Activated carbon produced from *Glycyrrhiza glabra* residue for the adsorption of nitrate and phosphate: batch and fixed-bed column studies

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Abstract

In the present study, *Glycyrrhiza glabra* residues (GGR) were used for the preparation of activated carbon, with a surface area of $959.22 \text{ m}^2 \text{ g}^{-1}$. Activated carbon was prepared through chemical activation using ZnCl_2 at optimum carbonization temperature, and impregnation ratio for nitrate, and phosphate removal. The effect of contact time and adsorbent dosage on the removal efficiency was investigated, and the pseudo-second-order kinetic model correlated well with the adsorption data. The response surface methodology was applied for the determination of the effect of initial concentration, pH, and temperature and their interaction on the removal efficiency in the batch adsorption system. The Langmuir isotherm generated a satisfactory fit with the experimental data, and the maximum adsorption capacity was 142.5 mg g^{-1} at 308 K and 92.5 mg g^{-1} at 298 K for nitrate and phosphate removal, respectively. The high adsorption capacity reveals the applicability of the GGR activated carbon for nitrate and phosphate removal. Furthermore, the fixed-bed column adsorption studies were carried out, and the effect of flow rate and influent concentration on the behavior of the breakthrough curve was studied. The breakthrough time decreased by increasing the flow rate and inlet concentration. The Thomas and Yoon–Nelson models were suitable models for the design of GGR activated carbon fixed-bed column. The LUB of 0.44 cm and 4.35 cm was obtained for nitrate and phosphate with the inlet concentration of 20 mg L^{-1} and a flow rate of 40 mL min^{-1} , respectively. GGR is a new adsorbent that has not been previously utilized for adsorption of phosphate and nitrate.

Keywords *Glycyrrhiza glabra* residue activated carbon · Nitrate removal · Phosphate adsorption · RSM · Fixed-bed column adsorption

1 Introduction

Urbanization, industrialization, high usage of agricultural fertilizers, combined with inappropriate treatment of wastewater, have led to contamination of the environment and groundwater resources by toxic pollutants including organic, and inorganic ions like nitrate and phosphate. Nitrogen and phosphorous are used in agriculture due to their high solubility in water and nutritious values for

the plants [1–3]. However, excessive release of nitrate and phosphate to the environment adversely affects the ecosystem and human health [4, 5]. Nitrate can cause several serious health problems including respiratory tract infection, diarrhea, hypertension, and blue baby syndrome for infants [3, 6]. Furthermore, nitrate could change to nitrite, a carcinogenic compound that increases the risk of cancer, and could potentially leach out from the soil to water, thus polluting the drinking water resources [2, 7]. Phosphate

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can lead to the formation of algal blooms, which could endanger human health by the production of cyanotoxins [8]. Phosphate and nitrate cause eutrophication, degrade freshwater and lead to loss of aquatic species [5, 9]. There is an increasing demand for the removal of phosphate and nitrate from water and wastewater, due to an increase in their pollution. High stability and solubility of nitrate and phosphate impose a great challenge for their removal [10]. Thus, the development of efficient methods and high-performance adsorbent for the removal of nitrate and phosphate is of crucial importance [9].

Physical, chemical and biological methods have been employed for nitrate and phosphate removal. Membrane separation, ion exchange, and other physical removal methods transfer or concentrate the contaminant without degrading the contaminant, leading to the formation of second contamination. The chemical reduction technique has reactivity and mobility issues and could potentially cause toxic products. Biological methods require carbon resources and a long period of microbial culturing [11, 12]. The substantial cost of these treatments and their complexity impairs the practicality of these techniques, thus cost-effective, and highly efficient technology for nitrate and phosphate removal should be developed. Adsorption is cost-, time-, and energy efficient, does not require high operating temperature or pressure and has proven to be efficient for the elimination of nitrate and phosphate [13, 14]. Various adsorbents for adsorption of these compounds have been applied, including fly ash, iron-based compounds, aluminum hydroxide, Ca-based adsorbents, clay, zeolite, chitosan, and carbon-based adsorbents [2, 15]. Low price, high adsorption capacity, selectivity to the pollutants and large surface area are important parameters for the adsorbent [2, 16].

Activated carbon has a high specific surface area, low density, microporous structure, high chemical resistance, high surface reactivity, and high adsorption capacity. It has been successfully utilized for adsorption of various chemical species [10, 14, 16, 17]. Due to the high demand for activated carbon, and subsequently, the high cost of this adsorbent, utilization of renewable sources as an alternative source for the production of activated carbon has gained attention [14]. Activated carbon adsorbent has been produced from environmental waste including rice husk, grape seed, maize cob, cocoa shell, bamboo fiber, palm shell, and kenaf fiber [14, 18]. Recently, there have been reports of *Glycyrrhiza glabra* as an activated carbon source for the removal of toluene from gaseous solutions. *Glycyrrhiza glabra* is a traditional herb with cylindrical, long, fibrous, thick, and multi-branched roots, with a high surface area. This herb has demonstrated suitable removal efficiency of Pb(II) and Ni(II) ions [19–21]. The utilization of agricultural waste as activated carbon precursors is

renewable and less costly and could convert waste into a valuable product [22]. The physical or chemical activation method could be applied for the preparation of the activated carbon [23, 24]. The chemical activation technique produces a higher porosity structure, involves shorter activation time and requires lower temperature [24]. Chemical activation by using ZnCl_2 has been reported to produce highly porous activated carbon with high surface area [23].

Batch adsorption was carried out for the measurement of the effective adsorption of pollutants and the determination of maximum adsorption capacity [25]. The batch adsorption studies are used for the determination of mass transfer coefficients and adsorption isotherm constants. Langmuir, Freundlich and Temkin isotherms could be applied for the evaluation of the suitability of an adsorbent for nitrate and phosphate removal [26]. Activated carbon has been used in the industrial scale fixed-bed column. The continuous column provides information regarding the practicality of the adsorption process in the wastewater treatment and in industrial scale [27]. The continuous fixed-bed adsorber does not operate under equilibrium conditions, and the effect of hydrodynamic parameters (flow conditions) influences the flow behavior downstream. Dynamics of the adsorption column impose difficulties on modeling due to nonlinearities in the adsorption equilibrium isotherms and mass transfer resistance [26, 28]. For effective design and efficient operation of a fixed-bed column, breakthrough curves developed under the operating conditions are important. The transport process in the fixed-bed column and within the adsorbent determines and influences the shape of the breakthrough curve [25]. The process parameters are important factors for the design of the adsorption system as they determine the model used for the prediction of effluent quality under the operating conditions [26].

In this study, the *Glycyrrhiza glabra* residues (GGR) were used for the preparation of activated carbon as a new adsorbent for nitrate and phosphate removal. To the best of authors' knowledge, this material has never been used before for the adsorption of nitrate and phosphate. The effect of carbonization temperature and the impregnation ratio of activated carbon with ZnCl_2 was studied. The optimum carbonization condition was determined, and the GGR activated carbon obtained from the optimum carbonization conditions was characterized using FE-SEM, FTIR, EDX, XRD, and BET. The effect of adsorbent dosage and contact time and presence of competitor anions (bicarbonate and sulfate) was studied in the batch adsorption system. The response surface methodology (RSM) was applied to investigate the effect of parameters (initial concentration, pH, and temperature) and their interaction on the removal efficiency. For this purpose, the central composite design (CCD) was used to predict

the mathematical models for removal efficiencies. Furthermore, the removal efficiency of nitrate and phosphate was studied in the laboratory scale fixed-bed column. The effect of inlet concentration and volumetric flow rate on the removal efficiency of nitrate and phosphate was studied. Adams-Bohart, Thomas, and Yoon–Nelson models were applied for the analysis of the breakthrough curves. Moreover, the desorbability of the GGR activated carbon was studied for 4 desorption–adsorption cycles.

2 Materials and methods

2.1 Preparation of activated carbon

The GGR was utilized as the precursor for the preparation of activated carbon. GGR was obtained from Rishmak Company, Shiraz, Iran. Initially, the dried samples were milled and were soaked in distilled water for 24 h. The sample was subsequently washed several times with distilled water. The samples were dried in the oven at 110 °C for the duration of 24 h. The sieve shaker was utilized for the separation of a fraction of the sample within the diameter range of 0.3–1 mm. Chemical activation of GGR granules was carried out using ZnCl_2 (1.467 mol L^{-1}). Initially, the dried GGR was mixed with different ratios (1:1, 1:1.5, 1:2) of ZnCl_2 and was subsequently allowed to soak for 24 h at room temperature. The GGR impregnated with ZnCl_2 was dried in the oven for 24 h at 110 °C. In the second step, the sample was carbonized in the furnace at the desired temperatures (450, 650 and 850 °C) under the nitrogen flow rate of 200 mL min^{-1} . The heating rate of the carbonization process was 10 °C min^{-1} from the ambient temperature to the desired temperature, and the sample was held at the final temperature for the duration of 1 h. The resultant activated carbon soaked in 2 M HCl for 2 h for the removal of residual zinc. Hot distilled water was used for washing the prepared activated carbon. The activated carbon was dried in the oven at 110 °C for 24 h and was subsequently stored in glass bottles. GGR activated carbon prepared at different conditions (temperature and impregnation ratio) was used for the evaluation of nitrate removal. For this purpose, the batch system was utilized to remove nitrate from the aqueous solution of nitrate. An amount of 1 g of prepared GGR activated carbon was added to 100 mL of 100 mg L^{-1} aqueous nitrate solution at a pH of 7 and a temperature of 25 °C for 180 min. The optimum activation conditions were achieved, and the characterization tests were conducted on the optimum prepared GGR activated carbon.

2.2 Characterization of the prepared adsorbents

Field emission scanning electron micrographs (Mira3 model, Tescan, Czech) were utilized to study the surface morphology of the adsorbent prepared at the optimum activation conditions. The adsorbent was coated with gold for charge dissipation during the FE-SEM imaging. The chemical structure of carbon and the functional group of the adsorbent were determined from the Fourier transform infrared spectrometer (6300 Jasco, Japan). FTIR spectra were measured from 400 to 4000 cm^{-1} at the resolution of 4 cm^{-1} [29]. The chemical analysis of the adsorbent was determined from the energy-dispersive X-ray (EDX) instrument [30]. X-ray diffraction (XRD) (D8 Advance, Bruker, Germany) patterns were collected by using Cu K_α radiation ($\lambda = 1.5405 \text{ Å}$) in the 2θ range of 5° – 80° . The surface area and pore distribution of the activated carbon were obtained through the surface area and pore size analyzer (BELSORP-mini II, Japan). The specific surface area of the adsorbent was determined from the Brunauer–Emmett–Teller (BET) method using N_2 adsorption data at 77 K. The density functional theory was used for the estimation of pore size distribution.

2.3 Batch adsorption

Adsorption of nitrate and phosphate from aqueous solution (100 mg L^{-1}) was carried out by using different adsorbent dosage (0.1–1 g in 100 mL) at 25 °C and pH of 7 for 180 min shaking period at 100 rpm. Batch nitrate and phosphate adsorption experiments were conducted by adding the optimum amount of GGR activated carbon to each of the aqueous solutions of nitrate and phosphate within the different range of initial concentrations. The 0.1 M H_2SO_4 or NaOH solution was used to adjust the pH. Samples were agitated in the shaking incubator (NB-205 V, Techno-park) at 100 rpm to control the temperature of the samples. Subsequently, the concentration of nitrate and phosphate in the solutions was determined by a UV–Vis spectrophotometer (DR-5000 Hach, USA) at 220 nm for nitrate and 430 nm for phosphate. The nitrate and phosphate adsorbed on the adsorbent were calculated according to Eq. 1. In Eq. 1, q_e (mg g^{-1}) is the equilibrium amount of adsorbate on the adsorbent, C_0 and C_e represent the initial and equilibrium concentration of adsorbate (mg L^{-1}), v is the solution volume (L), and m is the dosage of the adsorbent (g) in the mixture. The removal efficiency of the nitrate and phosphate ($R\%$) in the solution was determined from Eq. 2 [7].

$$q_e = v(C_0 - C_e)/m \quad (1)$$

$$R\% = 100(C_0 - C_e)/C_0 \quad (2)$$

2.3.1 Kinetic studies

The rate of adsorption of nitrate and phosphate on the activated GGR was studied at different time periods. In the kinetic studies for nitrate and phosphate adsorption, the specific amount of GGR activated carbon was, respectively, added to each of 100 mL of 50 mg L⁻¹ nitrate solution pH of 2 and 100 mL of 40 mg mL⁻¹ phosphate solution pH of 4. The mixtures were agitated in the shaking incubator at 100 rpm and different temperatures (25, 35, and 45 °C) until adsorption equilibrium was achieved. The effect of HCO₃⁻ and SO₄²⁻ anion on the adsorption kinetics of nitrate and phosphate was studied separately. For this purpose, 10 mg of KHCO₃ and 5 mg of K₂SO₄ were added to 100 mL of 50 mg L⁻¹ nitrate solution and 40 mg L⁻¹ phosphate solution [6].

2.3.2 Response surface methodology

To determine the effect of the studied parameters (A: initial concentration, B: pH, C: temperature) and their interaction on the removal efficiency of nitrate and phosphate, the central composite design (CCD) was used. Furthermore, CCD was applied for obtaining prediction models for the removal efficiencies. For the CCD, three levels ($\alpha = 1$) and three parameters were used, to determine the number and the conditions of the experiment to be carried out. Table 1 demonstrates the factors and levels of nitrate and phosphate adsorption. The pH range for phosphate was considered from pH 4, since phosphate exists as H₃PO₄, H₂PO₄⁻, HPO₄²⁻, and PO₄³⁻ at different pH. At acidic pH, the phosphate exists as H₃PO₄ which adsorbs weakly to the adsorption sites. Thus, the experiments were conducted in the pH range of 4–10 [31, 32].

2.4 Fixed-bed adsorption

Fixed-bed column adsorption studies were carried out for evaluation of the feasibility of the adsorbent in the continuous system in the 21 mm diameter and 300 mm height

column. The column was packed with GGR activated carbon to the height of 10 cm. The feed was introduced from the bottom of the column, to prevent the channeling effect. To study the effect of volumetric flow rate on the nitrate and phosphate removal, the peristaltic pump (DLX-MA/AD, ETATRON D.S.) was used for pumping the feed at the different rates of 10, 25, and 40 mL min⁻¹ from the solution containing nitrate (pH = 2) and phosphate (pH = 4) which had the concentration of 50 mg L⁻¹ and 40 mg L⁻¹, respectively (temperature of 25 °C). For evaluation of the impact of inlet feed concentration on nitrate and phosphate removal, the experiments were conducted with a fixed volumetric flow rate of 40 mL min⁻¹ at different concentrations of 20, 60 and 100 mg L⁻¹ for nitrate and phosphate. The effluent solutions were collected at regular time intervals and the nitrate and phosphate concentrations were tested. The breakthrough curve is determined from the experimental data of $\frac{C_t}{C_0}$ versus time (C_t is the concentration in the outlet at a given time, and C_0 is the inlet concentration). The length of the unused bed (LUB) was determined from Eq. 3, in which t_b (breakthrough time: the time at which the maximum allowable concentration of nitrate and phosphate is reached) was obtained from Eq. 4 and t^s (the time equivalent for a total capacity of the adsorption bed) was obtained from Eq. 5 [33, 34].

$$\text{LUB} = L \left(1 - \frac{t_b}{t^s} \right) \quad (3)$$

$$t_b = \int_0^{t_b} \left(1 - \frac{C_t}{C_0} \right) dt \quad (4)$$

$$t^s = \int_0^{t^s} \left(1 - \frac{C_t}{C_0} \right) dt \quad (5)$$

2.5 Desorption studies

To determine the reusing ability of the GGR activated adsorbent, it is important to investigate desorption of

Table 1 (a) Process variables and levels for nitrate adsorption, (b) process variables and levels for phosphate adsorption

a				b			
Factors	Levels			Factors	Levels		
	-1	0	+1		-1	0	+1
A: initial concentration (mg L ⁻¹)	20	60	100	A: initial concentration (mg L ⁻¹)	20	60	100
B: pH	2	6	10	B: pH	4	7	10
C: temperature (°C)	25	35	45	C: temperature (°C)	25	35	45

nitrate and phosphate from the GGR activated carbon. For this purpose, in the batch adsorption system, the adsorbent that was utilized for the adsorption of nitrate ($C_0 = 50 \text{ mg L}^{-1}$, $\text{pH} = 2$, and $T = 25^\circ\text{C}$) and phosphate ($C_0 = 40 \text{ mg L}^{-1}$, $\text{pH} = 4$, and $T = 25^\circ\text{C}$) was centrifuged. Desorption of the nitrate and phosphate from the GGR activated carbon was conducted by immersing the adsorbent in 100 mL of 0.1 M NaOH for 90 min and 120 min for nitrate and phosphate adsorbents, respectively. The used adsorbent was subjected to the desorption-adsorption process for 5 times, and the removal efficiency of each stage was obtained for nitrate and phosphate.

Desorption studies for the fixed-bed column were performed by initially pumping the distilled water at 40 mL min^{-1} for 5 min. Subsequently, an amount of 10 mL min^{-1} of 0.1 M NaOH solution was pumped in the fixed-bed column for 150 min and 180 min for nitrate and phosphate, respectively, at the temperature of 25°C . The used adsorbent was reused in 4 cycles of desorption-adsorption ($C_0 = 50 \text{ mg L}^{-1}$ for nitrate and $C_0 = 40 \text{ mg L}^{-1}$ for phosphate, $Q = 40 \text{ mL min}^{-1}$), and the breakthrough curves were obtained for each adsorption stage of each cycle [6].

2.6 Adsorption models

The adsorption data obtained from the batch and fixed-bed system were analyzed using the adsorption models

stated in Table 2. In this study, the pseudo-first-order, pseudo-second-order, and intra-particle diffusion models were studied. The Adams–Bohart, Thomas, and Yoon–Nelson models were used to describe the behavior of the fixed-bed column. The initial part of the breakthrough curved was described by the Adams–Bohart model. The Thomas model is applied for adsorption systems that possess no internal and external diffusions by assuming plug flow behavior [6]. The application of the Yoon–Nelson model for nitrate and phosphate removal considers that the reduction in the probability of adsorption of nitrate and phosphate is proportional to the probability of nitrate and phosphate adsorption and the breakthrough of nitrate and phosphate on the adsorbent [6]. The adsorption isotherms state the equilibrium amount of nitrate and phosphate in the adsorbent and the aqueous phase [20]. Langmuir isotherm considers a monolayer adsorption onto the finite adsorption surface sites and assumes independent adsorption enthalpy from the adsorbed amount of adsorbate. Freundlich isotherm assumes that by increasing the adsorption occupied sites the enthalpy of adsorption of a heterogeneous surface decreases logarithmically [35]. Temkin isotherm considers the interaction effect between adsorbate and adsorbent. Furthermore, this model considers that the enthalpy of adsorption in the adsorption layer reduces linearly by increasing the adsorption occupied sites [36]. The constants of each model are determined

Table 2 Batch equilibrium adsorption models, batch kinetic models, and column kinetic models [6, 9, 36, 40]

Experiments	Models	Equation	Linearized form	Parameters	Equations no.
Batch kinetic models	Pseudo-first order	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	$\ln(q_e - q_t) = \ln(q_e) - k_1 t$	k_1, q_e	(6)
	Pseudo-second order	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	k_2, q_e	(7)
	Interparticle diffusion	$\frac{dq_t}{dt} = k_{\text{int}} t^{-0.5} / 2$	$q_t = k_{\text{int}} t^{0.5} + C$	k_{int}, C	(8)
Batch equilibrium	Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$	q_m, K_L	(9)
	Freundlich	$q_e = K_F C_e^{1/n}$	$\ln(q_e) = \ln K_F + \frac{\ln C_e}{n}$	K_F, n	(10)
	Temkin	$q_e = B_T \ln(K_T C_e)$	$q_e = B_T \ln(K_T) + B_T \ln(C_e)$	K_T, B_T	(11)
Column kinetic models	Adams–Bohart	$\frac{C_t}{C_0} = \exp\left(K_{AB} C_0 t - K_{AB} N_0 \frac{Z}{U_0}\right)$	$\ln\left(\frac{C_t}{C_0}\right) = K_{AB} C_0 t - K_{AB} N_0 \frac{Z}{U_0}$	K_{AB}, N_0	(12)
	Thomas	$\frac{C_t}{C_0} = \left[\exp\left(\frac{K_{Th} m q_0}{Q} - K_{Th} C_0 t\right) + 1\right]^{-1}$	$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{K_{Th} m q_0}{Q} - K_{Th} C_0 t$	$K_{Th}, m q_0$	(13)
	Yoon and Nelson	$\frac{C_t}{C_0} = [\exp(K_{YN} \tau - K_{YN} t) + 1]^{-1}$	$\ln\left(\frac{C_t - C_0}{C_0}\right) = K_{YN} t - K_{YN} \tau$	K_{YN}, τ	(14)

C_e = equilibrium concentration (mg L^{-1}), q_e = amount of adsorbate per unit mass of adsorbent (mg g^{-1}), q_m = maximum amount of adsorbate (mg g^{-1}), K_L = Langmuir constant (L mg^{-1}), K_F = Freundlich constant (mg g^{-1}) (L mg^{-1}) $^{1/n}$, n = Freundlich constant, K_T = Temkin constant (L mg^{-1}), $B_T = RT/b_T$ (b_T constant related to heat of sorption kJ mol^{-1}), q_t = amount of adsorbate at time (mg g^{-1}), k_1 = rate constant of pseudo-first order (min^{-1}), k_2 = rate constant of pseudo-second order ($\text{g mg}^{-1} \text{min}^{-1}$), K_{int} = intra-particle diffusion constant ($\text{mg g}^{-1} \text{min}^{-0.5}$), the parameter C should be 0 if the intra-particle diffusion is the rate-controlling step. K_{AB} = kinetic constant ($\text{L mg}^{-1} \text{min}^{-1}$), U_0 = linear velocity (volumetric flow rate/column section area, cm min^{-1}), Z = bed length of the column (cm), N_0 = saturation concentration (mg L^{-1}), K_{Th} = Thomas rate constant ($\text{mL min}^{-1} \text{mg}^{-1}$), $m q_0$ = mass of adsorbate at the equilibrium (mg), C_0 = inlet concentration (mg L^{-1}), C_t = outlet concentration at time t (mg L^{-1}), Q = volumetric flow rate (mL min^{-1}), t = time (min), τ = time required for 50% adsorbate breakthrough (min), K_{YN} = rate constant (min^{-1})

from the linearized form of that model, as indicated in Table 2.

3 Results and discussion

3.1 Optimum preparation conditions of the GGR activated carbon

To prepare the GGR activated carbon with the highest nitrate removal potential, the GGR impregnation ratio ($m_p : m_{\text{ZnCl}_2}$, m_p is the mass of dried GGR, and m_{ZnCl_2} is the mass of ZnCl_2), and carbonization temperature was varied between 1:1, 1:1.5, 1:2, and 450, 650, and 850 °C, respectively. Table 3 demonstrates the nitrate removal efficiency obtained at different preparation conditions of the GGR activated carbon. The CCD was applied for the determination of the impact of the studied parameters on the

nitrate removal. Figure 1 demonstrates the effect of studied parameters on nitrate removal. According to Table 3 and Fig. 1, by increasing the carbonization temperature and impregnation ratio, the efficiency of the prepared GGR activated carbon was increased. At impregnation ratio of 1:2 and temperature of 850 °C, the nitrate removal efficiency was 79.12%. At higher carbonization temperatures, more volatile compounds were released, and thus a porous structure was formed. Therefore, the removal efficiency of nitrate increased. Similar trends were observed in other research studies [10, 11]. Phenol groups present in the activated carbon have acidic properties. The H from Phenol reacts with Cl of ZnCl_2 . Therefore the oxygen of phenol that has lost its H would enter the pair electrons into the empty orbital of Zn. Zn has two Cl and thus can react with two structures that have phenol groups and can form cross-link [41]. The ZnCl_2 develops cross-links, resulting in the creation of a rigid matrix; therefore, the nitrate removal would increase by increasing the ZnCl_2 ratio [42].

Table 3 Nitrate removal efficiency obtained from activated carbon prepared at different temperatures and ratios of the weight of the dried plant to ZnCl_2

No.	Carbonization temperature (°C)	$m_p : m_{\text{ZnCl}_2}$	$R_N\%$
1	450	1:1	59.68
2	650	1:1	61.36
3	450	1:2	67.16
4	850	1:2	79.12
5	850	1:1	65.78
6	450	1:1.5	65.36
7	650	1:2	73.14
8	850	1:1.5	76.12
9	650	1:1.5	72.65

3.2 Characterization of GGR activated carbon

Figure 2 demonstrates the FE-SEM of the prepared GGR activated carbon. This figure demonstrates the irregular and porous morphology of the adsorbent that has occurred due to the removal of volatile compounds and impurities during the activation process with ZnCl_2 . The activated carbon acquired at the temperature of 850 °C and the impregnation ratio of 1:2 had a porous surface, indicating a high surface area. The FTIR spectra of the GGR activated carbon are demonstrated in Fig. 3a. The displayed bands at 661.184 cm^{-1} and 673.035 cm^{-1} represent the C–Cl bonding. The peak at 1115.62 cm^{-1} is assigned to the S–O linkage or C–O stretching linkage

Fig. 1 **a** Contour plot and **b** response surface plot showing the effects of carbonization temperature and impregnation ratio on the nitrate removal

Fig. 2 **a** FE-SEM of GGR activated carbon at 1 μ m, **b** FE-SEM of GGR activated carbon at 200 nm

Fig. 3 **a** FTIR spectra of GGR activated carbon, **b** EDX spectra of GGR activated carbon, **c** XRD spectra of GGR activated carbon

from alcohols, ethers or hydroxyl groups. The band at 1563.02 cm^{-1} is indicative of C=C linkage. The peak at 2923.56 cm^{-1} is attributed to the C–H bonding of methyl and methylene groups. The peak at 3423.99 cm^{-1} represents the O–H bonding of hydroxyl, carboxyl group, and phenol or alcohol groups. The loading capacity of activated carbon is not determined from the pore structure alone, and the chemical nature of the surface of adsorbent is also important. Heteroatoms (oxygen, hydrogen, nitrogen) are present in the structure of activated carbon as single atoms or functional groups. Oxygen is the heteroatom present most in the matrix of activated carbon. The combination of oxygen–carbon in activated carbon has the highest impact on reactions and surface behavior of activated carbon [29]. The surface of activated carbon contains functional groups with oxygen sites and amino sites. Figure 3b depicts the EDX spectra with the elemental analysis of the GGR activated carbon. The table inset in the EDX spectra indicates the quantitative elemental analysis in weight % for the adsorbent, which was determined to have 83.24% carbon, 11.92% oxygen, 3.44% Cl, and 1.40% Zn. From the EDX spectra, it is evident that the highest component present is carbon; furthermore, Zn and Cl are present due to the utilization of ZnCl_2 as the precursor. The presence of Zn and Cl on the surface of adsorbent could

block the active sites and hinder the adsorption of nitrate and phosphate [30].

The X-ray diffraction profile of GGR activated carbon is shown in Fig. 3c. The lack of an exhibition of well-defined peaks in the XRD spectra indicates that the discrete mineral phase was not detected. Thus, the GGR activated carbon has an amorphous structure. The hump at 2θ of 25° indicates the high degree of disorder of the produced carbonaceous material.

Table 4 demonstrates the results of the BET analysis. The specific surface area was determined to be $959.22\text{ m}^2\text{ g}^{-1}$. The yield (mass of GGR activated carbon/mass of dried GGR) of GGR activated carbon was 40%.

3.3 Batch adsorption studies

3.3.1 Adsorbent dosage studies

To determine the effect of adsorbent dosage on the removal efficiency of nitrate and phosphate, the adsorbent dose was varied between 0.1 and 1 g in 100 mL aqueous solution (100 mg L^{-1}). According to Fig. 4, the removal efficiency of nitrate and phosphate increased with increasing the amount of adsorbent, due to an increased surface area. When the adsorbent amount increased from 1 to 4 g L^{-1} , the nitrate adsorption increased from 55.12 to 75.35%. Similarly, an increase in the adsorbent amount from 1 to 6 g L^{-1} increased the removal efficiency of phosphate from 41.56 to 76.09%. Furthermore, the adsorbent affinity toward adsorbing nitrate was higher than phosphate at low adsorbent dosage. At high adsorbent dosage, the equilibrium uptake of nitrate and phosphate did not increase considerably, due to the conglomeration of

Table 4 Results of BET analysis

Surface area ($\text{m}^2\text{ g}^{-1}$)	Total pore volume ($\text{cm}^3\text{ g}^{-1}$)	Mean diameters of pores (nm)	Yield %
959.22	0.5431	2.2227	40

Fig. 4 Effect of adsorbent dosage on nitrate and phosphate removal efficiency

adsorbent particles [35]. Therefore, the optimum GGR activated carbon dosage for nitrate and phosphate removal was 4 g L^{-1} and 6 g L^{-1} , respectively.

3.3.2 Adsorption kinetics

Figure 5 displays the adsorption kinetics of nitrate and phosphate separately and in the presence of competitive anions. These data were obtained at the temperatures of 25, 35, and 45 °C. According to Fig. 5a, b, the equilibrium time for nitrate removal was 90 min, while the equilibrium time for nitrate in the presence of competitor anions was prolonged to 150 min, and the adsorption capacity was decreased. This occurrence has resulted from the occupation of the adsorption sites with the competitor anions [7]. The adsorption kinetic study of phosphate (Fig. 5b, c) indicates that the equilibrium time for phosphate removal and phosphate removal in the presence of competitor anions was 120 min. According to Table 5, the pseudo-first-order, pseudo-second-order, and intra-particle diffusion models were applied to analyze the experimental data shown in Fig. 5. According to Table 2, by using the linearized form and plotting the $\ln(q_e - q_t)$ versus t (Eq. 6), $\frac{t}{q_t}$ versus t (Eq. 7), and q_t versus $t^{0.5}$ (Eq. 8), for pseudo-first-order, pseudo-second-order, and intra-particle diffusion, respectively, the adsorption kinetics parameters were obtained at the temperature of 25 °C. The coefficient of

determination of the pseudo-second-order for nitrate and phosphate was 0.9997 and 0.9914, respectively, which is close to 1 and the calculated q_e for nitrate and phosphate was in accordance with the experimental data. The linearity of the intra-particle diffusion model indicates the involvement of the intra-particle diffusion in the adsorption process. Passage of linear line through the origin indicates that the intra-particle diffusion is the rate-controlling step; else the rate of adsorption is controlled by the boundary layer and other kinetic models. According to Table 5, intra-particle diffusion is not in accordance with the experimental data, and thus, the rate of adsorption is not controlled by this model [37]. The pseudo-first-order model was determined to be the most suitable model for nitrate adsorption in the presence of competitor anions, with the coefficient of determination of 0.9922. On the contrary, the pseudo-second-order model was determined to be a suitable model for phosphate adsorption in the presence of competitor anion, with the coefficient of determination value of 0.996. The pseudo-second-order model considers that there is no external and internal mass transfer resistance in the adsorption procedure [35]. These results indicate that physical and chemical adsorption could be included in the adsorption.

Fig. 5 Adsorption kinetics of **a** nitrate, **b** nitrate with competitor anions, **c** phosphate, **d** phosphate with competitor anions

Table 5 Kinetic parameters for adsorption on the activated carbon from GGR at 298 K

Kinetic models	Analyte	K_1 (min ⁻¹)	q_e (cal)	R^2
Pseudo-first order	Nitrate (50 mg L ⁻¹)	0.0176	3.9	0.9814
	Phosphate (40 mg L ⁻¹)	0.0293	4.75	0.9888
	Nitrate (50 mg L ⁻¹) + (100 mg L ⁻¹ HCO ₃ ⁻ + 50 mg L ⁻¹ SO ₄ ²⁻)	0.0147	4.8544	0.9922
Pseudo-second order	Analyte	K_2 (g mg ⁻¹ min ⁻¹)	q_e (cal)	R^2
	Nitrate (50 mg L ⁻¹)	0.02	10.2354	0.9997
	Phosphate (40 mg L ⁻¹)	0.004943	6.51	0.9914
	Phosphate (40 mg L ⁻¹) + (100 mg L ⁻¹ HCO ₃ ⁻ + 50 mg L ⁻¹ SO ₄ ²⁻)	0.0099	4.91	0.996
Interparticle diffusion	Analyte	K_{int} (mg g ⁻¹ min ^{-0.5})	C (mg g ⁻¹)	R^2
	Nitrate (50 mg L ⁻¹)	0.1794	7.4948	0.8643
	Phosphate (40 mg L ⁻¹)	0.2497	2.5065	0.82

Bolded words show the boundary of tables or adsorption mechanisms

3.3.3 Response surface methodology

The CCD with three levels and three parameters (A: initial concentration of nitrate or phosphate mg L⁻¹, B: pH, C: Temperature °C) was accomplished by using the Design-Expert software 7.0.0 (Stat-Ease Inc., Minneapolis). The number of experiments for each of nitrate and phosphate was 20 with 6 central point experiments. The results are

tabulated in Table 6. A quadratic model was obtained for the prediction of nitrate removal, and a polynomial model was obtained for the prediction of phosphate removal. The analysis of variance (ANOVA) was used for the evaluation of the regression coefficients, and parameters of the model. Furthermore, it was applied for the determination of a mathematical model. The adequacy of the model was determined through the evaluation of the F value, p

Table 6 (a) Design matrix and the responses obtained from the CCD for nitrate adsorption, (b) design matrix and the responses obtained from the CCD for phosphate adsorption

a					b				
No.	C_0 (mg L ⁻¹)	pH	Temperature (°C)	$R_N\%$	No.	C_0 (mg L ⁻¹)	pH	Temperature (°C)	$R_P\%$
1	60.00	6.00	35	82.28	1	20.00	10.00	25	84.71
2	60.00	6.00	35	82.41	2	60.00	7.00	25	79.015
3	20.00	6.00	35	85.28	3	60.00	7.00	35	82.12
4	100.00	10.00	45	72.16	4	60.00	7.00	35	81.81
5	60.00	6.00	25	80.28	5	100.00	10.00	25	68.66
6	60.00	10.00	35	82.16	6	20.00	10.00	45	70.19
7	20.00	2.00	45	86.17	7	20.00	7.00	35	87.44
8	100.00	6.00	35	78.16	8	100.00	4.00	25	78.36
9	100.00	10.00	25	74.16	9	60.00	7.00	35	81.41
10	60.00	6.00	35	83.06	10	60.00	4.00	35	91.71
11	60.00	2.00	35	87.16	11	100.00	4.00	45	62.11
12	60.00	6.00	45	78.16	12	100.00	7.00	35	62.33
13	60.00	6.00	35	82.3	13	60.00	7.00	35	83.4
14	20.00	2.00	25	86.56	14	100.00	10.00	45	57.69
15	100.00	2.00	25	81.16	15	60.00	10.00	35	77.02
16	60.00	6.00	35	82.61	16	60.00	7.00	45	68.32
17	60.00	6.00	35	82.4	17	60.00	7.00	35	80.67
18	20.00	10.00	25	82.74	18	20.00	4.00	25	94.38
19	20.00	10.00	45	84.52	19	60.00	7.00	35	79.98
20	100.00	2.00	45	77.16	20	20.00	4.00	45	79.16

Table 7 The response surface method analysis of variance (ANOVA) for nitrate adsorption

Source	Sum of squares	df	F value	Prob > F	
Model	293.07	9	151.64	< 0.0001	Significant
A—C ₀	180.37	1	839.92	< 0.0001	
B—pH	50.4	1	235.11	< 0.0001	
C—tempera- ture	4.53	1	21.09	0.0010	
AB	5.33	1	24.82	0.0006	
AC	6.83	1	31.79	0.0002	
BC	2.17	1	10.12	0.0098	
A ²	1.72	1	8.01	0.0178	
B ²	12.70	1	59.14	< 0.0001	
C ²	29.78	1	138.69	< 0.0001	
Residual	2.15	10			
Lack of fit	1.72	5	4	0.0772	Not sig- nificant
Pure error	0.43	5			
Corrected total	295.22	19			

value, R^2 , R^2_{Adjusted} , and $R^2_{\text{Predicted}}$. Equations 15 and 16 are quadratic and polynomial models in terms of actual factors for the prediction of nitrate and phosphate removal, respectively.

According to Table 7, the F value (151.64) and P value (< 0.0001) of the predicted model for nitrate indicate that the model is significant. The F value of each term of this model is high, indicating the significance of each term of the model, and each parameter had an impact on the nitrate removal. The lack of fit of the model (LOF) is 0.0772, which indicates that the LOF is not significant. Based on Table 7, terms of A , B , and C^2 had F values of 839.92, 235.11,

Table 8 The response surface method analysis of variance (ANOVA) for phosphate adsorption

Source	Sum of squares	df	F value	Prob > F	
Model	1777.19	8	50.95	< 0.0001	Significant
A—C ₀	315.26	1	72.31	< 0.0001	
B—pH	225.15	1	51.64	< 0.0001	
C—tempera- ture	457.72	1	104.98	< 0.0001	
AC	0.79	1	0.18	0.6778	
A ²	68.75	1	15.77	0.0022	
B ²	55.19	1	12.66	0.0045	
C ²	106.31	1	24.38	0.0004	
AC ²	37.67	1	8.64	0.0135	
Residual	47.96	11			
Lack of fit	40.89	6	4.82	0.0572	Not sig- nificant
Pure error	7.07	5			
Corrected total	1825.14	19			

and 138.69, respectively, indicating that these terms had the highest impact on the nitrate removal efficiency. Based on Table 8, the predicted model for phosphate removal efficiency has an F value of 50.95 and a P value of < 0.001, demonstrating the significance of the model. The F values of each term of the mathematic model was high, and thus, each term had a significant influence on the phosphate removal efficiency. The LOF is 0.0572 which is not significant, which shows that the model fits. The terms of AC^2 and AC were added to obtain higher F value. The terms C , A , and B had the F values of 104.98, 72.31, and 51.64, respectively, showing that these terms had the highest impact on the phosphate removal efficiency. Figure 6 demonstrates the predicted values of nitrate and phosphate removal versus the experimental data.

$$N_{\text{removal}}\% = 53.4 + 0.0646C_0 - 2.323\text{pH} + 2.296\text{Temperature} \\ - 0.0051(C_0 \cdot \text{pH}) - 0.0023(C_0 \cdot \text{Temperature}) + 0.013(\text{pH} \cdot \text{Temperature}) \\ - 4.94C_0^2 + 0.134\text{pH}^2 - 0.0329\text{Temperature}^2 \quad (15)$$

$$P_{\text{removal}}\% = -16.077 + 1.519C_0 - 8.55\text{pH} + 8.723\text{Temperature} \\ - 0.0841(C_0 \cdot \text{Temperature}) - 0.00312C_0^2 + 0.4977\text{pH}^2 - 0.139\text{Temperature}^2 \\ + 0.001213(C_0 \cdot \text{Temperature}^2) \quad (16)$$

Fig. 6 Predicted versus actual for **a** nitrate removal, and **b** phosphate removal

Table 9 (a) Statistical parameters for the nitrate adsorption obtained from Eq. 15, b statistical parameters for the phosphate adsorption obtained from Eq. 16

<i>a</i>		<i>b</i>	
R^2	0.9927	R^2	0.9737
R^2_{Adjusted}	0.9862	R^2_{Adjusted}	0.9546
$R^2_{\text{Predicted}}$	0.9528	$R^2_{\text{Predicted}}$	0.8112
Adequate precision	44.905	Adequate Precision	27.433

According to Table 9, the regression coefficients R^2 were obtained to be 0.9927 and 0.9737 for nitrate and phosphate removal, respectively. The R^2_{Adjusted} was determined to be 0.9862 and 0.9546 for nitrate and phosphate removal, respectively, and these values are close to 1. The statistical suitability of the model is determined from the closeness of the R^2_{Adjusted} values to the R^2 [43]. The value of adequate precision of 44.905 and 27.433 (which are greater than 4), for nitrate removal and phosphate removal, respectively, indicates an adequate signal.

According to Fig. 7, increasing the pH of nitrate and phosphate solution causes a reduction in nitrate and phosphate removal efficiency. The pH is the main controlling parameter in the electrostatic interaction between the adsorbate and the adsorbent [9]. An increase in pH increases the hydroxyl ions, leading to competition between the hydroxyl group and nitrate and phosphate anions for the adsorbent sites, which decreases the nitrate and phosphate removal. At low pH, protons are present and the negativity of the surface of GGR activated carbon reduces. Therefore, the number of positively charged sites increases, which enhances adsorption [37, 38]. By increasing the initial solution concentration of nitrate and phosphate, the removal efficiencies decrease. This is due to the faster rate of occupation of active sites of adsorbent which

reduces the adsorption capacity [20]. Initially, by increasing the temperature the nitrate and phosphate removal increases, however, a further increase in temperature results in the reduction of nitrate and phosphate removal efficiencies. This effect is attributed to the endothermic adsorption at low temperatures and the physical adsorption mechanism at high temperatures [9].

According to Fig. 8a, c (the perturbation plot for the nitrate and phosphate removal), parameter A (the initial concentration of nitrate or phosphate) has the highest impact on the removal, followed by the pH and the temperature parameters. According to Fig. 8b, at low initial nitrate concentration, increasing the temperature increases the removal efficiency. However, by increasing the temperature at high initial nitrate concentration, the removal efficiency decreases. Based on Fig. 8d, at the low initial concentration of phosphate, increasing the temperature, increases the removal of phosphate, until an optimum temperature is reached at 32 °C. By increasing the temperature further than the optimum point, the phosphate removal efficiency decreases. For high initial concentrations of phosphate, increasing the temperature decreases the phosphate removal efficiency.

3.3.4 Adsorption isotherm

Adsorption isotherm tests were carried out at the pH of 2 and 4 for nitrate and phosphate removal, respectively. The Langmuir (Eq. 9), Freundlich (Eq. 10), and Temkin (Eq. 11) in Table 2 were applied to the experimental data. The constant of isotherms for nitrate and phosphate is given in Table 10. The experimental data were in good accordance with the Langmuir isotherm, which had the highest linear regression coefficient. The maximum adsorption capacity obtained for nitrate at 308 K was 142.58 mg g⁻¹ with the

Fig. 7 Response surface plot of nitrate removal (N removal) and phosphate removal (P removal) showing the effect of **a** pH and initial concentration for nitrate and phosphate removal, **b** tempera-

ture and initial concentration for nitrate and phosphate removal, and **c** temperature and pH on nitrate and phosphate removal

linear regression coefficient of 0.9977 (Fig. 9a), and the maximum adsorption capacity for phosphate at 298 K was 92.59 mg g^{-1} , with the linear regression coefficient of 0.9804 (Fig. 9c). The high linear regression coefficient demonstrates the monolayer adsorption of this process. Langmuir isotherm is evaluated by the separation factor (R_L), which is given in Eq. 17. The shape of isotherm is demonstrated with the R_L , and an R_L value between 0 and

1 is indicative of favorable adsorption, whereas R_L value greater than 1 and $R_L = 0$ indicate irreversible adsorption.

$$R_L = \frac{1}{1 + K_L C_0} \quad (17)$$

Fig. 8 **a** Perturbation plot for nitrate removal, **b** interaction of initial concentration and temperature parameters for nitrate removal, **c** perturbation plot for phosphate removal, **d** interaction of initial concentration and temperature for phosphate removal

Similarly, the isotherms were used to fit the experimental data of adsorption in the presence of competitor anions $100 \text{ mg L}^{-1} \text{HCO}_3^- + 50 \text{ mg L}^{-1} \text{SO}_4^{2-}$. According to Fig. 9b, d, the Langmuir isotherm was the best fit for the adsorption of nitrate and phosphate in the presence of competitor ions. The maximum adsorption capacity obtained for nitrate in the presence of competitor ion at 308 K was 47.39 mg g^{-1} with the linear regression coefficient of 0.984 (Fig. 9b), and the maximum adsorption capacity for phosphate at 298 K was 75.18 mg g^{-1} , with the linear regression coefficient of 0.9834 (Fig. 9d). According to Table 11, the maximum adsorption capacity for nitrate and phosphate had decreased by 66%, and 18%, respectively, in the presence of competitor anions.

The presence of bicarbonate and sulfate anions occupied the active sites of the adsorbent and blocked the adsorption of nitrate and phosphate. Sulfate has two valence charges and thus adsorbs stronger than the nitrate with one valence charge. Therefore, the presence of sulfate anion strongly decreases the adsorption of nitrate.

However, the sulfate and bicarbonate anion have less tendency to adsorb in the presence of phosphate. Therefore, the presence of competitor anions ($100 \text{ mg L}^{-1} \text{HCO}_3^- + 50 \text{ mg L}^{-1} \text{SO}_4^{2-}$) in the phosphate solution of 40 mg L^{-1} and does not significantly affect the adsorption of phosphate [6, 44].

3.3.5 Adsorption thermodynamics

The temperature behavior was studied to determine the adsorption thermodynamics and the nature of the adsorption process. The Gibbs free energy (ΔG° , kJ mol^{-1}) was obtained from Eq. 18. In Eq. 18, R is the gas constant ($8.314 \text{ J mol}^{-1} \text{K}^{-1}$), T is the temperature (K), and K is from the K_L in the Langmuir isotherm (L mol^{-1}). The ΔG° for nitrate was obtained at 298, 308, and 318 K and was determined to be -18.3 , -20.1 , and $-20.8 \text{ kJ mol}^{-1}$, respectively. The ΔG° was determined to be -16.7 , -17.1 , and $-18.2 \text{ kJ mol}^{-1}$ for phosphate removal at 298, 308, and 318 K, respectively. The negative values attained

Table 10 Isotherm parameters for adsorption from the activated carbon synthesized from GGR

Isotherms	Temperature K	Analyte	K_f (L mg ⁻¹)	q_0 (mg g ⁻¹)	R^2	R_f
Langmuir	298	Nitrate (50 mg L ⁻¹)	0.0285	136.98	0.9966	0.4123
	308	Nitrate	0.0413	142.58	0.9977	0.3262
	318	Nitrate	0.0423	128.20	0.9887	0.321
	298	Phosphate (40 mg L ⁻¹)	9.0429×10^{-3}	92.59	0.9804	0.734
	308	Phosphate	8.2753×10^{-3}	84.03	0.9856	0.751
	318	Phosphate	0.0103	79.92	0.9855	0.708
		Analyte	K_F (mg ^{1-1/n} L ^{1/n} g ⁻¹)	n	R^2	
Freundlich	298	Nitrate (50 mg L ⁻¹)	5.0319	1.6504	0.9442	
	308	Nitrate	6.5646	1.6934	0.9280	
	318	Nitrate	3.6659	1.5718	0.9591	
	298	Phosphate (40 mg L ⁻¹)	1.2289	1.3770	0.9632	
	308	Phosphate	1.0879	1.3960	0.9675	
	318	Phosphate	1.3396	1.4918	0.9597	
		Analyte	K_T (L mg ⁻¹)	$B_T = RT/b_T$	R^2	
Temkin	298	Nitrate (50 mg L ⁻¹)	0.9314	22.8820	0.8417	
	308	Nitrate	0.8374	35.2070	0.8723	
	318	Nitrate	0.6282	23.4740	0.8262	
	298	Phosphate (40 mg L ⁻¹)	3.5558	14.4900	0.8728	
	308	Phosphate	4.0172	13.2310	0.8879	
	318	Phosphate	3.3683	12.2460	0.8973	

for ΔG° indicate the spontaneous nature of adsorption. The enthalpy (ΔH° , kJ mol⁻¹) and entropy change (ΔS° , J mol⁻¹ K⁻¹) were obtained from Eq. 19. The value of ΔH° for nitrate and phosphate was obtained to be 15.55 kJ mol⁻¹ and 5.12 kJ mol⁻¹, respectively. The endothermic nature of adsorption is demonstrated by the positive value of enthalpy. The ΔS° for nitrate and phosphate adsorption was 114.36 J mol⁻¹ K⁻¹ and 73.37 J mol⁻¹ K⁻¹, respectively. The positive values of ΔS° propose the rise in randomness at the solid/solution interface of the adsorption process [37, 45].

$$\Delta G^\circ = -R \cdot T \cdot \ln K \quad (18)$$

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (19)$$

3.4 Fixed-bed adsorption studies

One of the important parameters utilized in the design of the adsorption process is the length of the unused bed (LUB). The maximum allowable limit of nitrate and phosphate in the drinking water is 10 mg L⁻¹ and 0.1 mg L⁻¹, respectively [46, 47]. The LUB values for the adsorption of nitrate and phosphate at different concentrations and flow

rate were determined from the analysis of breakthrough curves (

Figure 10 and Eq. (3)) and are stated in Table 12. The LUB for constant nitrate concentration of 50 mg L⁻¹ at the flow rate of 25 mL min⁻¹ was obtained to be 2.07 cm, and for constant phosphate concentration of 40 mg L⁻¹ at the flow rate of 25 mL min⁻¹ was determined to be 4.43 cm. The low value of LUB at high concentrations of nitrate and phosphate indicates high utilization of the GGR activated carbon bed capacity. A narrow mass transfer zone or small LUB is desirable to utilize the adsorbent efficiently and for the reduction in the cost of energy for regeneration [33].

Figure 10a, c demonstrates the breakthrough curves for the adsorption of nitrate and phosphate in the continuous fixed-bed column loaded with the GGR activated carbon. The adsorbent height in the column was kept at 10 cm. According to Fig. 10 a, c, by increasing the flow rate for nitrate (50 mg L⁻¹) and phosphate (40 mg L⁻¹) from 10 to 40 mL min⁻¹ the breakthrough time decreases from 76 to 41 min, and 66 to 32 min, respectively. When the flow rate is high, the adsorbate does not have sufficient time for diffusion inside the pores of the GGR activated carbon, and thus nitrate and phosphate leave the adsorption bed prior to reaching equilibrium, resulting in low utilization of the adsorption bed. At lower flow rates, nitrate and phosphate have a higher residence time in the adsorption

Fig. 9 Linearized Langmuir adsorption isotherm were obtained at 208 K, 308 K, 318 K and at pH of 2 for nitrate and pH of 4 for phosphate, **a** nitrate adsorption, **b** nitrate adsorption in the presence of

competitor anions, **c** phosphate adsorption, **d** phosphate adsorption in the presence of competitor anions

Table 11 Adsorption isotherms for nitrate and phosphate in the presence of competitor anions

Isotherms	Temperature K	Analyte	K_f (L mg ⁻¹)	q_0 (mg g ⁻¹)	R^2	R_l
Langmuir	298	Nitrate (50 mg L ⁻¹) + (100 mg L ⁻¹ HCO ₃ ⁻ + 50 mg L ⁻¹ SO ₄ ²⁻)	0.011	36.10	0.9901	0.645
	308	Nitrate (50 mg L ⁻¹) + (100 mg L ⁻¹ HCO ₃ ⁻ + 50 mg L ⁻¹ SO ₄ ²⁻)	0.0094	47.39	0.984	0.68
	318	Nitrate (50 mg L ⁻¹) + (100 mg L ⁻¹ HCO ₃ ⁻ + 50 mg L ⁻¹ SO ₄ ²⁻)	0.0091	29.49	0.9906	0.687
	298	Phosphate (40 mg L ⁻¹) + HCO ₃ ⁻ (100 mg L ⁻¹) + SO ₄ ²⁻ (50 mg L ⁻¹)	9.87×10^{-3}	75.18	0.9834	0.716
	308	Phosphate (40 mg L ⁻¹) + (100 mg L ⁻¹ HCO ₃ ⁻ + 50 mg L ⁻¹ SO ₄ ²⁻)	7.47×10^{-3}	72.99	0.9805	0.7699
	318	Phosphate (40 mg L ⁻¹) + (100 mg L ⁻¹ HCO ₃ ⁻ + 50 mg L ⁻¹ SO ₄ ²⁻)	6.5×10^{-3}	71.42	0.9763	0.793

bed, allowing a more efficient separation. Furthermore, by increasing the flow rate the breakthrough curve changes from concave-up to concave-down in the mid-ranges of time. This is because at low flow rate values the transport process is limited by the interparticle diffusion and the external mass transfer is slow, thus the adsorption rate is lower, and the length of the mass transfer zone would be longer [33].

The effect of the inlet concentration of nitrate and phosphate at 20, 60, and 100 mg L⁻¹ at the flow rate of

40 mL min⁻¹ (adsorbent bed height of 10 cm) was investigated. According to Fig. 10b, d, as the inlet concentration increases, the breakthrough curve becomes sharper. The breakthrough time decreases from 70 to 20 min, as the inlet concentration of nitrate increases from 20 to 100 mg L⁻¹, and decreases from 45 to 25 min as the phosphate inlet concentration increases from 20 to 100 mg L⁻¹. This is attributed to the rapid saturation of the adsorbent binding sites of the GGR activated carbon.

Fig. 10 The breakthrough curves **a** effect of volumetric flow rate at constant inlet concentration of nitrate (50 mg L^{-1}), **b** effect of inlet concentration of nitrate at constant volumetric flow rate

(40 mL min^{-1}), **c** effect of volumetric flow rate at constant inlet concentration of phosphate (40 mg L^{-1}), **d** effect of inlet concentration of phosphate at constant volumetric flow rate (40 mL min^{-1})

Table 12 (a) LUB for nitrate and phosphate removal at constant C_0 , (b) LUB for nitrate and phosphate removal at constant Q (volumetric flow rate)

a				b			
$C_0 = 50 \text{ (mg L}^{-1}\text{)}$				$Q = 40 \text{ (mL min}^{-1}\text{)}$			
$Q \text{ (mL min}^{-1}\text{)}$	10	25	40	$C_0 \text{ (mg L}^{-1}\text{)}$	20	60	100
$\text{LUB}_{\text{Nitrate}} \text{ (cm)}$	1.45	2.07	2.99	$\text{LUB}_{\text{Nitrate}} \text{ (cm)}$	0.44	3.89	5.18
$C_0 = 40 \text{ (mg L}^{-1}\text{)}$				$Q = 40 \text{ (mL min}^{-1}\text{)}$			
$Q \text{ (mL min}^{-1}\text{)}$	10	25	40	$C_0 \text{ (mg L}^{-1}\text{)}$	20	60	100
$\text{LUB}_{\text{Phosphate}} \text{ (cm)}$	3.13	4.43	5.18	$\text{LUB}_{\text{Phosphate}} \text{ (cm)}$	4.35	6	7.42

The behavior of the fixed-bed column was described with Adams–Bohart (Eq. 12), Thomas (Eq. 13), and Yoon–Nelson (Eq. 14) models (Table 2). The Adams–Bohart adsorption model was used to describe the first part of the breakthrough curve. According to Table 13, the values of K_{AB} decrease with increasing the flow rate and decrease with increasing the concentration. Therefore, lower flow rate and lower influent concentration increase the adsorption of nitrate and phosphate in the column. The coefficient of determination values reveals that this model is not in accordance with the experimental data. By increasing the volumetric flow rate, the model was not suitable for

fitting the experimental data; therefore, it is not reported in Fig. 10b, d. The values of K_{Th} decrease with increasing the inlet concentrations of nitrate and phosphate. This is due to the presence of the driving force between the inlet concentration of nitrate and phosphate adsorbed on the adsorbent and the nitrate and phosphate in the solution. By increasing the flow rate, the K_{Th} decreases, and the mq_0 increases. Therefore, lower inlet concentration and lower flow rate lead to higher adsorption of adsorbate in the column. Moreover, all the coefficients of determination for line fitting are more than 0.94, demonstrating an exceptional confidence level. The K_{YN} demonstrates

Table 13 Parameters of Adams–Bohart, Thomas, and Yoon–Nelson models under column adsorption process obtained from (a) nitrate removal breakthrough curve, (b) phosphate removal breakthrough curve

C_0 (mg L ⁻¹)	Q (mL min ⁻¹)	Adams–Bohart model			Thomas model			Yoon and Nelson model		
		$K_{AB} \times 10^{-4}$ (L mg ⁻¹ min ⁻¹)	N_0 (mg L ⁻¹)	R^2	K_{Th} (mL min ⁻¹ mg ⁻¹)	mq_0 (mg)	R^2	K_{YN} (min ⁻¹)	τ (min)	t_{exp} (min)
<i>a</i>										
50	10	11.2	1730	0.83	0.0026	44,914	0.98	0.127	89	90
50	25	9.92	3632	0.94	0.0022	90,621	0.98	0.107	72	75
50	40	9.04	5156	0.84	0.0021	115,381	0.94	0.104	57	60
20	40	17.8	2572	0.86	0.0046	58,811	0.95	0.092	73	72
60	40	5.6	6913	0.92	0.0013	144,021	0.96	0.078	60	60
100	40	3.3	8880	0.79	0.0009	164,418	0.98	0.085	41	39
<i>b</i>										
40	10	15.17	1423	0.88	0.0025	38,228	0.98	0.1	95	94
40	25	9.27	3343	0.79	0.0023	78,386	0.98	0.092	78	80
40	40	10	4720	0.82	0.0021	106,316	0.94	0.084	66	65
20	40	12.9	3462	0.54	0.0037	63,640	0.96	0.074	79	76
60	40	5.05	8441	0.65	0.0012	154,683	0.98	0.072	64	64
100	40	1.64	14,211	0.51	0.0007	211,558	0.95	0.07	52	47

Fig. 11 Adsorption–desorption of **a** nitrate in the batch system, **b** nitrate in the fixed-bed column, **c** phosphate in the batch system, **d** phosphate in the fixed-bed column

Table 14 Comparison of adsorption capacity of GGR activated carbon with the other adsorbents

Adsorbent	Analyte	q_m (mg L ⁻¹)	References
Rice husk	Nitrate	86.2	[7]
Sugar beet bagasse	Nitrate	27.5	[37]
Corn cob	Nitrate	49.9	[6]
Coconut copra		59.2	
Modified rice husk	Nitrate	55	[35]
Calcined waste eggshell	Phosphate	23	[39]
Zirconic chitosan beads	Phosphate	61.7	[9]
ZnCl ₂ activated coir pith carbon	Phosphate	5.1	[32]
Modified Wood-based activated carbon	Phosphate	16	[31]
Modified granular activated carbon	Nitrate	21.5	[1]
Activated carbons developed with potassium hydroxide	Nitrate	18.6	[48]
Composite of activated carbon and Fe ₂ O ₃ nanoparticles	Nitrate	17.7	[2]
Activated carbon	Nitrate	14.6	[24]
Activated carbon of residue	Phosphate	30.2	
Bayoxide E33 (E33)	Phosphate	37.7	[8]
E33/AgII		38.8	
Zinc chloride (ZnCl ₂)-treated coconut granular activated carbon	Nitrate	10.3	[10]
Mg–Al-layered double hydroxide	Nitrate	117	[49]
	Phosphate	26.4	
Iron–zirconium modified activated carbon nanofiber	Phosphate	26.3	[15]
Modified chitosan beads	phosphate	61.7	[9]
Activated carbon produced from <i>Prosopis juliflora</i>	Phosphate	13.55	[50]
	Nitrate	10.99	[50]
Modified activated carbon from tobacco stalk	Phosphate	41.6	[51]
Biochar from bamboo	Nitrate	5	[52]
<i>Glycyrrhiza glabra</i> residues activated carbon	Nitrate	142.5	Present study
	Phosphate	92.5	

the breakthrough curve shape. The values of τ were in accordance with the t_{exp} (time required for 50% adsorbate breakthrough). By increasing the flow rate and inlet concentration, τ decreases, as the saturation in the column takes place quickly [6, 33, 40].

3.5 Results of desorption studies

According to Fig. 11a, c, by increasing the number of desorption–adsorption stages the removal efficiency of nitrate and phosphate decreased from 78 to 62% and from 90 to 64%, respectively. This indicates that the GGR activated carbon adsorbent could be reused several times and has a high adsorption capacity. Equation 20 represents the total adsorption capacity in the fixed-bed column, where C_0 is the inlet concentration (mg L⁻¹), Q is the volumetric flow rate mL min⁻¹, and t^s was calculated from Eq. 5. Equation 21 indicates the desorbability, where q_{total}^n is the total adsorption amount at the n^{th} cycle and q_{total}^{n-1} is the total adsorption at the $n - 1$ cycle. According to Fig. 11b, the

nitrate adsorption amount with the fresh adsorbent was 117 mg and decreased to 84.1 mg at the end of the fourth desorption–adsorption cycle in the fixed-bed column. The desorbability of nitrate for each desorption–adsorption cycle was between 90 and 94%. Based on Fig. 11d, the phosphate adsorption amount with the fresh adsorbent was 105 mg and decreased to 70 mg at the end of the fourth desorption–adsorption cycle in the fixed-bed column. The desorbability of phosphate for each desorption–adsorption cycle was between 88–92%.

$$q_{total} = \frac{C_0 Q t^s}{1000} \quad (20)$$

$$\text{Desorbability \%} = \frac{100 q_{total}^n}{q_{total}^{n-1}}, \quad n \geq 1 \quad (21)$$

3.6 Comparison of adsorption capacity of GGR activated carbon with the other adsorbent

The monolayer adsorption capacities for nitrate and phosphate onto the GGR activated carbon are compared with other adsorbents for the removal of nitrate and phosphate. Based on Table 14 GGR activated carbon has high nitrate and phosphate adsorption capacity of 142.5, and 92.5 mg L⁻¹, respectively. Thus, it could be deduced that GGR activated carbon is an exceptional adsorbent for the removal of nitrate and phosphate.

4 Conclusion

According to this research, the GGR activated carbon was effectively utilized for the efficient removal of nitrate and phosphate from the wastewater. The carbonization temperature of 850 °C and ZnCl₂ impregnation ratio of 1:2 ($m_p : m_{ZnCl_2}$) lead to the formation of high surface area (959.22 m² g⁻¹) of GGR activated carbon. The optimum adsorbent dosage for removal of nitrate and phosphate was determined to be 4 g L⁻¹, and 6 g L⁻¹, respectively. According to the kinetic data, the pseudo-second-order kinetic model was a suitable correlation for the adsorption. The Langmuir isotherm provided the best fit for the experimental data. The maximum adsorption capacity was 142.5 mg g⁻¹ at 308 K and 92.5 mg g⁻¹ at 298 K for nitrate and phosphate, respectively. The presence of competitor ions (100 mg L⁻¹ HCO₃⁻ + 50 mg L⁻¹ SO₄²⁻) reduced the maximum adsorption capacity for nitrate and phosphate by 66% and 18%, respectively. The negative ΔG° demonstrates the spontaneous nature and thermodynamic feasibility of the adsorption process. The ΔH° was obtained to be 15.5 kJ mol⁻¹ and 5.12 kJ mol⁻¹ for nitrate and phosphate, respectively, revealing the endothermic nature of adsorption. The positive value of ΔS° indicates the increased randomness at the solid/solution interface of the adsorption process. The LUB for nitrate and phosphate with an inlet concentration of 20 mg L⁻¹ and a flow rate of 40 mL min⁻¹ was determined to be 0.44 cm, and 4.35 cm, respectively. These amounts indicate high utilization of the GGR activated carbon bed capacity. By increasing the flow rate and inlet concentration of nitrate and phosphate, the breakthrough time decreases. The Thomas and Yoon–Nelson models were obtained to be suitable models under different conditions for the design of GGR activated carbon fixed-bed column. Moreover, the desorbability of GGR activated carbon in the fixed-bed column was studied. The

adsorbed amount of nitrate and phosphate reduced from 117 to 84.1 mg, and from 105 to 70 mg, respectively, in the fourth desorption–adsorption cycle.

Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests

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