Sinopfbd, 2022; 7(1): 22-40 **https://doi.org/10.33484/sinopfbd.1013083**

Sinop Üniversitesi Fen Bilimleri Dergisi
Sinop Uni J Nat Sci

ISSN: 2536-4383
E-ISSN: 2564-4383

https://dergipark.org.tr/tr/pub/sinopfbd

Using Walnut Shell Based Activated Carbon for the Efficient Removal of Phosphate from Aqueous Solutions

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How to cite: Arslan, A., & Zeybek, Ş. (2022). Using walnut shell based activated carbon for the efficient removal of phosphate from aqueous solutions. *Sinop Üniversitesi Fen Bilimleri Dergisi, 7*(1), 22-40. https://doi.org/10.33484/sinopfbd.1013083

Research Article

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Received: 21.10.2021
Accepted: 23.02.2022

Abstract

In this study, walnut shell, which is abundant in Turkey and low-cost biomass waste, has been used for activated carbon production and phosphate removal from aqueous solutions with the produced activated carbon was investigated. $ZnCl_2$ was used to prepare adsorbent by chemical activation method. Produced activated carbons were characterized by moisture content, ash content, iodine number, Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM) analyses. The specific surface area was calculated as 415.433 m^2/g from the isotherms using the Brunauer-Emmett-Teller (BET) equation. The effects of pH, adsorbent amount, agitation speed and temperature were investigated. Different adsorption isotherm models were applied. It was found that the Langmuir isotherm provided the best fit for the experimental data. In the pseudo- second order kinetic model, the values found theoretically ($q_{e,cal}$) were very similar to those determined by experiments ($q_{e,exp}$). The results showed that the adsorption of phosphate on the WSAC fits the pseudo- second order kinetic model. According to the thermodynamics analysis, phosphate adsorption on WSAC was endothermic under the studied conditions.

Keywords: Phosphate, activated carbon, adsorption isotherms, walnut shell.

Sulu Çözeltilerden Etkin Fosfat Giderimi için Ceviz Kabuğu Bazlı Aktif Karbon Kullanımı

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Öz

Bu çalışmada Türkiye'de bol miktarda bulunan ve düşük maliyetli biyokütle atığı olan ceviz kabuğu aktif karbon üretimi için kullanılmıştır ve üretilen aktif karbon ile sulu çözeltilerden fosfat uzaklaştırılması araştırılmıştır. $ZnCl_2$ kimyasal aktivasyon yöntemi ile adsorbent hazırlamak için kullanılmıştır. Üretilen aktif karbonlar nem içeriği, kül içeriği, iyot sayısı, taramalı elektron mikroskopisi (SEM) ve Fourier transform kızılötesi spektroskopi (FT-IR) analizleri ile karakterize edilmiştir. Brunauer-Emmett-Teller (BET) denklemi kullanılarak aktif karbonun spesifik yüzey alanı 415.433 m^2/g olarak hesaplanmıştır. pH, adsorbent miktarı, karıştırma hızı ve sıcaklığın etkileri araştırılmıştır. Adsorpsiyon izotermi farklı izoterm modelleri ile analiz edilmiştir. Langmuir izoterminin deneysel veriler ile uyumlu olduğu görülmüştür. Sözde ikinci dereceden kinetik modelde, teorik olarak bulunan değerler ($q_{e,cal}$) deneylerle belirlenenlere çok yakındır ($q_{e,exp}$). Sonuçlar, WSAC üzerindeki fosfat adsorpsiyonunun sözde ikinci derece kinetik modele uyduğunu göstermiştir. Termodinamik analize göre, WSAC'deki fosfat adsorpsiyonu çalışılan koşullarda endotermiktir.

Anahtar Kelimeler: Fosfat, aktif karbon, adsorpsiyon izotermleri, ceviz kabuğu

Introduction

The abatement of elevated phosphorus levels in water bodies is of momentous urgency from the aspect of environmental management, due to its adverse impact on the aquatic ecosystems and human health [1]. In order to remove phosphorus from water and wastewaters, the state-of-the-art treatment methods can be physical, chemical and biological processes [2]. Precipitation as a chemical method is widely used for phosphorus removal [3]. Although chemical precipitation is an effective method, it causes problems such as the complexity of the control system, the use of chemical substances, the excess amount of phosphate sludge formed in the precipitation and disposal of the sludge [4]. Biological processes are lower cost alternatives to chemical treatment of wastewater. Biological phosphorous removal is based on stress-induced activity of the microorganisms for excessive adsorption than usual requirement for microbial growth [5]. Up to 97% of total phosphorus can be treated with advanced biological treatment, but difficulties may arise in operating the process [6]. In addition to the high cost of biological and physical-chemical methods in phosphorus treatment, difficult operating conditions limit the use of these methods. Therefore, it is crucial to use reliable and economical technologies for removing phosphorus from wastewater. Example methods can be stated as adsorption, ion exchange, membrane, electrocoagulation, reverse osmosis, and electrodialysis [7]. For phosphate removal, adsorption is evaluated as a useful and cost-effective method, considering readily available materials at hand [8-10]. Especially in studies with calcium carbonate, calcium kaolinite, red mud, half-burnt dolomite, fly ash, clinker, zeolite, pumice stone, titanium dioxide and coconut shell, very successful results have been obtained in removing phosphate from wastewater [11]. Activated carbon can be defined as an adsorbent material for which surface area and pore volume are highly improved by applying activation process to materials that contain high carbon [12]. Activated carbon can be produced from several raw materials containing low inorganic material and high carbon. In addition to wood, coal and coconut, which are commonly used substrates in activated carbon production, many agricultural wastes and products are also utilized as activated carbon materials for removing some compounds (both organic and inorganic) in liquid and gas phase [13]. Activated carbon contains carbon component within the range of 85-95% and other elements, for example hydrogen, oxygen, nitrogen, and sulfur. Typical activated carbon's elemental composition may be comprised of 88% C, 6-7% O, 0.5% N, 0.5% H and 1% S. The oxygen content of activated carbon may vary between 1-20% depending on the preparation of the substance [14]. Activated carbon's physicochemical properties can be changed by type of raw material used as well as activation conditions [15]. The application of various thermal and chemical treatments improves the pore structure of the raw materials and allows the formation of micropores [16].

Cost-effectiveness, availability, and unique content (high carbon and low inorganic) are the reason for preferring agricultural waste usage in activated carbon production in recent years [17]. Vegetative waste usage for activated carbon production makes an important contribution to the solution of environmental problems [18]. Within the sustainable environment approach, it is aimed to evaluate walnut shells from agricultural wastes formed in our country and to obtain an adsorbent that can be used as an alternative in the removal of phosphate, which is an important pollutant. Phosphate removal with different adsorbents has been studied in the literature. However, while the removal applications of pollutants such as dye and chromium with activated carbon obtained from walnut shell are more, phosphate removal applications are very few. This study aims to investigate whether activated carbon prepared from walnut shell is effective for phosphate removal from aqueous solution. Several important experimental conditions such as pH, adsorbent amount, agitation speed and temperature and also isotherm models, adsorption kinetic and thermodynamic were investigated in the present study.

Materials and Methods

Materials

Walnut shell (WS) was gathered as household waste. The composition of the WS was 47.22% C, 6.12% H, 1.33% N, 1.05% ash and 3.37% moisture. Different chemicals were used in the experimental stages of the study. For the activation of the raw materials, zinc chloride ($ZnCl_2$, Merck) was applied as activating agent. KH_2PO_4 (Merck) was utilized in the preparation of the stock phosphate solution. For pH adjustment NaOH (Merck) and H_2SO_4 (Merck) were used. During analysis of orthophosphate, $(NH_4)_6Mo_7O_{24}.4H_2O$ (Merck), $SnCl_2$ (Merck), $C_3H_8O_3$ (Merck) and phenolphthalein (Merck) were used. During the analysis of iodine number, concentrated hydrochloric acid (HCl, Merck), sodium thiosulfate ($Na_2S_2O_3.5H_2O$, Merck), sodium carbonate (Na_2CO_3, Merck), iodine (I_2, Merck), potassium iodide (KI, Merck) and starch (Merck) were used according to the standard procedure. All chemicals used were of analytical grade.

Equipments

Drying oven (NÜVE model FN 500), jaw crusher (ÜNAL model 100 x 100 mm), shaking bath (NÜVE model ST 30), laboratory type chamber furnace (PROTHERM), ash furnace (BLULAB), pH meter (Thermo Scientific ORION STAR model A111), magnetic stirrer (MTOPS MS300 HS) and spectrophotometer (HACH DR 5000) were used in the experiments and analyses.

Methods

The surface morphology of the raw shells and activated carbons was investigated with SEM (JEOL JSM-6060). Surface functional groups, or structure characterization of the raw shells and activated carbons, were analyzed through the FTIR transmission spectra recorded by using a FTIR spectrophotometer (FTIR-Bruker Alpha) in the wave number range of 4000-400 1/cm. BET analysis (Quantachrome Quadrosorb SI) was performed at Yıldız Technical University Science and Technology Application and Research Center. For ash and moisture contents, 1 g of activated carbon samples were weighed with an analytical balance. By placing the samples in the balanced crucibles, the ash content was determined by burning them at 650°C for 10 hours in furnace, and the moisture content was determined by drying them at 105°C for 24 hours in oven. To determine the iodine number, 1 g of activated carbon sample placed in a 250 mL titration flask was soaked with 10 mL of 5% HCl solution and then boiled for 30 seconds, later it was allowed to cool. 100 mL of stock iodine solution was added, and homogenization of the mixture was achieved using magnetic stirrer. It was then filtered through a filter paper and titrated with thiosulfate solution. After a pale-yellow color was obtained, titration was carried on with adding 2 mL of starch into the filtrate. The amount of iodine in the filtrate was calculated from the amount of thiosulfate spent up to the turning point [19]. Total phosphorus analyses were performed in accordance with the tin chloride method (4500-P D.Stannous Chloride Method) given in Standard Methods [20].

Synthesis of WSAC

The walnut shells were first washed several times with tap water to remove foreign particles. After, the shells were washed with distilled water and then dried in an oven at 105°C, for 12 hours. The shells dried in the oven were then crushed to the size of 1-3 mm using a 100x100 mm jaw crusher. For activation, the crushed shells were immersed in $ZnCl_2$ solution (30%) with the impregnation ratio of 1:1 and then stirred in a shaking bath at 80°C and 125 rpm, for 4 hours. The samples removed from the shaking bath were filtered through coarse filter paper and dried in the oven at 105°C, for 12 hours. Activated shells were carbonized in the ash furnace at 600°C, under nitrogen gas flow of 250 mL/min, for 60 min. After the carbonization processes, the activated carbon samples were washed with distilled water until pH 6-6.5 to remove the excessive chemicals used for activation. The ultimate samples were dried in the oven at 105°C, for 12 hours.

Characterization of WSAC

Synthesized activated carbon was characterized by several analysis which were moisture and ash content, iodine number, SEM, FT-IR and BET. The moisture and ash contents and also iodine number of the produced adsorbent was compared with similar studies in literature (Table 1). The BET specific surface area was calculated to be 415.433 $m^2.g^{-1}$. It has been determined that WSAC has a microporous structure.

Table 1. *Studies about activated carbon production and characteristics*

Shell	Activating Agent	Ash Content (%)	Moisture Content (%)	Iodine Number (mg/g)	References
Hazelnut Shell	$ZnCl_2$	1.23	11.02	-	[21]
Almond Shell Walnut Shell	$ZnCl_2$ H_3PO_4	-	-	A-S: 256 W-S: 958	[22]
Walnut Shell	$ZnCl_2$	-	-	400	[15]
Walnut Shell	KOH	-	-	303	[23]
Chestnut Shell Hazelnut Shell	$ZnCl_2$	-	-	C-S:785 H-S: 276	[24]
Peanut Shell	$ZnCl_2$	8.20	9.00	1114	[25]
Chestnut Shell	$ZnCl_2$	-	-	917	[26]
Hazelnut Shell	H_3PO_4	5.32	-	397.7	[27]
Hazelnut Shell	$ZnCl_2$	-	1.97	737	[28]
Hazelnut Shell	H_3BO_3 K_2CO_3	2.92	7.41	1009.71	[29]
Walnut Shell	**$ZnCl_2$**	**1.81**	**1.03**	**449**	**Current Study**

In the study, performed by [30], activated carbon was produced from pecans. Activated carbons were characterized by its pore structure, FTIR analysis and acidic surface groups. The raw pecans were reduced to a certain size and their activation was carried out with H_3PO_4 solution (30%). It was observed that the pore structure of the activated carbon was more improved at higher activation temperatures and 1130 m^2/g of BET surface area was achieved. [31] applied vacuum chemical activation to produce activated carbon from walnut shells. The highest surface area of the sample obtained at $ZnCl_2$:walnut shell ratio of 2:1 and activation temperature of 450°C was 1800 m^2/g. And it was stated that these activated carbon samples were good adsorbents for removing some organic pollutants in water. In their study with two different impregnation ratio, [28] concluded that the iodine number and the BET surface area of the activated carbon with a walnut shell: $ZnCl_2$ impregnation ratio of 1:1 were 760 mg/g and 803 m^2/g, respectively. On the other hand, the iodine number and the BET surface area of the sample with 1:0.5 impregnation ratio were 737 mg/g and 780 m^2/g, respectively. In the study performed by [32], activated carbon had 1452 m^2/g surface area and 1.970 nm average pore diameter which was obtained from 60 min-carbonization of 5 g walnut shell activated with $ZnCl_2$ with the impregnation ratio of 1:1.

SEM

In Figure 1a and b, SEM images softly are given to show the surface morphology of the raw walnut shell and the activated carbon. When the images are examined in Figure 1a, it is seen that the surface of the raw walnut shell was smooth and slightly indented. But then, in Figure 1b, it was obvious that after activation/carbonization, there occurred small pores inside the pores even if its inner walls seemed smooth and also the surface area was increased due to the formation of apparent indentations.

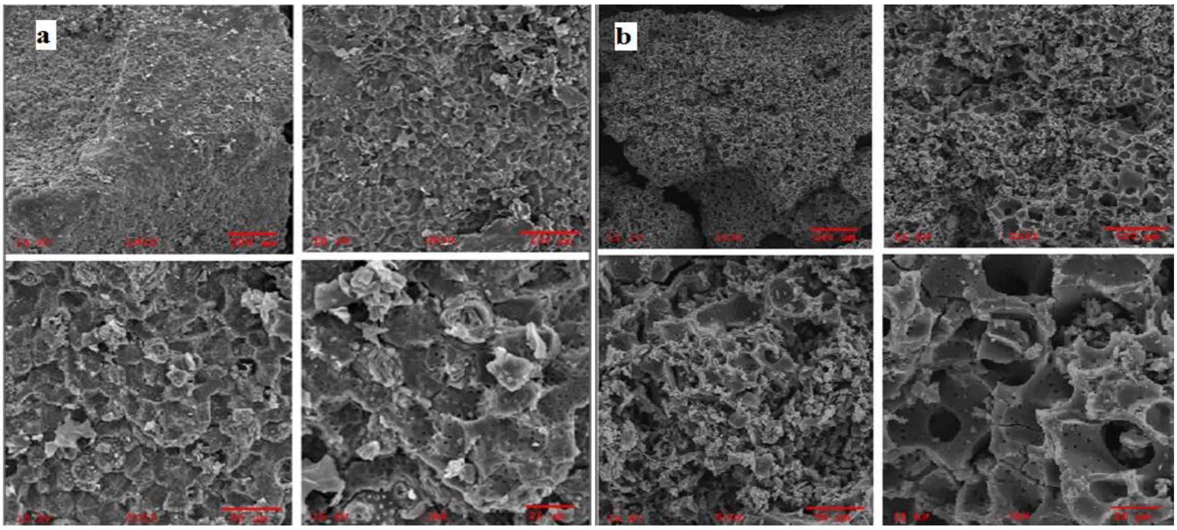

Figure 1. *(a) SEM images of walnut shell (100x, 250x, 500x, 1kx) (b) SEM images of activated carbon (100x, 250x, 500x, 1kx)*

FTIR

In Figure 2, the FTIR analysis is given, and it may be concluded that the apparent band intensity of organic molecules was weakened because of activation and the cellulosic organic structure of the walnut shell became disrupted.

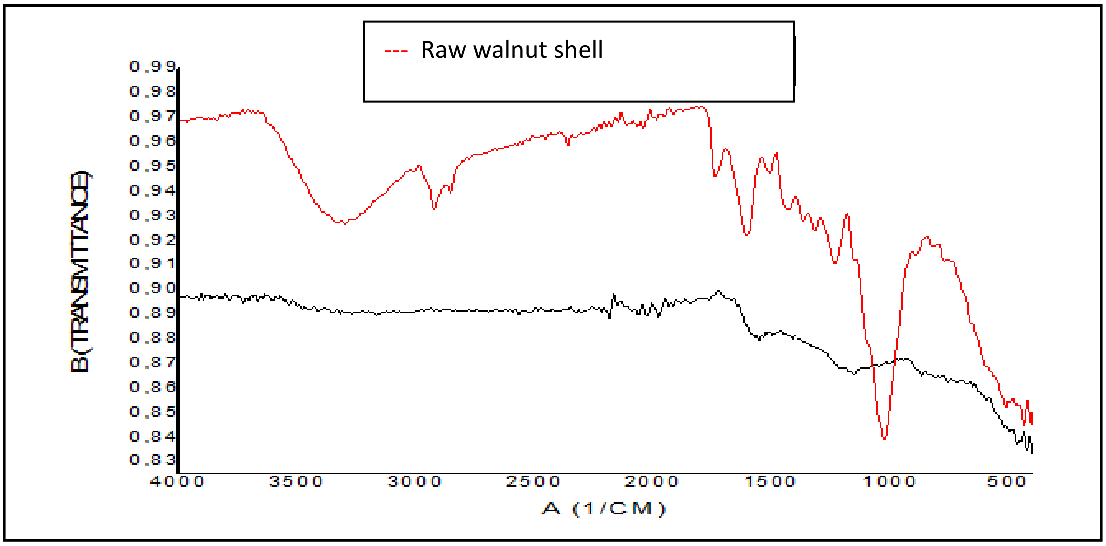

Figure 2. *FT-IR spectra of the acivated carbon samples and walnut shell*

Adsorption Experiments

In the experiments, the effects of pH, adsorbent amount, agitation speed and temperature were investigated on the adsorption process. The batch adsorption experiments were conducted using 100 mL synthetic phosphate solution of different initial concentrations (10, 20 and 30 mg/L). 0.5 g WSAC was added in 250 mL Erlenmeyer flasks. The flasks were placed in a shaker at a constant speed of 150 rpm and 25°C for 150 min. By determining the residual phosphate amount in the solution after adsorption, the adsorption capacity values (qe) and phosphate removal efficiencies were calculated according to the following equations:

$$q_e = \frac{(C_o\text{-}C_e)\ V}{M} \quad (1)$$

$$\text{Efficiency (\%)} = (C_0\text{-}C_e)/C_0 \times 100 \quad (2)$$

Where C_0 and C_e (mg/L) are the initial and equilibrium concentrations of phosphorus respectively. M (g) is the mass of the adsorbent and V(L) is the volume of the solution.

Results and Discussion

Effect of pH

For evaluating the effect of initial pH; the adsorption studies were conducted in the pH range of 2-10, with 0.5 g of adsorbent and 20 mg/L initial phosphate concentration, at 25°C and 150 rpm, for 150 min. The results are given in Figure 3.

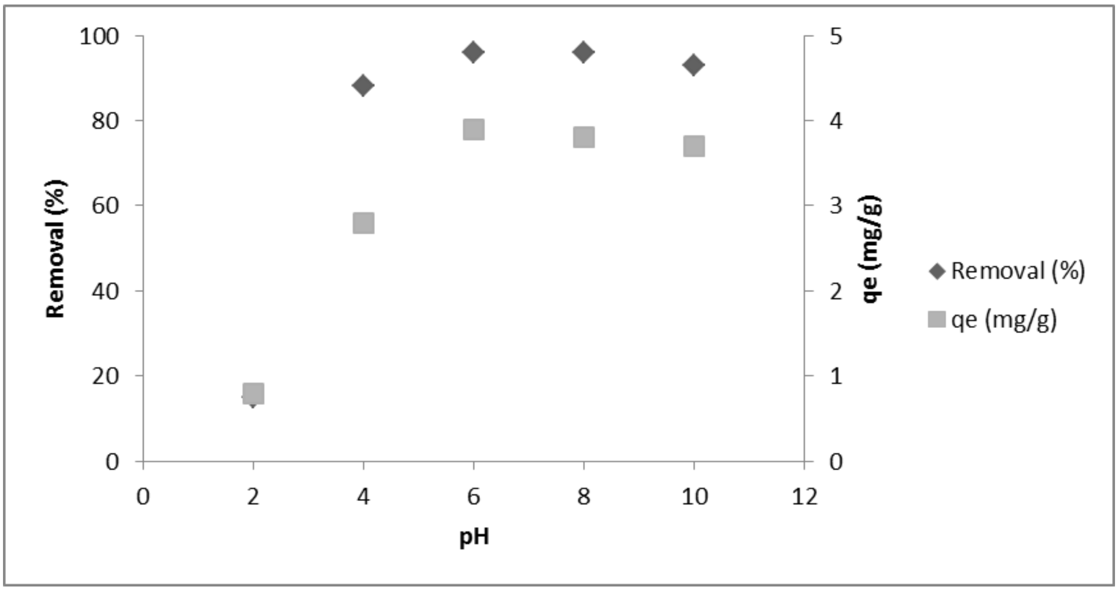

Figure 3. *The adsorption capacities and removal efficiencies at different pH (Co=20 mg/L, 150 min, 0.5 g adsorbent/100 mL, 150 rpm, 25°C)*

According to the Figure3, the phosphate removal efficiency tended to increase with the increment of pH in the range of 4-7. Because of the insignificant difference between the phosphate removal efficiencies of particular pH levels, the studies for other parameters were conducted at 6.5, original pH of the solution. Additionally, the highest adsorption capacities (q_e) were also achieved at pH 6.5. At low pH (2-4), phosphate adsorption capacity decreased with protonation caused by high H^+ ion concentration. Also, the decrease in the capacity, at pH higher than 8, could be due to the competition of phosphate and OH^- ions for the adsorption sites on the adsorbent surface [33-34].

Effect of Adsorbent Amount

The adsorption studies for investigating the effect of adsorbent amount were performed with amounts varying between 0.1-0.9 g. Other conditions were hold at pH 6.5, initial phosphate concentration of 20 mg/L, 25°C, 150 rpm and for 150 min (Fig. 4).

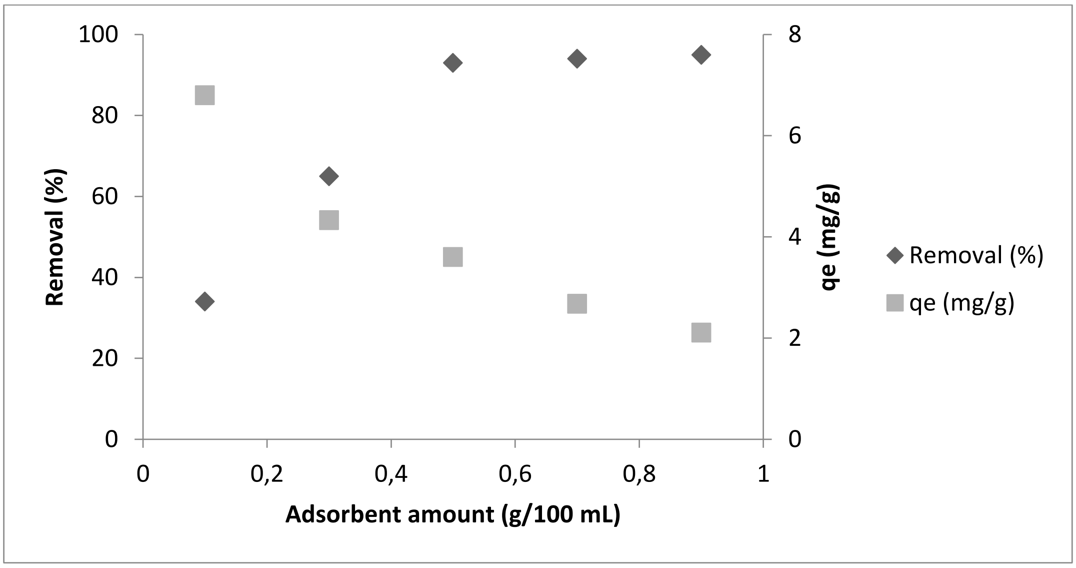

Figure 4. *The adsorption capacities and removal efficiencies with different adsorbent amount (Co=20 mg/L, 150 min, pH 6.5, 150 rpm, 25°C).*

It was observed that the phosphate removal efficiencies increased proportionally to the increase in the adsorbent amount. However, for applications higher than 0.5 g, the removal efficiencies remained close. Thus, the optimum adsorbent amount was determined as 0.5 g. The decrease in the adsorption capacity with the increase in the adsorbent amount is due to the unsaturation of the active sites during the adsorption process [35].

The Effect of Agitation Speed

In adsorption, the adsorbate must be in contact with the adsorbent in the most effective way to achieve high efficiency. Therefore, the adsorption studies to investigate the optimum agitation speed were carried out with the speeds ranged between 50-200 rpm. Other hold values were pH 6.5, initial phosphate concentration of 20 mg/L, adsorbent amount of 0.5 g, room temperature, and 150 min. The effect of the agitation speed is presented in Fig. 5. Phosphate removal efficiencies tended to increase with the increase in agitation speeds.

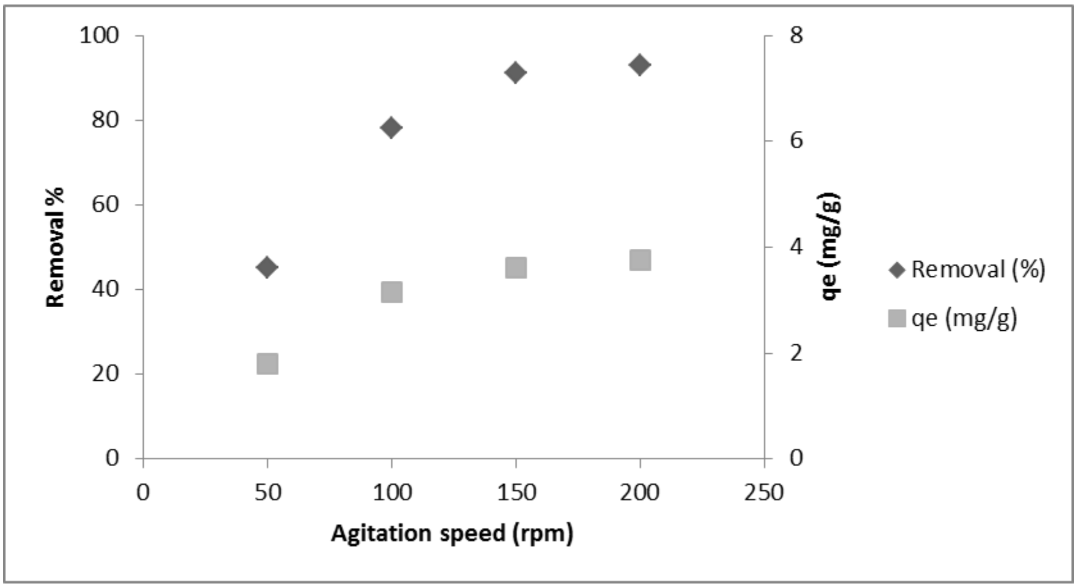

Figure 5. *The adsorption capacities and removal efficiencies at different agitation speeds (Co=20 mg/L, 150 min, pH 6.5, 0.5 g adsorbent/100 mL, 25°C).*

Effect of Temperature

Temperature is an important physochemical process parameter that changes adsorption capacity of adsorbent. The effect of temperature on the adsorption of phosphate by WSAC was examined in the range of 25-45°C with 20 mg/L initial phosphate concentration and 0.5 g adsorbent dosage, at pH 6.5 and 150 rpm, for 150 min. The results are shown in Fig. 6. There was no significant difference between the removal efficiencies of the studied temperature levels. Thus, the experiments were performed at room temperature.

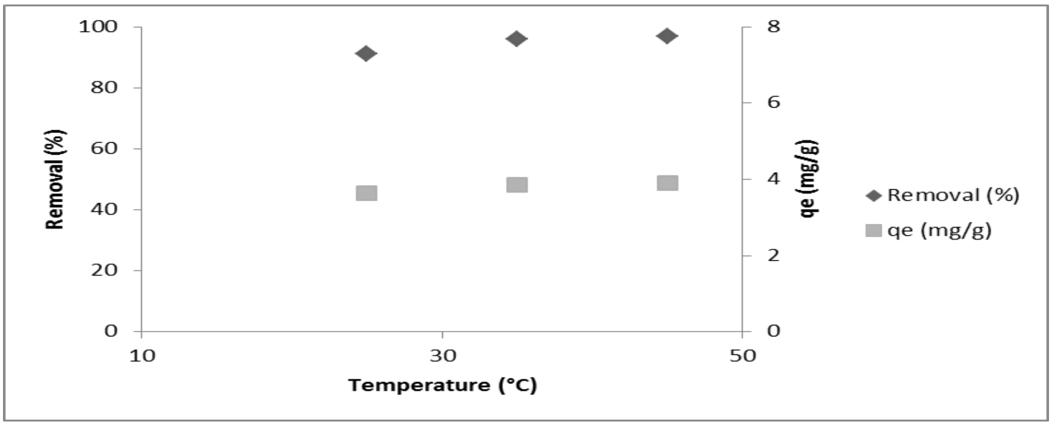

Figure 6. *The adsorption capacities and removal efficiencies at different temperatures (Co=20 mg/L, 150 min, pH 6.5, 0.5 g adsorbent/100 mL, 150 rpm)*

Adsorption Isotherms

The data obtained were applied to Freundlich, Langmuir, Temkin and Dubinin-Radushkevich adsorption isotherms.

Freundlich Isotherm

Freundlich isotherm is used to model adsorption on heterogeneous surfaces and is expressed in the following equations [36].

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad (3)$$

where K_f (mg/g) is the Freundlich adsorption constant and n Freundlich density constant and heterogeneity factor, which is a constant related to surface heterogeneity.

Langmuir Isotherm

Langmuir isothermia is the most widely used isotherm model and is used to describe single-layer homogeneous adsorption [37]. Langmuir isotherm is expressed by equality (2);

$$C_e/q_e = (1/k\ V_m) + (C_e/V_m) \qquad (4)$$

Where; qe indicates the amount of adsorped substance (mg/g), k equilibrium constant (L/mg), Ce: concentration of the substance remaining in the solution after adsorption (mg/L) and Vm adsorption capacity (mg/g).

The sizeless separation factor ($R_{L)}$ is calculated with the following equality help to determine whether langmuir adsorption isotherm is appropriate.

$$R_L = 1/\ (1 + a_L C_0) \qquad (5)$$

Where a_L(L/mg) refers to the Langmuir constant and C_0 is defined to the adsorbate initial concentration (mg/L).

The fact that the R_L value is greater than 1 indicates that the adsorption process is unfavorable, equal to 1 is linear, it is appropriate to have a value between 0 and 1, and if it is 0, adsorption is irreversible [38].

Temkin Isotherm

Temkin isotutery assumes that the decrease in adsorption energy is linear [39]. Temkin isotherm is calculated from the following equation;

$$q_e = B\ln A + B\ln C_e \qquad (6)$$

A: indicates the constant, which represents adsorbate-adsorbate interactions, and B: indicates a constant related to adsorption temperature.

Dubinin – Radushkevich Isotherm

D-R (Dubinin–Radushkevich) isothermia provides information about whether the adsorption process is physical or chemical adsorption [40]. D-R isotherm equality is as follows;

$$\ln q_e = \ln V'_m - K'\varepsilon^2 \qquad (7)$$

where q_e (mg/g) is the amount of substance adsorbed at equilibrium, V'_m (mg/g) is the capacity of adsorption, K' (mol^2k/J^2) is constant related to adsorption energy and ε is Polanyi potential.
Polanyi adsorption potential can be defined as follows;

$$\varepsilon = RT'\ln(1+ 1/C_e) \quad (8)$$

R, shows universal gas constant (kJ K^{-1} mol^{-1}) and T' :temperature (K).

The average free energy (E) of adsorption is free energy, which changes with the transfer of each mole adsorbate to the surface and is calculated using the following formula;

$$E= \left(-2K'\right)^{-0,5} \quad (9)$$

The size of the E value can be used to estimate the type of adsorption process [41]. All isoterm model parameters are given inTable 2.

Table 2. *Adsorption isotherm parameters*

Model	Model Parameters	R^2
Langmuir	Vm=7.61; k=0.38 R_L = 0.50	**0.97**
Freundlich	K_F=2.51; n=2.82	0.82
Temkin	A=5.632; B=1.4337	0.84
Dubinin-Radushkevich	K' = -0.3422 V'_m = 5.75 E = 1.21	0.85

It was shown that the best fitting of the experimental data for isotherm models achieved by the Langmuir isotherm. This is thought to be due to homogeneous distribution of active parts on the adsorbent surface. In this study, the maximum adsorption capacity on the WSAC was obtained 7.61 mg/g based on the Langmuir isotherm model. The sizeless constant separation factor ($R_{L)}$value is calculated as 0.50, and the fact that this value is between 0 and 1 indicates that adsorption is appropriate.

Kinetics of Adsorption

At this stage of the study, batch adsorption experiments were applied for different initial concentrations (10, 20 ve 30 mg/L) under the optimum conditions determined (pH 6.5, 0.5 g adsorbent, 150 rpm and at 25°C). Phosphate removal against time is seen in Figure 7 and adsorption capacity values are seen in Figure 8. The amount of phosphate adsorbed increases as the initial solution concentration increases. This increase is since the executive force of mass transfer becomes dominant with the increase of initial concentrations [42]. Low adsorption capacities also indicate that the active regions on the adsorbent surface do not reach fullness for low initial concentrations [43].

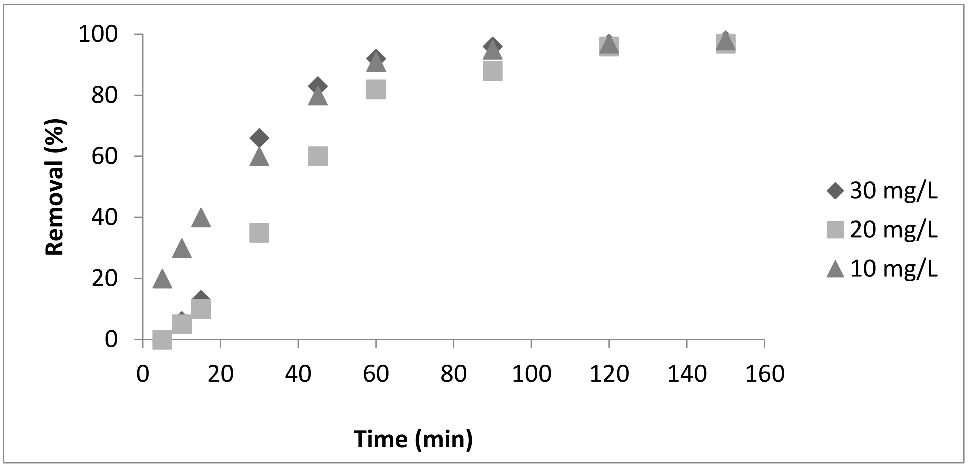

***Figure 7**. Relationship between contact time and initial concentration and phosphorus removal (pH 6.5, 0.5 g/100 mL, 25°C, 150 rpm)*

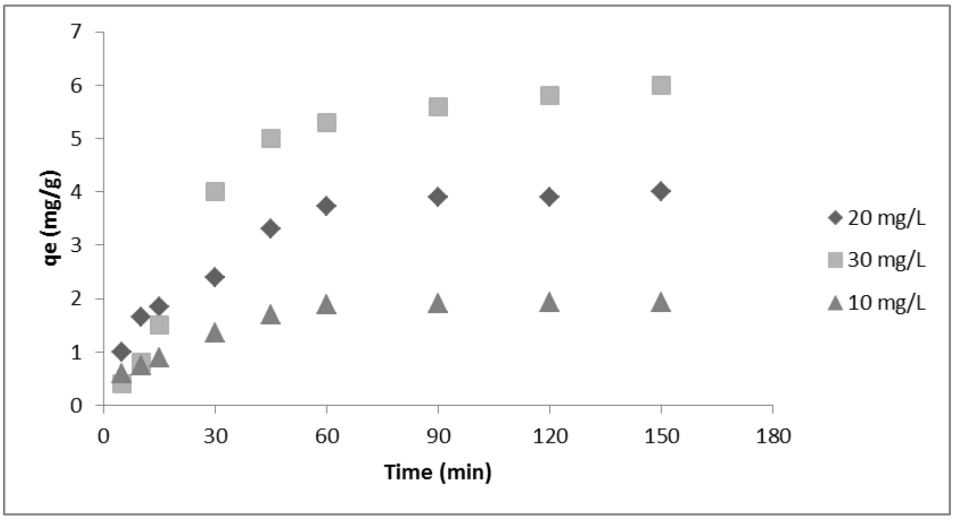

***Figure 8**. Effect of different initial concentration on adsorption capacity (pH 6.5, 0.5 g/100 mL, 25°C, 150 rpm)*

Pseudo-First-Order Reaction Kinetic

The pseudo first order speed equality developed by Lagergren is as follows [44];

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{10}$$

where q_e (mg/g) and q_t (mg/g) are the amounts of adsorbate on the sorbents at equilibrium and time t, respectively. k_1 (min^{-1}) is the pseudo-first order rate constant of adsorption.

Pseudo-Second-Order Reaction Kinetic

The Pseudo second order kinetic model based on adsorption equilibrium capacity is as follows.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{11}$$

k_2 (g/mg.dk) is the rate constant of pseudo-second-order adsorption.

Kinetic models were applied to the values given in Figure 9.

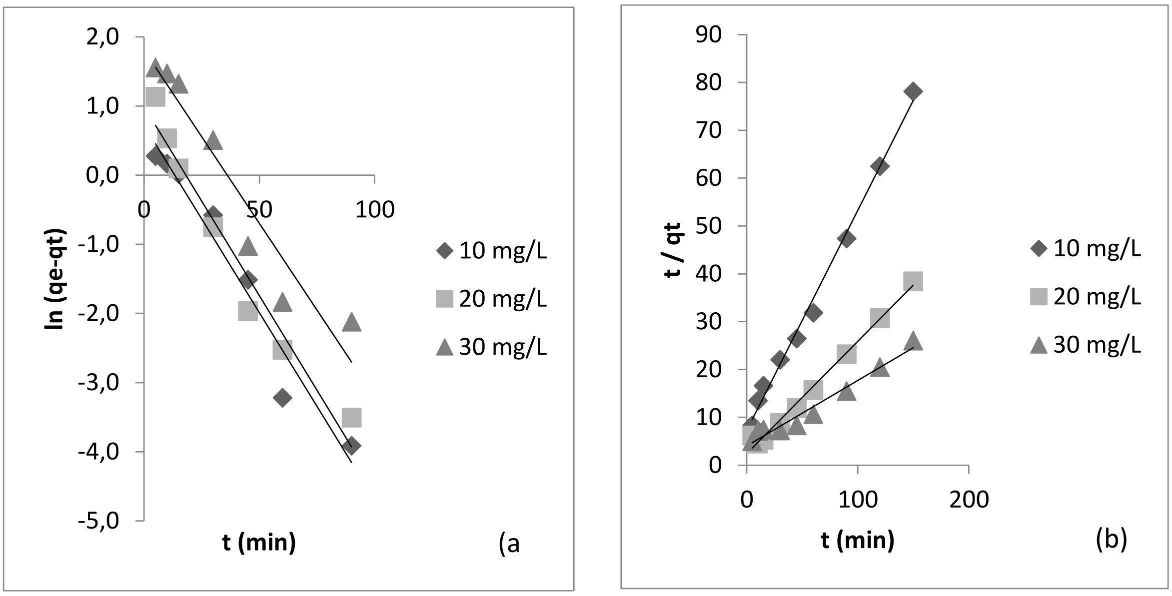

***Figure 9.** The kinetics models for adsorption of phosphate on the WSAC; (a) pseudo- first order model; (b) pseudo- second order model*

The results of kinetics data analysis were given in Table 3.

The values obtained from experimental data ($q_{e,exp}$) and theoretically ($q_{e,cal)}$ found are closer to each other in the pseudo-second-order kinetic model. According to these results, it can be said that phosphate adsorption with activated carbon obtained by $ZnCl_2$ activation of walnut shell was a second order adsorption process.

***Table 3.** Kinetic model constants of phosphate adsorption*

	pseudo first order kinetic model				pseudo second order kinetic model			
C_0(mg/L)	$q_{e,exp}$	$q_{e,cal}$	k_1	R^2	$q_{e,exp}$	$q_{e,cal}$	k_1	R^2
10	1.92	2.60	0.054	0.95	1.92	2.16	0.029	0.99
20	3.90	2.70	0.055	0.96	3.90	4.15	0.023	0.99
30	5.92	8.51	0.066	0.97	5.92	6.20	0.005	0.98

As a result of adsorption experiments carried out with different initial concentrations, adsorbent was filtered out of the solution and the pollutants in the structure of activated carbon was examined with SEM images. SEM images of activated carbons after adsorption are given in Figure 10. From the figure, it was observed that pollutants are holding onto the pores.

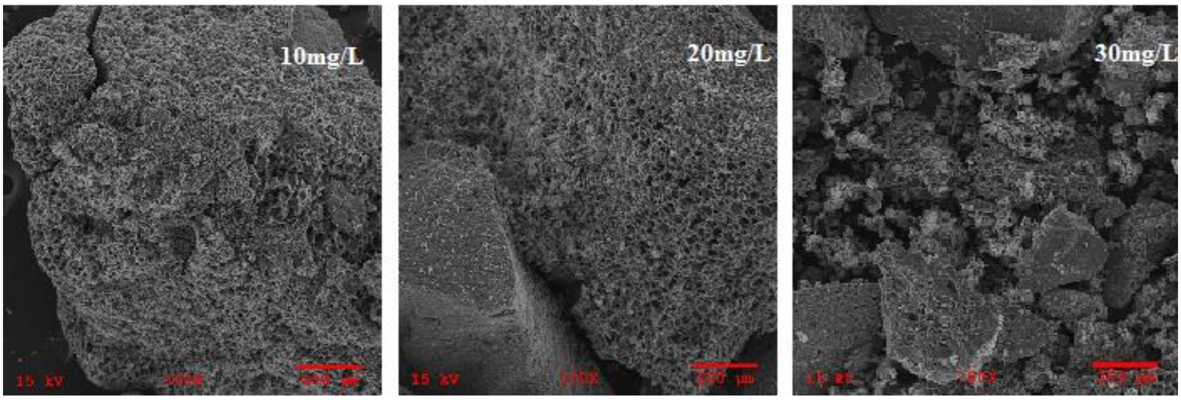

Figure 10. *SEM images of activated carbons after adsorption*

Thermodynamics of Adsorption

To learn about the thermodynamics of the system, the thermodynamic parameters of enthalpy (ΔH^0), entropy (ΔS^0) and Gibbs free energy (ΔG^0) were calculated according to the following equations [32].

$$K_C = {c_s}/{c_e} \tag{12}$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{13}$$

$$\Delta G^\circ = -RTlnK_c \tag{14}$$

Studies were carried out at temperatures of 298,308 and 318 K with an initial concentration of 20 mg/L, under optimum conditions (pH 6.5; 0.5 g adsorbent amount, 150 rpm mixing speed and 150 min contact time). The measurement results were evaluated based on gibbs free energy exchange principle.

Table 4. *Thermodynamic parameters of phosphate adsorption*

T(K)	K_c	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol K)
298	1.56	-1.11	1.56	0.00898
308	2.75	-2.59	1.68	0.01389
318	3.23	-3.10	1.75	0.01526

According to Table 4; negative ΔG^0 values indicate that adsorption of phosphate on activated carbon is a spontaneous type of adsorption and occurs without any external energy [45]; [46]. The positive entropy values ($\Delta S^{0)}$ indicate that irregularity increases on the solution-adsorbent interface during the adsorption process and shows the strong interest of carbons in phosphate molecules [47];[48]. The fact that the standard enthopaed change value($\Delta H^{0)}$ is positive indicates that adsorption is endothermic [46]. The results of the study were compared with the literature based on the adsorbent used and/or the pollutant removed (Table 5).

Table 5. *Comparison of study results with literature*

Adsorbent Type	Pollutant	Experimental Conditions	Removal	References
Alunite	Phosphate	C_0=5 mg/L C_0=200 mg/L	93% 53%	[8]
Calcium and magnesium-modified iron-based adsorbent	Phosphate	Fe/$CaCO_3$-PVA 1:1 Fe/$CaCl_2$-PVA 1:1	98.5% 93%	[49]
Al-intercalated acid activated bentonite	Phosphate	Al-ABn Al-ABn-AB	96.4% 93%	[50]
Rice husk and fruit juice residue	Phosphate	pH 6.0, 3g/L adsorbent	95.85%	[51]
Modifying walnut shell	Anionic dye	t=180 min, 0.5 g/L adsorbent	99.6%	[52]
Walnut Shell	Phosphate	C_0=20 mg/L, t=120 min	96%	**This study**

Conclusion

In this study, activated carbon was obtained from walnut shell by chemical activation and then used for phosphate adsorption. The physical and chemical properties of the produced activated carbon were investigated. The iodine number, moisture and ash contents were determined as 449 mg/g, 1.81% and 1.03%, respectively. The optimum conditions of process were initial solution pH of 6.5, 0.5 g adsorbent amount, 150 rpm agitation speed, 120 min reaction time and 25°C temperature. The maximum adsorbent capacity was obtained as 7.61 mg/g. The suitability of the data was examined with respect to the adsorption isotherms of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich. According to the results, the data was suitable for the Langmuir isotherm model with R-squared of 0.97. The second order kinetic model was evaluated as suitable for WSAC in the kinetic studies conducted with different initial concentrations. According to the thermodynamic studies, the adsorption of phosphate on the WSAC was spontaneous, endothermic in nature and also the randomness at solid /liquid interface increased with increasing temperature. This study is a good practice for the evaluation of walnut shells, which is a large amount of agricultural waste in Turkey. Synthesized activated carbon is environmentally friendly. As a result, it may be concluded that the activated carbon obtained from walnut shell can be an effective adsorbent for phosphate removal.

Acknowledgments -

Funding/Financial Disclosure The authors have no received any financial support for the research, authorship, or publication of this study.

Ethics Committee Approval and Permissions -

Conflict of Interests The authors stated that there are no conflict of interest in this article.

Authors Contribution Authors contributed equally to the study.

References

[1] Vikrant, K., Kim, K., Ok, Y. S., Tsang, D. C. W., Tsang, Y. F., Giri, B. S., & Singh, R. S. (2018). Engineered/designer biochar for the removal of phosphate in water and wastewater. *Science of the Total Environment, 616–617*, 1242–1260. https://doi.org/10.1016/j.scitotenv.2017.10.193

[2] Jiang, J., Kim, D. I., Dorji, P., Phuntsho, S., Hong S., & Shon, H. K. (2019). Phosphorus removal mechanisms from domestic wastewater by membrane capacitive deionization and system optimization for enhanced phosphate removal. *Process Safety and Environmental Protection*, *126*, 44–52. https://doi.org/10.1016/j.psep.2019.04.005

[3] Zelmanov, G., & Semiat, R. (2014). Phosphate removal from aqueous solution by an adsorption ultrafiltration system. *Separation and Purification Technology*, *132*, 487-495. https://doi.org/10.1016/j.seppur.2014.06.008

[4] Delaney, P., McManamon, C., Hanrahan, J. P., Copley, M. P., Holmes, J. D., & Morris, M. A. (2011). Development of chemically engineered porous metal oxides for phosphate removal. *Journal of Hazardous Materials*, *185*(1), 382-391. https://doi.org/10.1016/j.jhazmat.2010.08.128

[5] Mulkerrins, D., Dobson, A. D. W., & Colleran, E. (2004). Parameters affecting biological phosphate removal from wastewaters. *Environment International*, *30*(2), 249-259. https://doi.org/10.1016/S0160-4120(03)00177-6

[6] Clark, T., Stephenson, T., & Pearce, P. A. (1997). Phosphorus removal by chemical precipitation in a biological aerated filter. *Water Research*, *31*(10), 2557-2563. https://doi.org/10.1016/S0043-1354(97)00091-2

[7] Xing, B., Chen, T., Liu, H., Qing, C., Xie, J., & Xie, Q. (2017). Removal of phosphate from aqueous solution by activated siderite ore: Preparation, performance and mechanism. *Journal of the Taiwan Institue of Chemical Engineers*, *80*, 875-882. https://doi.org/10.1016/j.jtice.2017.07.016

[8] Özacar, M. (2003). Adsorption of phosphate from aqueous solution onto alunite. *Chemosphere*, *51*(4), 321–327. https://doi.org/10.1016/S0045-6535(02)00847-0

[9] Huang, X., Liao, X., & Shi, B. (2009). Adsorption removal of phosphate in industrial wastewater by using metal-loaded skin split waste. *Journal of Hazardous Materials*, *166*(2-3), 1261–1265. https://doi.org/10.1016/j.jhazmat.2008.12.045

[10] Fan, C., & Zhang, Y. (2018). Adsorption isotherms, kinetics and thermodynamics of nitrate and phosphate in binary systems on a novel adsorbent derived from corn stalks. *Journal of Geochemical Exploration*, *188*, 95–100. https://doi.org/10.1016/j.gexplo.2018.01.020

[11] Namasivayam, C., & Sangeetha, D. (2004). Equilibrium and kinetic studies of adsorption of phosphate onto ZnCl 2 activated coir pith carbon. *Journal of Colloid and Interface Science*, *280*(2), 359–365. https://doi.org/10.1016/j.jcis.2004.08.015

[12] Alslaibi, T. M., Abustan, I., Ahmad, M. A., & Foul, A. A. (2013). A review: Production of activated carbon from agricultural byproducts via conventional and microwave heating. *Journal of Chemical Technology & Biotechnology*, *88*(7), 1183–1190. https://doi.org/10.1002/jctb.4028

[13] Tsai, W. T., Chang, C. Y., & Lee, S. L. (1998). A low cost adsorbent from agricultural waste corn cob by zinc chloride activation. *Bioresource Technology*, *64*(3), 211–217. https://doi.org/10.1016/S0960-8524(97)00168-5

[14] Bansal, R. C., & Goyal, M. (2005). Activated Carbon Adsorption. CRC Press Taylor & Francis Group, USA.

[15] Kim, J. W., Sohn, M. H., Kim, D. S., Sohn, S. M., & Kwon, Y. S. (2001). Production of granular activated carbon from waste walnut shell and its adsorption characteristics for Cu^{2+} ion. *Journal of Hazardous Materials*, *85*(3), 301–315. https://doi.org/10.1016/S0304-3894(01)00239-4

[16] Yahya, M.A., Al-Qodah, Z., & Ngah, C.W.Z. (2015). Agricultural bio-waste materials as potential sustainable precursors used for activated carbon production: A review. *Renewable & Sustainable Energy Reviews*, 46, 218–235. https://doi.org/10.1016/j.rser.2015.02.051

[17] Girgis, B. S., Yunis, S. S., & Soliman, A. M. (2002). Characteristics of activated carbon from peanut hulls in relation to conditions of preparation. *Materials Letters*, *57*(1), 164–172. https://doi.org/10.1016/S0167-577X(02)00724-3

[18] Dias, J. M., Alvim-Ferraz, M. C. M., Almeida, M. F., Rivera-Utrilla, J., & Sánchez-Polo, M. (2007). Waste materials for activated carbon preparation and its use in aqueous-phase treatment: A review. *Journal of Environmental Management*, *85*(4), 833–846. https://doi.org/10.1016/j.jenvman.2007.07.031

[19] ASTM D4607-14 and ASTM (2006). Standard Test Method for Determination of Iodine Number of Activated Carbon 1, ASTM International, *94*, 1–5.

[20] *Standard Methods for the Examination of Water and Wastewater*, (2005). 21st edn, American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA.

[21] Tuna, M. (1996). *The usage of west Karadeniz region hazelnut shells as active carbon*. (Thesis no. 57082) [Master Thesis, Sakarya University].

[22] Çiçek, İ. (1998). *Production of activated carbon from agricultural wastes*. (Thesis no. 75384) [Master Thesis, Istanbul Technical University].

[23] Martínez, M. L., Torres, M. M., Guzmán, C. A., & Maestri, D. M. (2006). Preparation and characteristics of activated carbon from olive stones and walnut shells. *Industrial Crops and Products*, *23*(1), 23–28. https://doi.org/10.1016/j.indcrop.2005.03.001

[24] Özçimen, D. (2007) *Evaluation of various vegetable residues by carbonization*. (Thesis no. 223161) [Ph.D. Thesis, Istanbul Technical University].

[25] Malik, R., Ramteke, D. S., & Wate, S. R. (2007). Adsorption of malachite green on groundnut shell waste based powdered activated carbon. *Waste Management*, *27*(9), 1129–1138. https://doi.org/10.1016/j.wasman.2006.06.009

[26] Döşemen, Y. (2009) *Production of activated carbon from chestnut shell*. (Thesis no. 251540) [Master Thesis, Istanbul Technical University].

[27] Şen, N. (2009). *Production of activated aarbon from hazelnut shells and characterization*. (Thesis no. 246951) [Master Thesis, Fırat University].

[28] Zabihi, M., Haghighi, Asl A., & Ahmadpour, A. (2010). Studies on adsorption of mercury from aqueous solution on activated carbons prepared from walnut shell. *Journal of Hazardous Materials, 174*(1-3), 251–256. https://doi.org/10.1016/j.jhazmat.2009.09.044

[29] Sayın, Z. E., Kumaş, C., & Ergül, B. (2016). Activated carbon production from hazelnut shells. *Afyon Kocatepe University Journal Science and Engineering, 16,* 409–419. https://doi.org/10.5578/fmbd.28129

[30] Guo, Y., & Rockstraw, D. A. (2007). Activated carbons prepared from rice hull by one-step phosphoric acid activation. *Microporous Mesoporous Materials, 100*(1-3), 12–19. https://doi.org/10.1016/j.micromeso.2006.10.006

[31] Yang, J., & Qiu, K. (2010). Preparation of activated carbons from walnut shells via vacuum chemical activation and their application for methylene blue removal. *Chemical Engineering Journal*, *165*(1), 209–217. https://doi.org/10.1016/j.cej.2010.09.019

[32] Nazari, G., Abolghasemi, H., & Esmaieli, M. (2016). Batch adsorption of cephalexin antibiotic from aqueous solution by walnut shell-based activated carbon. *Journal of the Taiwan Institue of Chemical Engineers*, *58*, 357–365. https://doi.org/10.1016/j.jtice.2015.06.006

[33] Xu, X., Gao, B., Tan, X., Zhang, X., Yue, Q., Wang, Y., & Li, Q. (2013). Nitrate adsorption by stratified wheat straw resin in lab-scale columns. *Chemical Engineering Journal, 226*(1-6), 1–6. https://doi.org/10.1016/j.cej.2013.04.033

[34] Qiao, H., Mei, L.,Chen, G., Liu, H., Peng, C., Ke, F., Hou, R., Wan, X., & Cai, H. (2019). Adsorption of nitrate and phosphate from aqueous solution using amine cross-linked tea wastes. *Applied Surface Science*, *483*, 114–122. https://doi.org/10.1016/j.apsusc.2019.03.147

[35] Özacar, M., & Şengil, I. A. (2005). Adsorption of metal complex dyes from aqueous solutions by pine sawdust. *Bioresource Technology*, *96*(7), 791–795. https://doi.org/10.1016/j.biortech.2004.07.011

[36] Arslan, A., & Veli, S. (2012). Zeolite 13 X for adsorption of ammonium ions from aqueous solutions and hen slaughterhouse wastewaters. *Journal of The Taiwan Institute of Chemical Engineers, 43*(3), 393-398. https://doi.org/10.1016/j.jtice.2011.11.003

[37] Tan, I. A. W., Hameed, B. H., & Ahmad, A. L. (2007). Equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon. *Chemical Engineering Journal*, *127*(1-3), 111–119, https://doi.org/10.1016/j.cej.2006.09.010

[38] Annadurai, G., Ling, L. Y., & Lee, J. F. (2008). Adsorption of reactive dye from an aqueous solution by chitosan: isotherm, kinetic and thermodynamic analysis. *Journal of Hazardous Materials, 152*(1), 337–346. https://doi.org/10.1016/j.jhazmat.2007.07.002

[39] Günay, A., Arslankaya, E., & Tosun, İ. (2007). Lead removal from aqueous solution by naturel and pretreated clinoptilolite: Adsorption equilibrium and kinetics. *Journal of Hazardous Materials*, *146*(1-2), 362-371. https://doi.org/10.1016/j.jhazmat.2006.12.034

[40] Alberti, G., Amendola, V., Pesavento, M., & Biesuz, R. (2012). Beyond the synthesis of novel solid phases: Review on modelling of sorption phenomena. *Coordination Chemistry Reviews, 256*(1-2),28–45. https://doi.org/10.1016/j.ccr.2011.08.022

[41] Kilislioglu, A., & Bilgin, B. (2003). Thermodynamic and kinetic investigations of uranium adsorption on amberlite IR-118H resin. *Applied Radiation Isotopes, 58*(2), 155–160. https://doi.org/10.1016/S0969-8043(02)00316-0

[42] Tan, I.A.W., Ahmad, A.L., & Hameed, B.H. (2009). Adsorption isotherms, kinetics, thermodynamics and desorption studies of 2, 4, 6-trichlorophenol on oil palm empty fruit bunch-based activated carbon. *Journal of Hazardous Materials*, *164*(2-3), 473–482. https://doi.org/10.1016/j.jhazmat.2008.08.025

[43] Tomar, V., Prasad, S. & Kumar, D. (2014). Adsorptive removal of fluoride from aqueous media using Citrus limonum (lemon) leaf. *Microchemical Journal*, *112*, 97-103. https://doi.org/10.1016/j.microc.2013.09.010

[44] Alyüz, B., & Veli, S. (2009). Kinetics and equilibrium studies for the removal of nickel and zinc from aqueous solutions by ion exchange resins. *Journal of Hazardous Materials*, *167*(1–3), 482–488. https://doi.org/10.1016/j.jhazmat.2009.01.006

[45] Eren, E., & Afsin, B. (2007). Investigation of a basic dye adsorption from aqueous solution onto raw and pre-treated sepiolite surfaces. *Dyes and Pigments*, *73*(2), 162–167. https://doi.org/10.1016/j.dyepig.2005.11.004

[46] Dahri, M. K., Kooh, M. R. R., & Lim, L. B. L. (2014). Water remediation using low cost adsorbent walnut shell for removal of malachite green: Equilibrium, kinetics, thermodynamic and regeneration studies. *Journal of Environmental Chemical Engineering*, *2*(3), 1434–1444. https://doi.org/10.1016/j.jece.2014.07.008

[47] Hamdaoui, O., Saoudi, F., Chiha, M. & Naffrechoux, E. (2008). Sorption of malachite green by a novel sorbent, dead leaves of plane tree: Equilibrium and kinetic modeling. *Chemical Engineering Journal*, *143*(1-3), 73-84. https://doi.org/10.1016/j.cej.2007.12.018

[48] Alkan, M., Demirbaş, Ö., & Doğan, M. (2007). Adsorption kinetics and thermodynamics of an anionic dye onto Sepiolite, *Microporous and Mesoporous Materials*, *101*(3), 388-396. https://doi.org/10.1016/j.micromeso.2006.12.007

[49] Han, C., Lalley, J., Iyanna, N., & Nadagouda, N. M. (2017). Removal of phosphate using calcium and magnesium-modified iron-based adsorbents, *Materials Chemistry and Physics*, *198*, 115-124. http://dx.doi.org/10.1016/j.matchemphys.2017.05.038

[50] Pawar, R., Gupta, P., Lalhmunsiama, Bajaj, H. C., & Lee, S. (2016). Al-intercalated acid activated bentonite beads fort he removal of aqueous phosphate, *Science of the Total Environment*, *572*, 1222-1230. https://doi.org/10.1016/j.scitotenv.2016.08.040

[51] Yadav, D., Kapur, M., Kumar, P., & Mondal, M.K. (2015). Adsorptive removal of phosphate from aqueous solution using rice husk and fruit juice residue, *Process Safety and Environmental Protection*, *94*, 402-409. https://doi.org/10.1016/j.psep.2014.09.005

[52] Cao, J., Lin, J., Fang, F., Zhang, M., & Hu, Z. (2014). A new adsorbent by modifying walnut Shell fort he removal of anionic dye: Kinetic and thermodynamic studies, *Bioresource Technology*, *163*, 199-205. https://doi.org/10.1016/j.biortech.2014.04.046