. They reported that the positively charged sites on the adsorbent that created at low pH were favors adsorption of nitrate anions due to electrostatic attraction. Similar results were reported by *Demiral & Gunduzogˇlu* [14].

Point of zero charges (pH_{pzc})

The point of zero charges (pH_{pzc}) is the pH value that all the positive and negative charges on the adsorbent surface are equal [13]. PH_{pzc} effectively affects the adsorption process [15]. The result showed that the pH_{pzc}
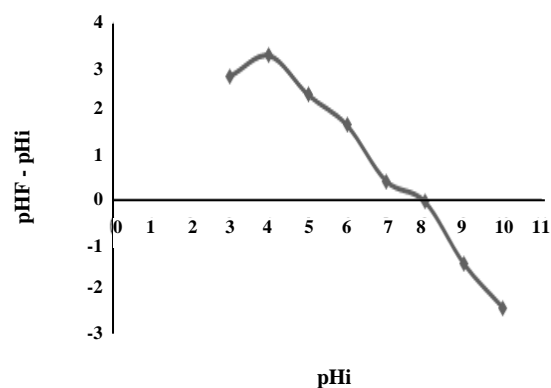
of palm leaf biochar is about 8 (Fig. 4) and according to the result of Fig. 3 the most adsorption of nitrate was obtained at pH 2, much lower than the pH_{pzc} of palm leaf biochar. At pH values lower than the pH_{pzc} (pH<pH_{pzc}), due to the adsorption of additional H⁺ of the solution on the surface of biochar, the net charge of biochar becomes positive and causes a high ability for nitrate adsorption [13]. However at pH values higher than the pH_{pzc} (pH>pH_{PZC}), due to neutral or negative charge on the surface of the biochar, the capacity of nitrate adsorption decreases indicating that the nonspecific adsorption of nitrate is predominated [27]. It is noticeable that the adsorption of nitrate at pH>pH_{pzc} by palm leaf biochar which has been shown in Fig. 4, could be because the degree of protonation was not immediately fall to zero and also the mechanism of anion exchange was probably effective in nitrate adsorption on neutral sites of the biochar [28].

Adsorption isotherms

The fit of experimental data to different isotherm models could be effective to assess an appropriate isotherm that well describes the pattern of adsorption, [14]. In these isotherms the high value of coefficients of determination (R^2) for equilibrium data is essential for analyzing the adsorption process [29].

Result of fitting experimental data to six models of equilibrium, adsorption showed that Langmuir 1, Redlich–Peterson, Van Huay and Tempkin models could not be chosen as appropriate models due to their high values of Standard Errors (SE) of estimate and low values

of coefficients of determination (R^2), but the nitrate adsorption data showed excellent fits to both Langmuir 2 and Freundlich, as evidenced by their relatively low values of standard errors of estimate (SE) and high values of coefficients of determination (R^2). Our results are in agreement with those of *Yao et al.* [30], *Li et al.* [10], *Demiral & Gunduzoğlu* [14] and *Kilpimaa et al.* [16]. Parameters and the statistical data of the best-fitted models, Langmuir 2 and Freundlich, are given in Table 2.

The fit of experimental data to Freundlich isotherms was obtained by plotting log q_e vs. log C_e values and that of Langmuir 2 isotherm was obtained by plotting $1/q_e$ vs. $1/C_e$ values. According to the Freundlich model, ion adsorption occurs on the heterogeneous surface of the adsorbent, energy of adsorption sites is different [2] and concentration of ions at equilibrium is effective on adsorption capacity [20]. While according to the Langmuir model a monolayer ion adsorption occurs on the homogenous surface and all the adsorption sites have equal energy [2]. Maximum adsorption in the Langmuir model occurs when a saturated layer of adsorbed molecules creates on the surface of adsorbent [20].

The values of Freundlich parameters, $1/n$ (adsorption intensity criterion) and K (adsorption capacity criterion) were 0.8543 and 0.8383, respectively (Table 2). When the value of parameter $1/n$ in Freundlich isotherm is between 0 and 1, implies that normal adsorption processes occur on all site of adsorbent surface and shows that the interaction between the adsorbent and ion is strong [29]. Also, the value of n, the affinity of adsorbent to ion, equals a number between one and ten indicates that the adsorption process is favorable [20]. In the present study, the values of $1/n$ and n were obtained 0.8543 and 1.1705, respectively (Table 2) indicating equal adsorption energies for all sites on palm leaf biochar and favorable of NO_3^- sorption on biochar surface. The high value of adsorption capacity (K) in Freundlich isotherm could be due to the increased micropores and specific surface area of palm leaf biochar produced under the pyrolysis process that improves the accessibility of ions to adsorption sites. *Kim et al.* [31] reported that increasing pyrolytic temperature significantly influenced on ion adsorption process by biochar that it could be because at higher temperature biochar has higher aromatic structure, fewer polar functional groups, and more pore space because of the escape of volatile substances such as cellulose and hemicelluloses.

Marzi et al. [26] and *Demiral & Gunduzoğlu* [14] found the same results for the influence of pyrolytic temperature on increasing biochar absorption capacity for nitrate removal from aqueous solution.

Experimental data related to NO_3^- adsorptions onto palm leaf biochar were fitted to the Langmuir 2 isotherm as well as Freundlich isotherm. The values of b (maximum adsorption capacity of adsorbent) and k_L (Langmuir constant) were 42.55 (mg/g) and 0.01759 (L/mg), respectively (Table 2). The relatively high value of parameter b indicated relatively high adsorption capacity of palm leaf biochar for the removal of nitrate ions. A useful criterion derived from the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L) and defined by Eq. (10) [10].

$$R_L = \frac{1}{1 + K*C} \tag{10}$$

The R_L values for all the initial concentrations (25, 50, 100 and 200 mg/L) were between 0 and 1 (0.695, 0.532, 0.362 and 0.221, respectively) and imply favorable nature of adsorption process [10, 29, 32].

The fits of both Freundlich and Langmuir 2 models were satisfied as evidence by R^2 exceeding 0.96. In this case, *Marzi et al.* [26] reported that if parameter n (absorption intensity) in Freundlich isotherm was between 1 and 10, it shows that Langmuir could fit experimental data better than Freundlich. In the present study, the value of parameter n derived from Freundlich isotherm was 1.1705, which was more than one and indicated that the Langmuir isotherm was more suitable than Freundlich. Furthermore the value of the *SE* in Freundlich isotherm was higher than that of Langmuir isotherm. *Hikmat et al.* [9] studied lead adsorption from aqueous solution onto petiole and fiber of palm tree and found that due to the saturated monolayer on the surface of petiole and fiber of palm tree the experimental data showed better fit to Langmuir than Freundlich. *Haleem and Abdulgafoor* [21] and *Sadeek et al.* [20] reported the same results concerning the homogenous sites on the palm leaf surface in the removal of heavy metals from aqueous solution.

Adsorption kinetics

Several kinetic models (zero-order, first-order, second-order, pseudo-first-order, pseudo-second-order, simplified Elovich, Intraparticle diffusion, and power function)

Table 2: Parameters of Langmuir 2 and Freundlich isotherms for adsorption of nitrate by palm leaf biochar.

Isotherm	Parameters				
Freundlich	k_f (mg/g)	n	1/n	R^2	SE
	0.8383	1.1705	0.8543	0.9667	0.0859
	Parameters				
Langmuir 2	k_e (L/mg)	b (mg/g)		R^2	SE
	0.01759	42.55		0.9698	0.0593

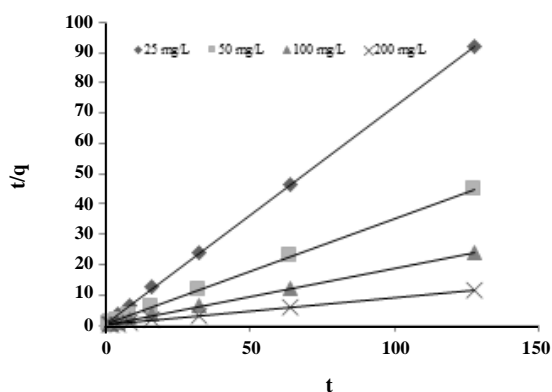*Fig. 5: Pseudo-second-order for nitrate adsorption by palm leaf biochar.*

Fig. 6: Power function for nitrate adsorption by palm leaf biochar.

were applied to describe the kinetics of NO_3^- adsorption by palm leaf biochar. The result indicated that the best-fitted models for the adsorption of nitrate ions by palm leaf biochar were pseudo-second-order, power function, Intraparticle diffusion and simplified Elovich due to their relatively low values *SE* and high values of R^2. The parameters of the best-fitted models are presented in Table 3.

The kinetic data were fitted very well to the pseudo-second-order (Eq. (6)). The *qe* (cal) and K_4 were obtained by plotting t/q_t vs. *t* values (Fig. 5 and Table 3). The approximately good agreement of calculated *qe* (cal) values and experimental *qe* (exp) values and high R^2 (higher than 0.99) (Table 3) for all of the initial concentration in comparison with other models, implied that the adsorption kinetics of NO_3^- by palm leaf biochar was more favorably conformed to pseudo-second-order kinetic model. The parameter K_4 in the pseudo-second-order kinetic model is a criterion of the time required to achieve equilibrium and its high values indicated that maximum sorption was achieved in a short time. Although sharing or exchange of electrons between biochar and NO_3^- ions in chemical adsorption may be a rate-limiting step [3].
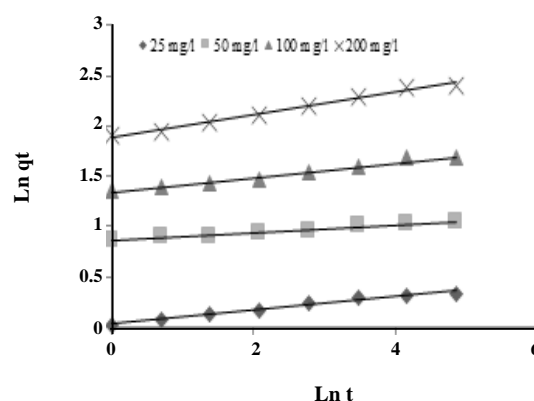
Similar results were also reported by other workers for nitrate adsorption kinetics [3, 5, 6, 14, 17, 20, 32]. The parameter $t_{1/2}$ is a half adsorption time (Eq. (11)) which implies the time required for half of the ions to be adsorbed at equilibrium and mostly used as a measure of the adsorption rate [33].

$$t_{1/2} = \frac{1}{K_4 q_e} \tag{11}$$

Where K_4 is the pseudo-second-order adsorption rate constant (g/mg.min). The values of $t_{1/2}$ for initial concentration 25, 50, 100 and 200 mg NO_3/L were 0.9717, 0.9418, 1.5294 and 2.2203, respectively. Relatively low $t_{1/2}$ values demonstrated a high affinity between the adsorbent and ions and also the instantaneous nature of the adsorption process [25].

In case of the power function model (Eq. (9)) and simplified Elovich model (Eq. (7)) the values of K_f and B_s for each of the initial concentration were obtained by plotting lnq_t vs. ln_t values and q_t vs. Ln_t values, respectively (Fig. (6) and Fig. (7), respectively) and given in Table 3. There was not a high difference between

Table 3: Kinetic model parameters for adsorption of nitrate by palm leaf biochar.

Concentration (mg/L)	Power function				
	q_e (exp)	K_f (mg g^{-1})	q_e (cal)	R^2	SE
25	1.2267	0.0675	1.0354	0.9701	0.0217
50	2.6059	0.0402	2.3582	0.9899	0.0075
100	4.5967	0.0713	3.8412	0.9764	0.0203
200	8.8085	0.1108	6.6266	0.9842	0.0258
Concentration (mg/L)	Intraparticle diffusion				
	q_e (exp)	k_p (mg g^{-1}min$^{1/2}$)	q_e (cal)	R^2	SE
25	1.2267	0.035	1.0683	0.8099	0.0661
50	2.6059	0.0479	2.3893	0.9258	0.0528
100	4.5967	0.1505	3.9155	0.9144	0.1793
200	8.8085	0.4372	6.8297	0.8979	0.5742
Concentration (mg/L)	Simplified Elovich				
	q_e (exp)	B_s (mg g^{-1})	q_e (cal)	R^2	SE
25	1.2267	12.254	1.0287	0.9755	0.0237
50	2.6059	9.5238	2.3512	0.9869	0.0222
100	4.5967	3.0414	3.7991	0.9671	0.1113
200	8.8085	1.3167	6.4571	0.978	0.2665
Concentration (mg/L)	Pseudo-second-order				
	q_e (exp)	K_4 (g mg^{-1} min^{-1})	q_e (cal)	R^2	SE
25	1.2267	0.7367	1.3968	0.9999	0.3148
50	2.6059	0.3694	2.8743	0.9998	0.2446
100	4.5967	0.1208	5.4171	0.9994	0.2079
200	8.8085	0.0404	11.148	0.9992	0.1213

calculated q_e (cal) values and experimental q_e (exp) values in both models (Table 3) but their R^2 were different, a little larger for pseudo-second-order. Relatively high values of the simplified Elovich constant, (β (mg/g)) as shown in Table 3 indicated that the rate of chemical adsorption of nitrate was increased [25] and might be controlled by multiple processes [11]. Transfer of ions from solution onto the sorbent surface usually occurred through an intraparticle process and determines that the adsorption is a multi-step process [17]. The intraparticle diffusion model (Eq. (8)) was obtained by plotting q_t vs. $t^{1/2}$ values and shown in Fig. 8. The fit of adsorption data to this model is linear and without passing through the origin which respectively indicated that the adsorption process included the intraparticle diffusion and there was a boundary layer control. These results also imply that the intraparticle diffusion was not the only model involved in adsorption nitrate and other kinetic models may operate at the same time and control the rate of adsorption process [14]. Similar results were reported by other researchers where linear plots of the intraparticle diffusion model do not pass through the origin for nitrate adsorption [13, 14, 17]. Inspection of Fig. 7 also showed that there were three stages for the ion adsorption process by adsorbent that could be seen well especially at higher initial concentration (S$_1$, S$_2$ and S$_3$, Fig. 8).
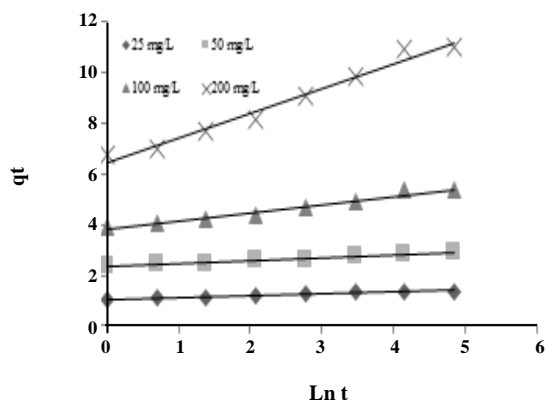
Fig. 7: Simplified Elovich for nitrate adsorption by palm leaf biochar.

Fig. 8: Intraparticle diffusion for nitrate adsorption by palm leaf biochar (S_1, S_2 and S_3 show stages 1, 2 and 3, respectively, at 200 mg nitrate/L).

Sadeek et al. [20] found similar results and reported that at the first stage the adsorption process occurred on the exterior surface of biochar. In the second stage, the nitrate ions enter the pores of the biochar surfaces. The third stage occurred when ions in the solution and the adsorbed ions are at the equilibrium. *Yao et al.* [30] suggested that due to the high amount of mesopores on biochar surface which derived from anaerobically digested sugar beet tailings, the intraparticle surface diffusion may play an important role in controlling the ion adsorption.

CONCLUSIONS

The nitrate adsorption capacity of biochar was dependent on initial pH values, as maximum removal of nitrate (90 %) was observed at pH 2. The pH_{pzc} of palm leaf biochar was obtained about 8. Nitrate adsorption data was the best fitted to Langmuir 2 model with favorable nature. The pattern of nitrate removal from the solution well conformed to the pseudo-second-order model indicated that the chemical adsorption was the main mechanism involved in nitrate adsorption onto palm leaf biochar. It appears that nitrate adsorption is a multi-step process and intraparticle surface diffusion may play an important role in nitrate adsorption onto the biochar. Due to the high effectiveness of palm leaf biochar in removing nitrate from the solution, the application of this low-cost material is promising in the decontamination of nitrate-polluted solutions. A comparison of percent removals in the present study with those reported in different researches demonstrated that palm leaf biochar is among the most efficient sorbents for nitrate removal from aqueous
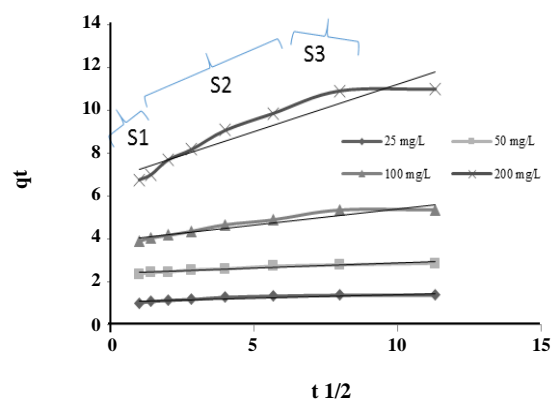
solutions. Since the presence of other anions such as sulfate and phosphate due to their high negative charge may affect nitrate adsorption, further research on the influence of competitive ions on nitrate removal from aqueous solution is warranted.

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