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Effect of Hydrogen Ion Presence in Adsorbent and Solution to Enhance Phosphate Adsorption

Tae-hoon Kim and Byungryul An *

Department of Civil Engineering, Sangmyung University, Cheonan 31066, Korea; gdb01449@gmail.com

* Correspondence: bran@smu.ac.kr

Abstract: In this paper, the effect of hydrogen ions on the adsorption onto granular activated carbon (GAC) with the inorganic contaminant phosphate, which exists as a form of four species depending on the solution pH, is investigated. Various batch isotherm and kinetic experiments were conducted in an initial pH 4 as an acid, a pH 7 as neutral, and a pH 9 solution as a base for the GAC conditioned with deionized water and hydrochloric acid, referred to as GAC and GACA, respectively. The physical properties, such as the total surface area, pore volume, pore size distribution, and weight of the element, obtained from Brunauer–Emmett–Teller (BET) and scanning electron microscopy coupled with energy-dispersive X-ray spectrometry (SEM–EDX) represent no significant differences. However, the hydrochloric acid (HCl) condition results in an alteration of the pH of the point of zero charge from 4.5 to 6.0. The optimized initial pH was determined as being acid for the GAC and as being neutral for the GACA. According to the Langmuir isotherm, the relatively high Q_m was obtained as being acid for the GAC and clearly distinguishes the pH effect as being the base for the GACA. An attempt was made to assess the adsorption mechanism using the pseudo-first-order (PFO), the pseudo-second-order (PSO), and the intraparticle diffusion models. The higher R^2 for the PSO in the entire pH range indicated that chemisorption was predominant for phosphate adsorption, and the pH did not change the adsorption mechanism. A prolonged Bed Volume (BV) for the GACA demonstrated that the hydrogen ions on the surface of the GAC enhanced phosphate adsorption.

Keywords: adsorption; isotherm; kinetic; GAC; pH

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1. Introduction

The presence of phosphorus in a water body has been acknowledged, although its concentration is relatively lower than that of nitrogen due to the main causes of eutrophication therein—the concentration of total phosphorus (T-P) was set to 0.2 mg/L in the effluent of the sewage treatment plant in Korea [1]. Since phosphorus (P) only rarely exists by itself in nature, instated P usually occurs as a form of phosphate [2], and improvement of the removal efficiency of the phosphate discharged is required to control the T-P. Since some issues such as ineffective removal efficiency and further treatment at low concentrations of phosphate remain [3], adsorption is a cost-effective and efficient approach, with low chemical sludge production and easy recovery of the adsorbed phosphate [4], when compared with chemical precipitation [5], biological removal [6], and ion exchange (IX)/adsorption [7,8].

Currently, although various adsorbents have been developed, as listed in Table S1, GAC is still widely applied in the field of organic and inorganic contaminant removal, with the benefits of high removal efficiency, easy operation, and availability of regeneration. To increase the removal efficiency of GAC, the following physical and chemical attempts have been made to modify GAC's properties: temperature control for altering the surface area, pore volume and diameter [9], acid and base treatment for use of the functional group [10], and impregnation of the metal [11].

During the phosphate removal process, the adsorption capacity of the adsorbent is highly dependent on the adsorption conditions (e.g., pH, initial concentration, and the

presence of co-ions), which are also related to the adsorption mechanism. According to Chitrakar et al. [12], the effect of pH is important in the adsorption of phosphates to goethite and akaganeite, being closely related to factors such as the net positive charge of the adsorbent and concentration of the hydroxide and phosphate species. A possible explanation is that phosphate has three pK_a values, i.e., 2.12, 7.21, and 12.44, and exists as a form of four species, i.e., H_3PO_4 , $H_2PO_4^-$, HPO_4^{2-} , and PO_4^{3-} , depending on the pH of the solution. Table S1 shows various adsorbents for the removal of phosphates including activated carbon, and the optimized solution pH was found to vary, confirming that the adsorption capacity depended on the adsorbent, the experimental conditions, and the adsorption mechanism.

Adsorption is the process of mass transfer of a target contaminant from the liquid phase to the solid phase. Adsorption isotherm and kinetic experiments have usually been undertaken to describe the adsorption mechanism. The adsorption isotherm model, which uses the relationship between the uptake at equilibrium and a certain time, is used to describe the mechanism and quantify the adsorbate distribution in the interface of the liquid and solid phases. Among a variety of isotherm models, currently, the Langmuir [13] and Freundlich [14] models are widely used. For a porous adsorbent, adsorption occurs over three stages, including external diffusion (film diffusion), internal diffusion (pore diffusion), and adsorption on the active sites [15,16]. The pseudo-first-order model (PFO) [17] and the pseudo-second-order model (PSO) [18] have been developed, and furthermore, the intraparticle diffusion model has been applied to determine the rate-limit step [19].

This study was to investigate the hydrogen-ion effect on the increase in phosphate adsorption and the mechanism onto porous GAC in the presence of the adsorbent and a solution of hydrogen. The specific objectives were to (1) assess the inherent physical properties of GAC; (2) test the optimized solution pH; (3) determine the effect of the pH on adsorption uptake using the isotherm and kinetic rates, the pseudo-first-order and pseudo-second-order reactions, and the interparticle diffusion model; and (4) estimate the enhancement in the fixed column.

2. Material and Methods

2.1. Chemicals

Commercial GAC was purchased from Green Activated Carbon (Hwasung, Korea). All the reagents, hydrochloric acid (HCl), sodium hydrate (NaOH), and KH_2PO_4 were purchased from Sigma-Aldrich and ACS grade and were used without further purification.

2.2. Preparation of the GAC and GACA

The raw GACs were first washed in deionized water (DI) several times until the effluent DI no longer turned black. The GAC was sieved to obtain a size of 0.85–1.7 mm using 11–22 mesh. The selected GAC was stored in 1% (w/w) HCl solution for one week at a 1:1 ratio of the GAC to the solution. The GACA was washed several times with the DI until the pH of the solution became 4–5 and was then dried in an oven at 60 °C.

2.3. Physical Properties

An image of the surface and the chemical composition was obtained using scanning electron microscopy (SEM) (Model: VEGA3 SBH, CZH) coupled with energy-dispersive X-ray spectrometry (EDX) (X-act, High Wycombe, UK). The surface area, pore size distribution, and pore volume for the GAC and GACA were calculated by the Brunauer–Emmett–Teller (BET) method (ASAP 2020, Micromeritics, Norcross, GA, USA). The zeta potentials (ξ) of the GAC and GACA were measured with a Zetasizer (NanoZS, Malvern, UK).

2.4. Batch Adsorption Tests

A series of batch tests were carried out to determine the removal efficiency (%) and uptake (mg/g) of phosphate at different initial solution pH values without and with pH adjustment, which was carried out by the addition of dilute HCl or NaOH at the desired time (0.17, 0.5, 1.3, 6, 12, and 24 h). Two sets of batch isotherm tests were initiated by adding 0.2 g of the GAC and the GACA into the 50 mL solution that contained from 1 to 50 mg/L of phosphate. The mixture was then gently rotated at 20 rpm for 48 h. The initial pH was first set to 4.0 ± 0.2 , 7.0 ± 0.2 , and 9.0 ± 0.2 , and the pH was adjusted for one set of batch isotherm tests. Other tests were also performed at various initial pH of 3, 4, 5, 6, 7, 8, and 9, to investigate the optimized pH and the effect of the solution pH on the phosphate removal. The adsorption rate of the phosphate was explored for 96 h by adding 2 g of the GAC and the GACA into 500 mL of a solution containing 15 mg/L of phosphate at pH values of 4.0 ± 0.2 , 7.0 ± 0.2 , and 9.0 ± 0.2 with or without pH adjustment. At predetermined time intervals, an aliquot of the sample was removed and stored in a refrigerator at 5 °C until analysis.

The phosphate uptake was calculated based on the following mass balance equation:

$$q_e = \frac{(C_0 - C_e)V}{M}, \quad (1)$$

where C_0 and C_e are the initial and final concentrations of the phosphate (mg/L), respectively. V and M are the volumes of the solution (L) and the mass of the GAC or GACA (g), respectively.

2.5. Fixed Column Tests

The pH effect on the phosphate was tested by comparing the breakthrough behavior for the GAC and the GACA using a fixed-bed column (3 cm in diameter, 7 cm in bed height, and 49.6 mL in bed volume) in the down-flow mode. The influent was set to 1 mg/L of phosphate and an initial pH of 7.2, operated with an empty bed contact time (EBCT) of 49.6 min and a superficial liquid velocity (SLV) of 0.09 m/h. The effluent was automatically collected and the pH was also measured to verify the pH shift during adsorption.

2.6. Chemical Analyses

The concentration of phosphate in the solution was analyzed using a portable water analyzer (Model: HS 1000 plus Humas, Daejeon, Korea) or ion chromatography (IC) (Model:ICS-100, Dionex, Sunnyvale, USA).

3. Results and Discussion

3.1. Characteristics of the GAC and GACA

Figure 1 and Table 1 show the images of the surface morphology and the element composition of the GAC and GACA from the SEM-EDX, respectively. After the HCl condition, the surface of the GACA (Figure 1b) was smoother than that of the GAC (Figure 1a), corresponding to the fact that the Al and Si had been removed from the GAC and the apparent concentration of the element composition approximately maintained the original values in Table 1. The BET surface area, micro and total pore volumes, and the mean pore sizes for the GAC and GACA are shown in Table 2. The values of the structural properties have been shifted by less than 5% after the HCl condition. Therefore, this negligible structural shift suggests that there were no effects on the physical properties of the phosphate adsorption capacity and the reaction rate.

Figure 1. Scanning electron microscope (SEM) image of granular activated carbon conditioned with deionized water (GAC) (a) and with hydrochloric acid (GACA) (b).

Table 1. Energy-dispersive X-ray (EDX) spectroscopy analysis of GAC and GACA.

Element	GAC		GAC-A	
	Apparent Concentration	wt. %	Apparent Concentration	wt. %
C	11.87	78.35	12.99	83.58
N	0.00	0.00	0.00	0.00
O	4.77	11.88	4.00	10.18
Al	0.95	2.83	-	-
Si	1.00	3.13	-	-
S	1.03	3.81	1.68	6.24

Table 2. Brunauer–Emmett–Teller (BET) analysis results of activated carbon.

Adsorbent	BET Surface Area (m ² /g)	Total Pore Volume (cm ³ /g)	Micropore Volume (cm ³ /g)	Average Pore Diameter (nm)
GAC	1038	0.54	0.47	2.09
GACA	991	0.52	0.45	2.10
Δ(%)	−4.51	−3.7	−4.2	

Negative indicates the value reduced for GACA.

3.2. Zeta Potential (ζ)

When the solid acted as an adsorbent in the solution, a region of the solid surface was dispersed with a positive or a negative charge due to the electrical inhomogeneity at the solid–solution interface, i.e., the electrical double layer. This can be defined as the zeta potential (ξ) that characterizes the electrical properties of the solid particles [4,20]. The zeta potential is one of the surface properties of the GAC that is used to understand the adsorption mechanism between the adsorbent and the ions, this being related to the surface charge. Figure 2 shows the zeta potential of the GAC and GACA at different solution pH values. Regardless of the type of adsorbent, the surface charge decreases with the increase in the solution pH, and the pH of the point of zero charge (pH_{pzc}) estimates to be 4.5 and 6.0 for the GAC and GACA, respectively. The pH_{pzc} of 4.5 for the GAC was similar to that of commercial GAC, which is measured at approximately 4–4.5 [21], and the increased pH_{pzc} was observed when the GAC was in the presence of the NaCl and FeCl₃ solutions [22,23]. Therefore, the increased pH_{pzc} could be explained by the presence of the pretreated hydrogen ions on the surface of the GAC, resulting in enhanced protonation.

Figure 2. Zeta potential as a function of pH for GAC and GACA.

3.3. Solution pH Effect

The effect of pH on phosphate adsorption was investigated at various initial pH ranging from 3 to 9. The removal efficiency and pH of the final solution are shown at the left and the right y-axis in Figure 3a, respectively. It should be noted that the initial pH of the solution was not fixed although the initial pH of the solution was adjusted to the initial pH at desired times during the experiment. At pH 3, the removal efficiency is only ~35% regardless of the GACs. With an increase in the pH, there is a difference, as described. For the GAC, removal efficiency of 70% is achieved at the acid condition. Since the initial pH is 7, the removal efficiency rapidly decreases with the increase of pH, finally being ~20% at an initial pH of 9.

Figure 3. Cont.

Figure 3. The removal efficiency of phosphate and final pH (a) and uptake and fraction of species of phosphate at initial pH of 3–9 (b).

The removal efficiency for the GACA is to be 65~70% at a pH of less than 7; this was comparable to that of the GAC, and ~55% efficiency can be reached, being reduced only by ~15% even at a pH of 9. Therefore, it could be observed that significant and mild phosphate removal efficiency occurred for the GAC and the GACA at base conditions. This could be explained by the effect of the solution pH. Based on the final pH of the solution during the experiment described in Figure 3 at the first y-axis, for the GAC, the initial pH of 4 and 5 is finally increased to 5.5 and 6.0, respectively, although the solution pH was adjusted, while the initial and final pH do not exhibit large differences at the base condition. For the GACA, the phenomena are reversed—the initial pH of 8 and 9 is finally decreased to 6.5 and 7.5, respectively. As a result, the optimized pH on the phosphate removal for the GAC or GACA can be determined at weak acid conditions, showing comparable values as those in Table S1, and the higher removal efficiency for the GACA at the base condition was due to the lower solution pH effect, which will be mentioned in Section 3.5.

The dotted line is the fraction of phosphate species (right y-axis) in Figure 3b with phosphate uptake (left y-axis). At a lower pH than 6.5 and a higher pH than pH 8, the species of $H_2PO_4^-$ and HPO_4^{2-} are dominated by over 80%, respectively. Ideally, when electrostatic force governs the interaction between the surface of a solid and the ions in solution, the two negative charges of the phosphate at pH 8 can interact more with the positively charged surface of the solid at the base condition. However, the contrary result is due to (1) the pH_{pzc} of the adsorbent and (2) the real solution pH. According to Figure 2, the pH_{pzc} and its values are 4.5 and 6.0 for the GAC and GACA, respectively. Therefore, electrostatic force results in increased phosphate adsorption for the GACA. However, at a pH of 3, the highest positive ξ , is revealed because the phosphate species of H_3PO_4 exists, and the removal efficiency is obtained at a pH of less than 4, which ideally attempts to interact with only a few H_3PO_4 .

3.4. Isotherm Tests

A series of batch isotherm tests were conducted at initial pH of 4, 7, and 9 with and without pH solution adjustment. Among several mathematical models to fit the experimental data of the adsorption isotherms, such as Elovich [24], Themkin [25], Langmuir [13], and Freundlich [14], the Langmuir and Freundlich isotherm equations are widely used and follow below.

$$q_e = \frac{bQ_m C_e}{1 + bC_e}, \quad (2)$$

where q_e and Q_m are the equilibrium uptake (mg/g) and the maximum phosphate capacity (mg/g) in the solid phase, respectively. C_e is the equilibrium concentration of phosphate in the aqueous phase (mg/L), and b is the Langmuir affinity coefficient related to the sorption (binding) energy between the sorbent and sorbate.

$$q_e = k_f C^{1/n}, \quad (3)$$

where q_e is the C is the aqueous phosphate concentration at equilibrium, k_f is the adsorption capacity, and $1/n$ is the sorption intensity.

Briefly, certain concepts describe both adsorption isotherms. The shapes of the adsorption isotherms were classified into four main groups, such as L, S, H, and C [26]. According to the classification, all of the isotherms displayed the L-curve pattern that is called the Langmuir isotherm, indicating the flat adsorption of the molecules on the surface and lack of strong competition during the adsorption process [26,27]. As shown in Equations (2) and (3), the Freundlich equation is expressed by an exponential equation assuming that the uptake of the adsorbate increases with the increasing adsorbate concentration [27]. The assumption for Langmuir and Freundlich is the mono and multi-adsorption layer, and this shows better fit data at low and high experimental concentrations, respectively [28].

Figures 4 and 5 are the nonlinear Langmuir and Freundlich isotherm models, respectively, and the parameters calculated are listed in Table 3. Based on the coefficient of determination (R^2), it is hard to determine which is a better fit for both isotherm equations. Among the three pH experiments, pH 7 shows less difference of the Q_m obtained to over 3 mg/g than those of pH 4 and 9 for both the GAC and the GACA, corresponding to approximately less pH shift around 6–7. However, the value of Q_m is clearly shown to be twice as high for the GAC at the acid condition and for the GACA at the base condition, respectively. This result has a similar tendency to that in Figure 3 at the base condition but is the opposite at the acid condition. This is because of sufficient concentration of the phosphate compared with Figure 3, describing that the removal efficiency does not show significant differences at the acid condition for the GAC and GACA. Additionally, the pH adjustment at the acid condition does not have a significant effect on the Q_m of phosphate for the GAC and GACA, whereas Q_m decreases from 3.96 to 2.59 mg/g (35% reduction) for the GACA at the base condition. With regard to the electrostatic force between the surface charge of the GAC and phosphate species at the acid condition, the higher Q_m for the GAC is estimated to be the shift species from H_2PO_4^- to HPO_4^{2-} , which is possible due to the Donnan effect [29]. At a pH of 9, the higher Q_m for the GACA is attributed to the maintenance of the solution at a pH of approximately 7 during the experiment, while the pH increases to 8 and 9 for the GAC. The reduction from 3.96 to 2.56 mg/g will be explained in Section 3.5.

The values of Q_m and k_f show the same trends in all of the experimental conditions. The value of n indicates the adsorption process as follows: (a) linear adsorption at $n = 1$ (b) chemical process $n < 1$, physical process $n > 1$ [30]. n within the range of 1–10 is considered to be good adsorption [31]. Table 3 shows that all the values of n are greater than 1 and are in the range of 1.86–4.10. The physical adsorption process would have dominated the phosphate adsorption regardless of the pH of the solution.

Figure 4. Langmuir isotherm for GAC and GACA with/without pH adjustment at initial pH of 4 (a), 7 (b), and 9 (c).

Figure 5. Freundlich isotherm for GAC and GACA with/without pH adjustment at initial pH of 4 (a), 7 (b), and 9 (c).

Table 3. Values of the Langmuir and Freundlich parameters for nonlinear equations.

pH	Condition	Langmuir				Freundlich			
		$Q_{\max}$ (mg/g)	b (L/mg)	ΔG° (kJ/mol)	R^2	k_f	$1/n$	n	R^2
4	GAC-wo	3.36 (0.196) *	0.419 (0.107)	−25.8	0.979	1.10 (0.130)	0.329 (0.0401)	3.04	0.976
	GAC-w	3.94 (0.457)	0.134 (0.0461)	−23.0	0.967	0.722 (0.127)	0.446 (0.0583)	2.24	0.972
	GACA-wo	1.53 (0.109)	0.598 (0.217)	−26.7	0.955	0.643 (0.164)	0.244 (0.0843)	4.10	0.848
	GACA-w	1.7 (0.118)	0.438 (0.141)	−25.9	0.963	0.640 (0.173)	0.268 (0.0893)	3.73	0.853
7	GAC-wo	3.59 (0.715)	0.0732 (0.0353)	−21.6	0.946	0.401 (0.0994)	0.539 (0.0783)	1.86	0.964
	GAC-w	3.00 (0.172)	0.296 (0.0367)	−25.0	0.986	0.790 (0.130)	0.407 (0.0606)	2.46	0.969
	GACA-wo	3.71 (0.566)	0.237 (0.136)	−24.4	0.911	0.857 (0.172)	0.420 (0.0671)	2.38	0.959
	GACA-w	3.77 (0.129)	0.398 (0.0564)	−25.7	0.993	1.23 (0.192)	0.328 (0.0543)	3.04	0.955
9	GAC-wo	1.29 (0.240)	0.406 (0.341)	−25.8	0.783	0.441 (0.190)	0.301 (0.139)	3.33	0.736
	GAC-w	1.46 (0.284)	0.284 (0.227)	−24.9	0.804	0.385 (0.163)	0.373 (0.134)	2.68	0.815
	GACA-wo	3.96 (0.173)	0.291 (0.0476)	−24.9	0.991	1.11 (0.192)	0.363 (0.0597)	2.75	0.954
	GACA-w	2.59 (0.159)	0.543 (0.148)	−26.5	0.970	0.972 (0.214)	0.284 (0.0749)	3.52	0.891

* indicate stand error using SigmaPlot 12.5.

Although linearization from Equations (2) and (3) was attempted to define the higher model fitting using Equations (4) and (5) [32], none of the cases obtained relatively higher values (data not shown).

$$\frac{1}{q_e} = \frac{1}{b_L} \frac{q_e}{C_e} + q_{mL} \quad (4)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e. \quad (5)$$

This result clearly confirms that the transformation of the nonlinear equation to linear has a bias [27].

From the Langmuir coefficient (b , L/mg), the adsorption thermodynamics can be estimated using the following Van 't Hoof Equations (6) and (7) [33,34]:

$$\Delta G^\circ = -RT \ln K_e \quad (6)$$

$$K_e = \frac{1000 \times b \times M \times c^\circ}{\gamma}, \quad (7)$$

where ΔG° is Gibbs energy change (kJ/mol), R is the universal gas constant (8.314 J/mol), T is the absolute temperature (K), K_e is thermodynamic constant (dimensionless), M is the molar mass of the adsorbate, c° is the standard concentration of adsorbate (1 mol/L), and γ is the dimensionless coefficient of activity, which is usually assumed to be (1). The value of ΔG° in Table 3 is negative for all cases and ranges from −21.6 to −26.7 kJ/mol. Therefore, adsorption is a spontaneous process.

3.5. Kinetic

3.5.1. Removal Efficiency

The phosphate removal efficiency for 96 h is drawn at different initial solution pH in Figure 6. The tendency of removal efficiency (%) is strongly associated with the isotherm equations (Q_m) except for the GAC-w at pH 4 and the GACA-w at pH 9. At the acid condition, GAC-wo obtains ~70% removal efficiency, this being the highest value in the current experimental condition, while others finally reach ~60%. For the GAC-w, the removal behavior is almost the same as that of the GAC-wo until 6 h, and it decreases by 10% to ~60% after 6 h, corresponding to desorption. At a pH of 7, 60% removal is obtained, except for GAC-wo, indicating that the pH effect is slight. At the base condition, regardless of the pH adjustment, the GAC shows only 40% removal efficiency, this being the lowest. Both GACAs obtain ~60% removal efficiency but this is finally decreased to 40% after 6 h for the GACA-w; this is also likely for the GAC-w at pH 4.

Figure 6. Phosphate removal efficiency (%) (left y-axis) and removal efficiency ratio (R_t/R_0) (right y-axis) as a function of time (h) at initial pH of 4 (a), 7 (b), and 9 (c).

Another drawing was added to Figure 6 with the right y-axis calculating the ratio of removal efficiency at equilibrium (R_e) to removal efficiency at a certain time (R_t). The red solid line can indicate the achievement of 90% adsorption per total adsorption. A period of 9 h is sufficient to reach 90% removal for the GACA regardless of the initial pH and the pH adjustment, while the GAC requires 20 and 48 h at pH 7 and 9, respectively. The removal efficiency shapes with rapid and slow slopes at the beginning and later has been accounted for by Choi et al. (2007) [35], who proposed the two-site irreversible sorption model at the exterior site by instantaneous occurrence and at the interior site by intraparticle diffusion.

3.5.2. PFO and PSO

The PFO and PSO models were used to calculate the variables. Equations (8) and (9) were used for the modeling of the nonlinear PFO and PSO shown in Figures 7 and 8, and the calculated variables are listed in Table 4.

$$q_t = q_e \left(1 - e^{-K_1 t}\right) \quad (8)$$

$$q_t = \frac{K_2 q_e^2 t}{1 + K_2 q_e t}. \quad (9)$$

Based on Table 4 and Figures 7 and 8, the mean of R^2 obtains 0.941, ranging from 0.863–0.995 for the GAC and 0.980, ranging from 0.940–0.996 for the GACA. This indicates that the PSO accomplishes a higher R^2 than the PFO in all the experimental conditions except for the GACA-w at pH 9. It should be considered that the PFO does not express the time of 3–9 h in Figure 7, whereas the mild curve line is included at the PSO. In general, the PFO and PSO were related to physisorption and chemisorption, respectively [16,36].

The rate constants, K_1 and K_2 , can be compared to the reaction rate. Due to the following observation that a higher K was associated with a higher q_e at pH 7 and 9, the relationship was questionable at pH 4. To determine the value of K clearly, an attempt was made to linearize Equations (8) and (9) to the following Equations (10) and (11), respectively:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (10)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t. \quad (11)$$

Figure 7. Nonlinear pseudo-first-order (PFO) kinetic for GAC and GACA at initial pH of 4 (a), 7 (b), and 9 (c) (red lines indicate the phosphate desorption experiment).

Figure 8. Nonlinear pseudo-second-order (PSO) kinetic for GAC and GACA at initial pH of 4 (a), 7 (b), and 9 (c) (red lines indicate the phosphate desorption experiment).

Table 4. Variables of nonlinear PFO and PSO.

Model	Parameter	pH 4				pH 7				pH 9			
		GAC-wo	GAC-w	GACA-wo	GACA-w	GAC-wo	GAC-w	GACA-wo	GACA-w	GAC-wo	GAC-w	GACA-wo	GACA-w
PFO	K_1	1.06 (0.169) *	1.41 (0.168)	1.91 (0.329)	1.91 (0.326)	1.05 (0.133)	0.63 (0.127)	1.76 (0.218)	1.85 (0.091)	0.851 (0.209)	0.796 (0.173)	1.75 (0.237)	2.25 (0.433)
	q_e	2.64 (0.077)	2.39 (0.048)	2.25 (0.058)	2.24 (0.057)	2.03 (0.048)	2.29 (0.098)	2.36 (0.045)	2.44 (0.018)	1.42 (0.068)	1.46 (0.065)	2.37 (0.049)	2.1 (0.055)
	R^2	0.942	0.969	0.943	0.944	0.963	0.907	0.969	0.995	0.863	0.889	0.963	0.939
PSO	K_2	0.616 (0.066)	1.07 (0.189)	1.36 (0.195)	1.4 (0.193)	0.738 (0.078)	0.358 (0.090)	1.23 (0.064)	1.43 (0.129)	0.811 (0.201)	0.727 (0.108)	1.23 (0.149)	2.94 (1.569)
	q_e	2.78 (0.040)	2.48 (0.050)	2.35 (0.035)	2.34 (0.033)	2.15 (0.031)	2.48 (0.019)	2.46 (0.071)	2.53 (0.022)	1.52 (0.055)	1.57 (0.023)	2.47 (0.048)	2.13 (0.082)
	R^2	0.989	0.974	0.985	0.987	0.989	0.969	0.996	0.995	0.94	0.958	0.994	0.9

* indicate stand error using SigmaPlot 12.5.

The linear PFO and PSO are drawn in Figures S1 and S2. As shown in Figure S1, it would be difficult to prepare one linear line. Therefore, the linear regression was separated into two parts [16]. Table S2 lists the parameters calculated from the linear PFO at 0–96 h and 0–6 h, in addition to those from the linear PSO. Although the separation of the PFO improves the R^2 , the values of q_e appear to be inexplicable, and R^2 is still poor. By contrast, the linearization of the PSO accomplishes at least 0.998 up to 1.00 (0.99996) of R^2 , which is higher than that of the nonlinear PSO. Furthermore, the desorption process was obviously distinguished with the negative K_2 for the GAC-w at pH 4 and the GACA-w at pH 9. Additionally, the order of K_2 is very similar to the 0.9 ratios of R_t/R_e in Figure 6. Based on K_2 , it could be concluded that the acid condition (pH 4) achieves an increased adsorption rate, and the pH adjustment (decreasing solution pH) assists in accelerating the adsorption reaction.

3.5.3. Intraparticle Diffusion

In the solid–solution adsorption process, the adsorbate (target contaminant) was diffused through external mass transfer (boundary-layer diffusion) and intraparticle diffusion (mass transfer through the pores) [37]. To determine the late-limit step, a linear model was recommended. The intraparticle diffusion model was developed by Weber and Morris (1963) [38], followed by Equation (12),

$$q_t = K_i t^{0.5} + C, \quad (12)$$

where q_t is the uptake of phosphate at time t (mg/g), K_i is the intraparticle diffusion constant (mg/g hr^{0.5}), and C is the arbitrary constant representing the thickness (or resistance) of the boundary layer [37,39]. When applied in previous studies, intraparticle diffusion was described by separating the whole segment into one [36,40], two [21,41], or three [37,42]. Various interpretations have shown that the multiple adsorption processes are involved in the overall adsorption rate [43]. In Figure 9, it can be seen that there are two main linear segments. The multiple adsorption process takes into consideration that at the beginning of adsorption, the external mass transfer (film diffusion) is governed and, later, the intraparticle diffusion leads to the adsorption rate. According to Table 5, the effect of pH adjustment is not significant, and at values of 7 and 9, the K_i for the GACA is higher than that for the GAC, indicating that the presence of hydroxide in the solution decreases the external mass transfer.

Figure 9. Intraparticle diffusion plot for GAC and GACA at initial of pH 4 (a), 7 (b), and 9 (c) (solid line: regression from 0 to 6 h).

Table 5. Intraparticle diffusion parameters calculated from 0 h to 6 h.

Parameter	pH 4				pH 7				pH 9			
	GAC-wo	GAC-w	GACA-wo	GACA-w	GAC-wo	GAC-w	GACA-wo	GACA-w	GAC-wo	GAC-w	GACA-wo	GACA-w
K_i	0.966	0.997	0.805	0.801	0.778	0.760	0.877	0.960	0.470	0.493	0.863	0.920
C	0.480	0.448	0.594	0.599	0.328	0.306	0.586	0.614	0.256	0.237	0.602	0.560
R^2	0.856	0.875	0.735	0.729	0.856	0.895	0.761	0.762	0.835	0.862	0.748	0.766

3.6. Fixed Column Tests

Fixed column tests were carried out to investigate the effect of the pH of the GAC by determining the phosphate breakthrough profiles. Figure 10 shows the phosphate and the pH of the effluent solution for the DI and the phosphate at the left (solid line) and the right (dash) of the y-axis, respectively. The breakthrough occurs after 580 and 720 BV, and the effluent concentration reaches that of the influent at 812 and 951 BV for the GAC and the GACA, respectively, indicating a 24% extension of operation for the GACA. In addition, the phosphate adsorption capacity of 1.45 and 1.76 mg/g is calculated to 1.45 and 1.76 mg/g for the GAC and GACA, respectively, which improves 21% which is similar with the BV increase. These continuous experimental results reinforce the batch isotherm and kinetic results and clearly confirm that the solution pH determines the phosphate adsorption capacity. The effluent solution pH initiated at 7.2 ± 0.2 shows significantly different behavior. For the GAC, the solution pH is maintained at approximately 7. However, the initial pH was sharply decreased to 4.7 and gradually recovered to the initial pH of the GACA. The additional pH profiles included a condition for only the DI without phosphate, exhibiting a very similar profile in the presence of phosphate. Therefore, the rapid decrease of pH at the beginning of the operation could be attributed to the desorption of the hydrogen from solid to liquid and not because the ion exchange process replaces hydrogen ions with phosphate. Consequently, it is confirmed that the extended BV operation for the GACA is due to the extended pH_{pzc} and lower solution pH.

Figure 10. Phosphate breakthrough profiles for GAC and GACA and the effluent solution pH for deionized water (DI) and phosphate.

4. Conclusions

In this study, the effect of hydrogen ions on the GAC and solution was tested on phosphate adsorption. The primary findings are summarized as follows:

- The HCl condition for the GAC shifted the pH_{pzc} from 4.5 to 6, but the modification of other physical properties, such as total surface area, pore volume, and pore size distribution, was negligible;
- The optimized solution pH of the phosphate removal using GAC was determined at the weak acid condition by electrostatic interaction and an increase of the pH_{pzc} from 4.5 to 6 for the GAC, extending the segment to a neutral pH;
- At the base condition, the positive surface charge of the GAC, in spite of the species of HPO_4^{2-} and PO_4^{3-} , led to a rapid decrease in phosphate removal, and the hydrogen

ions, excluded from the GAC in solution, deferred the reduction rate. Additionally, desorption of phosphate occurred with the increase of the solution pH;

- The PSO kinetic rate was more suitable than that of the PFO to describe the chemisorption of phosphate, and the rate constant (K_2) was relatively faster at the acid condition than at other solution pH values;
- The fixed column tests confirmed that the phosphate was removed by adsorption because the hydrogen ion release onto the surface of the GAC was not due to an ion exchange process.

Supplementary Materials: The following are available online at <https://www.mdpi.com/2076-3417/11/6/2777/s1>, Table S1: Experiment and optimized solution pH for the removal of phosphate at various adsorbents, Table S2: Variables of linear PFO and PSO, Figure S1: Linear PFO kinetic for GAC and GACA at initial pH of 4(a), 7(b), and 9(c).

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