



# Article Preparation and Optimization of the Adsorbent for Phosphorus Removal Using the Response Surface Method

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**Abstract:** A diatomaceous earth (DE)-based adsorbent DE-Ce was prepared and optimized to remove phosphorus from wastewater. DE was modified through purification–cerium loading, improving its phosphorus adsorption capacity and recycling ability. The preparation conditions were optimized using the Box–Behnken design, and the response surface method was employed to analyze the effects of roasting temperature, cerium concentration, and HCl concentration on the preparation of DE-Ce. Scanning electron microscopy, X-ray fluorescence spectrometry, and X-ray photoelectron spectroscopy were used for characterization, with results indicating that HCl washing can effectively remove impurities. Cerium was mainly loaded onto DE in the form of Ce(OH)<sub>3</sub>, and pore size and capacity increased following cerium loading, with the formation of a macroporous structure. The obtained DE-Ce adsorbent removed 98.30% phosphorous, with the removal process following the secondary kinetic and Langmuir models. According to material characterization and model analysis results, the phosphorus removal mechanism primarily involves electrostatic adsorption, ligand exchange, and precipitation. Overall, the findings indicate that cerium modification can effectively improve the adsorption capacity of DE.

Keywords: cerium-modified diatomaceous earth; adsorbent; response surface method

# 1. Introduction

Phosphorus is highly associated with the eutrophication of water bodies, affecting water quality, destroying the ecological environment, and threatening human health [1,2]. Phosphorus can be removed using biological [3,4], adsorption [5–7], chemical precipitation [8,9], and membrane [10,11] methods; among them, the simple process, low cost, and environmental friendliness of adsorption indicates that it is ideal for removing phosphorus [12,13], with the adsorbent used being the key to successful phosphorus removal [14,15]. Traditional adsorbents have the disadvantages of poor regeneration performance, low adsorption capacity, and high costs, which limits their application in phosphorus-containing wastewater. Diatomaceous earth (DE) is a natural mineral that primarily comprises amorphous silica (SiO<sub>2</sub>–nH<sub>2</sub>O), and its unique physicochemical properties, such as high porosity and permeability, abundant hydroxyl functional groups, and strong adsorption capacity has led to its use as an ideal adsorbent [16–19]. Porosity is conducive to metal oxide loading and pollutant removal from wastewater [20]; thus, DE has received extensive attention as an adsorbent in the field of water treatment. However, the micropores on the surface of DE often become blocked with organic matter or other impurities, restricting the number



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**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). of available active sites and limiting the adsorption and removal capacity, and DE is considered insufficient for the adsorption of negative-charged species, such as  $HPO_4^{2-}$  and  $H_2PO_4^{-}$  [21,22]. DE is also known to have trouble with solid–liquid separation when used for water treatment. Therefore, improving the adsorption performance and reuse rate of DE-based adsorbents is the focus of much research, and commonly-used metals such as Al, La, Ce, Mg, and Zn, which have been widely used for DE modification, have excellent adsorption capacities for pollutants [14].

Cerium is a rare-earth element that is characterized by abundant storage capacity and a nontoxic nature, and it is the only lanthanide element that includes both Ce(III) and Ce(IV) bivalent states, lowering the effects of pH [23–25]. Cerium is a paramagnetic substance, indicating that its characteristics are mainly dependent on the incomplete filling of its 4f electron layer [26]. Its oxide has been associated with room-temperature ferromagnetism, primarily owing to its abundant oxygen vacancies, indicating a high potential for application as an adsorbent. Several studies [27-32] have shown that cerium occurs mainly in the forms of cerium oxide (CeO<sub>2</sub>) and cerium hydroxide (Ce–OH), and cerium modification can effectively enhance the removal capacity of adsorbents for arsenate, phosphate, and heavy metals (Table 1), and the high phosphate affinity and low cost of cerium renders it a preferred material for phosphorus removal [16,33]. Liu et al. [34] used impregnation-roasting-impregnation to load hydrated cerium oxide onto natural zeolite, resulting in the adsorbent HCO-MZ that mainly worked via the interchange of Ce-OH with  $H_2PO_4^-$  or  $HPO_4^{2-}$ , which clearly demonstrated phosphorus removal effects. In another study, Li et al. [35] loaded cerium oxide onto porous silica microspheres and showed that electron conversion between Ce(III) and Ce(IV) provided abundant chemisorption sites for the adsorption of phosphorus. The results of these experiments indicate that cerium can optimize the material properties of an adsorbent, improving its phosphorus removal effect. At present, most studies investigating phosphorus removal are focused on single DE adsorbents and cerium-based adsorbents, with only few studies examining the use of cerium-modified DE.

Material	Ce Type Method		Pollutant	Capacity (mg/g)	Ref.	
BC-Ce	Ce(NO <sub>3</sub> ) <sub>3</sub> (CeO <sub>2</sub> ) *	impregnation– precipitation– pyrolysis	Cr(VI)	47.83	[27]	
NaY@Ce	CeCl <sub>3</sub>	coprecipitation	Sb(III)	24.65	[29]	
	(cerium hydroxide) *	method	Sb(V)	7.28	[20]	
Cu <sub>45</sub> Zn <sub>3</sub> Ce <sub>1</sub> /AC	$Ce(NO_3)_3 \cdot 6H_2O$	impregnation method	PH <sub>3</sub>	61.86	[29]	
Ce-bentonite	corium sulfato		Р	1.261	[30]	
	Certuin Sunate		NH <sub>3</sub> -N	0.884	[30]	
CHP	cerium hydroxide *	hydrothermal method	phosphates	86.7	[31]	
Ce-MIL-101-NH <sub>2</sub>	CeCl <sub>3</sub> ·eC <sub>2</sub> O (cerium hydroxide) *	solvothermal method	phosphate As(V)	341.5 249	[32]	

Table 1. Application of cerium-loaded materials.

Note: "\*" indicates the loading form of cerium in the materials.

In this experiment, DE and paramagnetic cerium were used as raw materials to prepare a DE-based adsorbent via cerium loading (referred to as DE-Ce). The response surface method (RSM) was employed to optimize the roasting temperature, cerium concentration, and HCl concentration of the prepared DE-Ce adsorbent and to explore the involved chemical interactions. DE-Ce was prepared under optimal conditions and comprehensively characterized using scanning electron microscopy (SEM), X-ray diffractometry (XRD), and other characterization tools, allowing investigation of the phosphorus removal mechanism. The results of this study are expected to provide technical support for the treatment of phosphorus-containing wastewater and eutrophication management in water bodies.

# 2. Materials and Methods

### 2.1. Materials and Chemicals

DE was purchased from Yunnan, China, and screened two-three times using a 100-mesh sieve before adding deionized water at a solid-liquid ratio of 1:10. Samples were then stirred until homogenous and left until the bottom layer could be removed, dried at 105 °C, removed, cooled to 25 °C, ground, and passed through a 100-mesh sieve to obtain pretreated DE. XRF analysis showed that the main chemical components of the treated DE were SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>3</sub>O<sub>4</sub>, with contents of 90.51%, 3.78%, and 0.59%, respectively. HCl, Ce(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O, and (NH<sub>4</sub>)<sub>6</sub>MO<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O were analytically pure, while NaOH and KH<sub>2</sub>PO<sub>4</sub> were of excellent purity.

#### 2.2. Synthesis Procedure

DE was modified using the purification–cerium loading method. The experimental method is presented in Figure 1.



**Figure 1.** Flow chart showing material preparation (DE, diatomaceous earth; PDE, purified DE; DE-Ce, magnetic DE-based adsorbent).

Appropriate amounts of pretreated DE were weighed in a beaker, and different concentrations of HCl (1–8 mol/L) added at a solid–liquid ratio of 1:4. Samples were then reacted in a water bath at 80 °C for 4 h and washed repeatedly with deionized water until a neutral pH was achieved. The samples were then filtered and the filter cake was dried at 105 °C, and cooled to 25 °C before roasting at 300 °C–700 °C for 2 h. The samples were then ground and passed through a 230-mesh sieve to obtain purified DE (PDE).

PDE was weighed into a beaker, and different concentrations of a cerium sulfate solution (0–0.2 mol/L) were added to achieve a liquid–solid ratio of 50:1 before adjusting to obtain a pH of 10.0. Ce impregnation was then performed over a period of 0.5–24 h. The impregnated material was filtered, and the filter cake was dried at 80 °C before cooling to 25 °C. The material was then heated for 0.1–4 h at 200 °C–800 °C in a muffle furnace, ground, and passed through a 230-mesh sieve to obtain DE-Ce, which was then sealed and stored.

### 2.3. Characterization

SEM (Gemini SEM 300, Shanghai, China) was performed with an accelerating voltage of 3 kV and gold spraying for 45 s at 10 mA to observe the morphological changes on the surfaces of the adsorption materials. XRF spectrometry (K-Alpha, Thermo Fisher Scientific, Waltham, MA, USA) was used to analyze the main DE-Ce elements and determine if cerium compounds were successfully loaded. The adsorption and desorption curves of the materials were determined at -196.15 °C using N<sub>2</sub> as an adsorbent. Vacuum degassing was performed for 12 h at 250 °C using a Mack ASAP2460 (McMurdoch (Shanghai) Instrument Co., Ltd., Shanghai, China), and the specific surface area and pore size were calculated. The crystal structure of the adsorption materials was analyzed using XRD (Panaco X'Pert

PRO, PANalytical B.V., Almelo, The Netherlands) with Cu-targeted K  $\alpha$ -rays as the X-ray source. Scanning was performed continuously over  $10^{\circ}-90^{\circ}$  at  $4^{\circ}/\text{min}$ . The magnetic properties of the materials were analyzed using a vibrating sample magnetometer (VSM, 7404, LakeShore, Columbus, OH, USA). All test samples were prepared under the optimal preparation conditions.

#### 2.4. Adsorption Experiment

 $KH_2PO_4$  was dried at 110 °C for 2 h, and the obtained material was used to prepare a 50-mg/L phosphorus standard reserve solution, which was then diluted to 1 mg/L to simulate wastewater.

A conical flask containing experimental water and an appropriate amount of DE-Ce was then placed in a gas bath thermostatic shaker. The reaction was shaken at 25  $^{\circ}$ C and 200 r/min to obtain supernatant, which was then centrifuged over the designed reaction period; ammonium molybdate spectrophotometry was used to determine the phosphorus content. Absorbance was measured using an ultraviolet–visible spectrophotometer (DR6000, HACH, Loveland, CO, USA).

The experimental data obtained for DE-Ce phosphorus removal were fitted using the pseudo-first-order and pseudo-second-order kinetic models [36]:

$$\ln(q_e - q_t) = \ln q_e - K_{1t} \tag{1}$$

$$\frac{t}{q_{t}} = \frac{1}{K_{2}q_{e}^{2}} + \frac{1}{q_{e}},$$
(2)

where t is the contact time between DE-Ce and phosphorus,  $q_e$  is the amount of phosphorus at which equilibrium adsorption is achieved using DE-Ce,  $q_t$  is the adsorption capacity of DE-Ce for phosphorus at time t of the reaction,  $K_1$  is the adsorption rate constant for the pseudo-first-order model, and  $K_2$  is the adsorption rate constant of the pseudo-second-order model.

In the utilized adsorption isotherm model, Langmuir describes monolayer adsorption and Freundlich describes multilayer adsorption [19]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}K_L}$$
(3)

$$\log q_e = \log K_F + \frac{1}{n} \log C_e, \tag{4}$$

where  $C_e$  is the equilibrium concentration of DE-Ce,  $q_e$  is the equilibrium adsorption capacity of DE-Ce for phosphorus adsorption,  $q_{max}$  is the maximum of phosphorus adsorption achieved using DE-Ce,  $K_L$  is the constant in Langmuir's adsorption model,  $K_F$  is the constant in Freundlich's adsorption model, n is the Freundlich constant, and 1/n can be used to represent the adsorption capacity.

#### 3. Results and Discussion

3.1. RSM

3.1.1. RSM Design

In the previous experiment, we considered five factors. The orthogonal experiments demonstrated that the studied factors influenced material preparation in the following order: roasting temperature > cerium concentration > HCl concentration > impregnation time > transition temperature, in which the impregnation time and transition temperature have no obvious effect on the removal of phosphorus. Therefore, in the subsequent experiments, they were set to 2 h and 250 °C, respectively.

Based on the results obtained, the RSM was used to identify the key influencing factors and determine the effects of interactions among the factors during synthesis. At a transition temperature of 250  $^{\circ}$ C and an impregnation time of 2 h, three factors were selected as independent variables: roasting temperature ( $X_1$ ), cerium concentration ( $X_2$ ), and HCl concentration ( $X_3$ ). The response surface model was then established using the phosphorus removal rate as the response value (Y, %). All independent variables and levels are shown in Table 2.

Table 2. Experimental factors and levels.

Variable	Scope and Level				
variable	Factor Coding	-1	0	+1	
Roasting temperature (°C)	X <sub>1</sub>	500	550	600	
Cerium concentration (mol/L)	X <sub>2</sub>	0.07	0.11	0.15	
HCl concentration (mol/L)	X <sub>3</sub>	2.0	3.0	4.0	

3.1.2. Experimental Results of RSM

The Box–Behnken optimization experiments were designed to include 17 groups. Table 3 presents the experimental scheme and results.

Serial		Variable Value			Actual Value	Response Value (Y, %)	
Number	<b>X</b> <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	X₁ (°C)	X <sub>2</sub> (mol/L)	X <sub>3</sub> (mol/L)	(P Removal Rate)
1	-1	-1	0	500	0.07	3	90.49
2	+1	$^{-1}$	0	600	0.07	3	92.64
3	-1	+1	0	500	0.15	3	92.15
4	+1	+1	0	600	0.15	3	93.52
5	$^{-1}$	0	-1	500	0.11	2	92.75
6	+1	0	-1	600	0.11	2	94.81
7	$^{-1}$	0	+1	500	0.11	4	92.8
8	+1	0	+1	600	0.11	4	92.98
9	0	$^{-1}$	-1	550	0.07	2	95.15
10	0	+1	-1	550	0.15	2	96.59
11	0	$^{-1}$	+1	550	0.07	4	94.34
12	0	+1	+1	550	0.15	4	95.42
13	0	0	0	550	0.11	3	99.28
14	0	0	0	550	0.11	3	99.02
15	0	0	0	550	0.11	3	98.91
16	0	0	0	550	0.11	3	98.57
17	0	0	0	550	0.11	3	98.67

Table 3. Box-Behnken design and results.

The Design Expert 10 software was used to sort the experimental data so that a quadratic polynomial regression equation could be obtained (Equation (5)). The similarity between the predicted results and those obtained from the experiment (Figure 2) indicates a good model fit, the accuracy of the quadratic model is verified [37,38].

$$Y = 98.89 + 0.72 X_1 + 0.63 X_2 - 0.47 X_3 - 0.20 X_1 X_2 - 0.47 X_1 X_3 - 0.090 X_2 X_3 - 4.37 X_1^2 - 2.33 X_2^2 - 1.19 X_3^2.$$
(5)

*p*-values of <0.05 indicate that the results of the prediction model are significant, whereas *p*-values that are >0.1000 are frequently considered nonsignificant [39]. As seen in Table 4, an F-value of 188.25 with a *p*-value of <0.0001 was obtained using the model, indicating that the roasting temperature, cerium concentration, and HCl concentration considerably affect the performance of the adsorbent. A correlation coefficient R<sup>2</sup> of 0.9959 and an adjusted correlation coefficient R<sup>2</sup><sub>(Adj)</sub> of 0.9906 obtained for the model (Table 4) demonstrates good simulation capabilities with high accuracy and reliability.



Figure 2. Model predictions and experimental results. The colored squares are the actual result values.

Source	Sum of Squares	Freedom	Mean Square	F	p > F	Significance
Mode	128.29	9	14.25	188.25	< 0.0001	Significant
X <sub>1</sub>	4.15	1	4.15	54.77	0.0001	-
X <sub>2</sub>	3.20	1	3.20	42.27	0.0003	
X <sub>3</sub>	1.77	1	1.77	23.34	0.0019	
$X_1X_2$	0.15	1	0.15	2.01	0.1993	
$X_1X_3$	0.88	1	0.88	11.67	0.0112	
$X_2X_3$	0.032	1	0.032	0.43	0.5339	
X1 <sup>2</sup>	80.22	1	80.22	1059.46	< 0.0001	
$X_2^2$	22.76	1	22.76	300.58	< 0.0001	
$X_3^2$	5.96	1	5.96	78.74	< 0.0001	
Residual	0.53	7	0.076			
Lack of fit	0.20	3	0.070	0.87	0.5252	Not significant
Pure error	0.32	4	0.080			0
Cor total	128.82	16				
$R^2 = 0.9959$		R <sup>2</sup> (Ad	(j) = 0.9906	А	$_{deq}$ Precision = 39	.031

Table 4. Results of variance analysis for phosphorus removal rate.

The primary terms  $X_1$ ,  $X_2$ , and  $X_3$ , interaction term  $X_1X_3$ , and secondary terms  $X_1^2$ ,  $X_2^2$ , and  $X_3^2$  have *p*-values that are considerably less than 0.05 and are thus considered significant, indicating the considerable contributions of these factors to the adsorbent performance [40,41]. *p*-values of <0.0001 for  $X_1^2$ ,  $X_2^2$ , and  $X_3^2$  indicate their significance. In the model, the F-values of  $X_1$ ,  $X_2$ , and  $X_3$  are 54.77, 42.27, and 23.34, respectively, indicating that these three factors influence the performance of DE-Ce in the following order: roasting temperature ( $X_1$ ) > cerium concentration ( $X_2$ ) > HCl concentration ( $X_3$ ). In terms of interaction,  $X_1X_3$  shows the largest effect, while  $X_2X_3$  shows the smallest effect.

The results of the RSM were used to produce a response surface graph, allowing further analysis of the influencing factors. The interaction effects of roasting temperature, cerium concentration, and HCl concentration on the phosphorus removal rate are presented in Figure 3.





The upward convex spherical surfaces in the response surface plots of Figure 3 indicate that the maximum phosphorous removal rate occurs under the interaction of two influencing factors. The convex red points in Figure 3a,c,e represent the optimum interaction conditions.

The density of the contour lines within the plots reflects the significance of the interaction between the three influencing factors in terms of phosphorus removal, with all three factors interacting to achieve phosphorus removal. The steep slope, dense contours, and elliptical shape in the response surface plots obtained for roasting temperature and HCl concentration in Figure 3c,d indicate that interaction between roasting temperature and HCl concentration has the greatest effect on phosphorus removal.

The results of the regression model optimization demonstrate a predicted phosphorus removal rate of 99.02% under the obtained optimal preparation conditions, which are a roasting temperature of 555  $^{\circ}$ C, a cerium concentration of 0.12 mol/L, and an HCl concentration of 2.76 mol/L. Preparation was, therefore, performed under these conditions, with

two sets of parallel tests used to verify the practicality of the established prediction model. The average phosphorus removal rate of 98.30% that was obtained under these conditions is similar to the removal rate predicted by the model, with only -0.72% deviation. These findings indicate the reliability of the model analysis and prediction.

# 3.2. *Characterization* 3.2.1. SEM

Figure 4a,b show a complete DE-Ce structure with abundant macroporous structures following cerium loading. Comparison of DE (Figure 4c) with PDE (Figure 4d) shows considerably lower amounts of surface and pore impurities and higher pore numbers for PDE, indicating that acid washing effectively removes impurities [42]. Figure 4b shows partially agglomerated or unevenly distributed cerium compounds both on the surface and in the pores. The presence of the cerium compounds in the pores reduces the pore size; however, they are not completely blocked and macroporous structures are clearly visible. The DE-Ce surface is covered by large amounts of modified material, rendering it rough and uneven.



Figure 4. SEM images of DE-Ce and DE, PDE.

# 3.2.2. XRF

The elemental composition of DE-Ce was determined using XRF, with O, Ce, and Si being the most abundant in terms of percentage. Cerium shows the highest abundance, except for O, with its mass fraction of 24.32% indicating successful loading.

# 3.2.3. BET

The results also show that, compared to DE, the specific surface area of PDE increased by 9.71 m<sup>2</sup>/g, the total pore volume increased by 0.0087 cm<sup>3</sup>/g, and the average pore size increased by 1.51 nm. These findings indicate that acid washing–roasting purification can effectively remove impurities from the surface of DE while also widening the pore channel. The average pore size of DE-Ce is 3.5 times of that of DE, with a higher abundance of macropores, resulting in a larger observed average pore size. The total pore volume of DE-Ce is 2.1 times of that of DE. However, the specific surface area of PDE is four times of that of DE, which is likely due to the alkaline method (pH = 10) used for the process of cerium of loading and, more specifically, owing to the surface-stacking capacity of Ce(OH)<sub>3</sub> under alkaline conditions, which becomes attached to the DE-Ce surface [43]. The accumulation

of  $Ce(OH)_3$  on the surface of DE leads to the formation of new pore size, increasing the total pore volume, and the formation of new cerium compounds during roasting may lead to a reduction in the DE-Ce surface area.

#### 3.2.4. XRD

Figure 5 shows sharp diffraction peaks for DE and PDE at  $2\theta = 26.6^{\circ}$ , which generally corresponds to quartz impurities. The reduced diffraction peak obtained for PDE as compared to DE is mainly due to the reduced number of impurities on the surface following purification. This finding is the same as that observed using SEM. The presence of the SiO<sub>2</sub> diffraction peak at  $2\theta = 26.6^{\circ}$  suggests that the original structure is not altered by cerium loading. However, the weaker diffraction peaks may be due to the presence of cerium compounds on the surface. It can be seen from the DE-Ce results in Figure 5, the diffraction peaks at  $27.4^{\circ}$ ,  $28.2^{\circ}$ ,  $31.7^{\circ}$ ,  $42.4^{\circ}$ ,  $47.5^{\circ}$ ,  $48.9^{\circ}$ , and  $50.3^{\circ}$  are associated with the Ce(OH)<sub>3</sub> (110), (101), (200), (210), (002), (211), and (102) crystal planes, respectively. Diffraction peaks indicating CeO<sub>2</sub> at  $28.6^{\circ}$  and  $59.0^{\circ}$  correspond to the (111) and (222) crystal planes, respectively, and may be attributed to the decomposition of Ce(OH)<sub>3</sub> and the production of CeO<sub>2</sub> during baking, respectively; however, the weaker intensity of the CeO<sub>2</sub> diffraction peaks indicates that either the CeO<sub>2</sub> content or its crystallinity is low, suggesting that cerium is mainly loaded in the form of Ce(OH)<sub>3</sub> both in the pores and on the surface.



**Figure 5.** XRD patterns of DE, PDE, and DE-Ce. a, XRD pattern of DE; b, XRD pattern of PDE; c, XRD pattern of DE-Ce.

#### 3.2.5. VSM

In order to explore the magnetic properties of DE-Ce, VSM analysis was performed on the material, and the results are shown in Figure 6. The M-H curve of DE-Ce is linear. It can be seen from the characteristics of the magnetization curve that the curve passes through the origin and exhibits central symmetry. With the increase in the applied magnetic field, the magnetization of DE-Ce increases continuously. When the applied magnetic field strength is zero, the magnetization of DE-Ce is also zero. DE-Ce does not have ferromagnetism and is a paramagnetic material.



Figure 6. M-H curve of DE-Ce.

## 3.3. Adsorption Kinetic Analysis

Figure 7 shows that phosphorus adsorption by DE-Ce can be divided into three stages. The first and fastest adsorption stage at 0–0.5 min is associated with rapid reaction, which is followed by gradual deceleration over a period of 0.5–240 min and further rate reduction after 240 min, resulting in equilibrium at 720 min, at which point, the phosphorus removal rate reaches 98.64%.



**Figure 7.** Adsorption kinetic fitting curve. The black squares in the figure represent the amount of phosphorus adsorbed by DE-Ce at different times.

According to Table 5, the pseudo-second-order kinetic model, with an  $R^2$  of 0.981, could explain the phosphorus adsorption by DE-Ce. The theoretical adsorption of 0.998 mg/g is similar to the 0.986 mg/g achieved via experimentation, indicating that chemical adsorption dominates the removal process.

Pseudo-First-Order	r Kinetic Model	Pseudo-Second-Order Kinetic Model		
$K_1 (min^{-1})$	0.927	$K_2 (min^{-1})$	5.074	
q <sub>e</sub> (mg/g)	3.004	q <sub>e</sub> (mg/g)	0.950	
$R^2$	0.968	$R^2$	0.981	

Table 5. Model parameters in the DE-Ce phosphorus adsorption kinetics.

# 3.4. Adsorption Isothermal Analysis

The isothermal adsorption models were also investigated to further analyze the adsorption type. The pH values of the reaction solution were adjusted to 4.0, 7.0, and 10.0 using 1.0 mol/L NaOH solution or 1.0 mol/L HCl, respectively.

According to Figure 8 and Table 6, the correlation coefficient values of  $R^2$  (0.994, 0.974, and 0.983) obtained using the Langmuir model were greater than those obtained by Freundlich (0.876, 0.919, and 0.868) under the three pH conditions. The q<sub>e</sub> obtained by fitting the Langmuir isothermal adsorption equation is close to the values obtained for adsorption. The phosphorus adsorption that was achieved using DE-Ce could therefore be explained using the Langmuir model, which is associated with monolayer adsorption. The weak adsorption capacity of DE is associated with a 0.440-mg/g peak for maximum phosphorus adsorption. By contrast, the best theoretical phosphorus adsorption capacity of DE-Ce (17.133 mg/g) indicates a 39-fold increase in the adsorption capacity for phosphorus following modification.



**Figure 8.** Fitting curve obtained for the DE-Ce adsorption model. (a) The fitting curve of the DE-Ce adsorption model under the condition of 25 °C and pH = 4.0; (b) The fitting curve of the DE-Ce adsorption model under the condition of 25 °C and pH = 7.0; (c) The fitting curve of the DE-Ce adsorption model under the condition of 25 °C and pH = 10.0. Black square is the adsorption capacity of DE-Ce to phosphorus at different concentrations of phosphorus.

Samples –	Langmuir			Freundlich		
	q <sub>m</sub> (mg/g)	K <sub>L</sub> (L/mg)	<b>R</b> <sup>2</sup>	n	$K_F$ ((mg/g) (mg/L) <sup>-n</sup> )	<b>R</b> <sup>2</sup>
pH = 4.0	16.317	3.838	0.994	4.246	8.231	0.876
pH = 7.0	17.133	3.867	0.974	3.912	8.379	0.919
pH = 10.0	15.794	2.977	0.983	4.125	7.689	0.868

**Table 6.** Parameters in the isothermal model of phosphorus adsorption.

The favorability for adsorption can be judged in accordance with  $R_L$  (Table 6). The expression  $0 < R_L < 1$  that was obtained using the Langmuir model indicates good adsorption performance for the DE-Ce adsorbent, while the expression 0 < 1/n < 0.5 obtained using the Freundlich model indicates that phosphorus adsorption is achievable using DE-Ce [44].

#### 3.5. Adsorption Mechanism

#### 3.5.1. Electrostatic Adsorption and Sedimentation

XRD was performed to further investigate the mechanism of phosphorus adsorption by DE-Ce. The XRD results after DE-Ce adsorption are presented in Figure 9. Based on these results and the findings of the JCDPS card analysis, the diffraction peak intensities at 20.1°, 41.7°, and 44.6° correspond to the (101), (211), and (103) crystallographic planes, respectively, in CePO<sub>4</sub> (No. 04-0632). Ce(HPO<sub>4</sub>)<sub>2</sub> (No. 34-0466) exhibits characteristic absorption peaks at 18.7°, 30.2°, 32.7°, 43.5°, and 47.1°, with the presence of CePO<sub>4</sub> and Ce(HPO<sub>4</sub>)<sub>2</sub> diffraction peaks in the XRD pattern indicating the formation of CePO<sub>4</sub> and Ce(HPO<sub>4</sub>)<sub>2</sub> crystal structures during adsorption.



**Figure 9.** XRD pattern following DE-Ce adsorption. a, XRD pattern of DE-Ce before adsorption; b, XRD pattern of DE-Ce adsorption.

The form that phosphate takes in water is heavily influenced by pH, while the form of DE-Ce-adsorbed phosphorus is only slightly dependent on pH as Ce<sup>3+</sup> is strongly attracted to  $PO_4^{3-}$  under acidic conditions [45]. As the pH increases,  $H_3PO_4$  is gradually deprotonated to become  $H_2PO_4^{-}$  and  $HPO_4^{2-}$  [44]. Figure 10 shows that the zeta point position of DE-Ce is 5.26 and that the surface of DE-Ce is positively charged in solutions where pH < 5.26. In this pH range, DE-Ce exhibits a strong electrostatic adsorption effect on negatively charged phosphates such as  $H_2PO_4^{2-}$ . As the pH increases, DE-Ce becomes negatively charged ( $pH_{PZC} = 5.26$ ) and the increased negative charge enhances the electrostatic repulsion effect of DE-Ce toward anions such as  $H_2PO_4^{2-}$  [46]. Moreover, phosphate competes with the increasing number of OH<sup>-</sup> molecules in an alkaline solution [47]. The weaker affinity of phosphate for Ce–OH on the DE-Ce surface as compared to the attraction to OH<sup>-</sup> in solution results in most active sites on the DE-Ce surface becoming occupied by OH<sup>-</sup>, limiting the phosphorus removal [42]. However, the continuing high removal rate may be due to Ce(III) hydrolysis leading to the formation of Ce–OH, at which time, the adsorption of phosphorus by DE-Ce is dominated by ligand exchange [48]. When DE-Ce adsorbs phosphorus,  $Ce^{3+}$  reacts with phosphate to generate CePO<sub>4</sub> precipitate and Ce(OH)3 reacts with hydrogen phosphate to generate Ce(HPO4)2 via ligand exchange, leading to phosphate capture.



Figure 10. Zeta potential analysis of DE-Ce. The black squares are the potentials at different pH values.

#### 3.5.2. Ligand Exchange

XPS was performed on DE-Ce before and after the reaction to further explore the phosphorus removal mechanism for DE-Ce.

The P 2p spectra are presented in Figure 11a,b. The obvious P 2p peak and resulting binding values of P  $2p_{3/2}$  and P  $2p_{1/2}$  at 133.8 and 134.9 eV, respectively, following adsorption correspond to HPO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup>, respectively, indicating the successful adsorption of phosphorus by DE-Ce. The stronger P 2p peak at 133.8 eV indicates that the phosphate is mainly loaded onto the DE-Ce surface in the form of HPO<sub>4</sub><sup>2-</sup> [48]. The lower binding energy as compared to that of purified KH<sub>2</sub>PO<sup>4</sup> (~134.0 eV) is likely due to the interaction between cerium and phosphate, thus demonstrating that DE-Ce removes phosphorus by chemisorption [24].

Four pairs of spin–orbit double peaks are present in the Ce 3d spectrum of cerium in DE-Ce [Figure 11c,d], with photoelectron peaks indicating Ce  $3d_{3/2}$  and Ce  $3d_{5/2}$  at 882.9/901.3, 886.0/904.3, 888.9/907.7, and 898.4/916.8 eV, respectively. The spin–orbit double peaks observed at binding energies of 882.9/901.3, 888.9/907.7, and 898.4/916.8 eV correspond to the characteristic chemical state of Ce<sup>4+</sup>, while the double peak at 886.0/904.3 eV corresponds to the chemical state of Ce<sup>3+</sup>. This finding indicates that cerium occurs is in the forms Ce<sup>3+</sup> and Ce<sup>4+</sup> in DE-Ce, which is likely due to the oxidation of Ce<sup>3+</sup> during preparation [49]; however, this observation may also be due to the fact that Ce(OH)<sub>3</sub> and Ce(OH)<sub>4</sub> form when cerium and OH<sup>-</sup> are combined and that Ce(OH)<sub>3</sub> is sensitive to air, thus forming Ce(OH)<sub>4</sub> [50]. The percentage of cerium in the different valence states can be estimated from the peak area, and the ratio of Ce<sup>3+</sup> to Ce<sup>4+</sup> content is 1:3.2 [51]. The slight displacement of Ce<sup>3+</sup> following phosphorus absorption may be due to electron transfer between Ce<sup>3+</sup> and phosphate, which leads to the generation of a Ce–O–P complex, indicating a strong affinity and interaction between phosphate and cerium [21,23].

Peaks are also observed at approximately 529.7, 531.6, and 532.6 eV in the O 1s profiles of DE-Ce [Figure 11e]. The photoelectron peaks at 529.7, 531.63, and 532.6 eV, which correspond to lattice O, surface-active O (O–H), and carboxylic acid O (O–C=O), respectively, are weaker after phosphorus adsorption than they are before adsorption, indicating that lattice O has transformed into surface-active O [52]. This phenomenon may be explained by the production of Ce–O–P under the coordination of Ce<sup>3+</sup> with phosphate. The considerable decrease in the peak area of Ce–OH further confirms the production of Ce–O–P [53].



**Figure 11.** XPS patterns before and after the reaction of DE-Ce. Explanations for subfigures (**a**–**f**): (**a**,**b**), P 2p; (**c**,**d**), Ce 3d; (**e**,**f**), O 1s.

The analysis results indicate that the adsorption of phosphorus by DE-Ce is the result of interaction between physical and chemical adsorption, with chemical adsorption playing a dominant role. The main mechanisms by which phosphorus is removed by DE-Ce include electrostatic adsorption, ligand exchange, and precipitation, as shown in Figure 12. DE-Ce has a pH<sub>PZC</sub> value of 5.26, which means that at pH values of <5.26, its surface is positively charged and it has a strong electrostatic adsorption effect on the negatively charged phosphate. Moreover, Ce<sup>3+</sup> interacts with PO<sub>4</sub><sup>3-</sup> to form CePO<sub>4</sub> precipitate on the DE-Ce surface. However, at a pH of >5.26, the hydrolysis of Ce(III) produces Ce–OH, providing additional exchange sites, and phosphate generates Ce–O–P inner sphere compounds via ligand exchange.



Figure 12. DE-Ce phosphorus removal mechanism.

## 4. Conclusions

An effective DE-Ce adsorbent was synthesized using cerium-modified DE, and the effects of roasting temperature, cerium concentration, and HCl concentration on adsorbent preparation were examined using the RSM. The significance of these parameters for adsorption is as per the following order: roasting temperature > cerium concentration > HCl concentration. Among the interaction effects, those of the roasting temperature and HCl concentration are the strongest. Combined with the previous experiments, the optimal preparation conditions are a roasting temperature of 550  $^{\circ}$ C, a cerium concentration of 0.12 mol/L, an HCl concentration of 2.76 mol/L, a transition time of 30 min, and an impregnation time of 2 h. The characterization results and adsorption experiments indicate that phosphorus adsorption by DE-Ce conforms to the secondary kinetic model, or chemisorption, and the Langmuir model, or unimolecular layer adsorption. The successful loading of Ce(OH)<sub>3</sub> onto DE can effectively increase the number and size of the pores observed on the DE surface and improve its structure. DE-Ce is a paramagnetic material. The mechanisms of phosphorus adsorption include electrostatic adsorption, precipitation, and ligand exchange. The overall results show that cerium loading is favorable for improving the adsorption capacity of DE. DE-Ce has a good removal effect on phosphorus, but its removal effect on other pollutants and its recyclability need to be further studied.

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