# AN INTEGRATED OVAT-RSM DESIGN TO GAPS-FILLING IN THE STUDY OF PHOSPHATE SORPTION PROCESS ONTO CATIONIC MODIFIED BOTTLE GOURD SHELL

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The conventional approach to researching the phosphate sorption process using a modified bottle gourd sorbent (the quaternary ammonium *Lagenaria vulgaris* shell), regardless of a large number of conducted experiments, indicated certain shortcomings in the prediction of the optimal process conditions. To fill the gaps in previous research, a design study involving conventional (comparative kinetic, thermodynamic and equilibrium) and "One-Variable-At-a-Time" (OVAT) experimental approaches integrated with “Design of Experiments” (DoE) methodology was carried out. The integrated experimental design is implemented in the phosphate sorption process optimization to evaluate significant factors (optimal sorption conditions), and their influence on the response (sorption efficiency), and to predict the maximum sorbent capacity in accordance with the sorption mechanism. The critical factors of the sorption process were determined through the OVAT method. The evaluation of factors’ interactive effects was realized using a central composite design (CCD) method within response surface methodology (RSM). A statistical software (JMP Pro16) was applied for planning the experiments, data processing and statistical analysis of the obtained results, which randomly generated a CCD matrix with 4 factors (initial concentration - $C_o$, pH value, temperature - $T$, time - $t$) on three levels (-1, 0, +1). The derived second-order polynomial model of phosphate sorption proved to be highly significant ($p<0.0001$). A statistically significant factor interaction is between the pH value and the initial concentration of phosphate ions. The experimental maximum sorption capacity (17.48 mg/g), very close to the predicted value (17.58 mg/g), indicated the capability and applicability of the regression model. The model finds a potential application in the optimization of the phosphate-contaminated wastewater treatment processes using the environmentally friendly cationic bottle gourd shell.

**Keywords:** Experiment design, RSM-CCD, OVAT, Phosphate sorption, *Lagenaria vulgaris* shell.

## Introduction

Eutrophication as a phenomenon greatly affects aquatic ecosystems and represents a serious ecological problem due to the high concentration of nutrients, especially phosphates and nitrates [1]. The causes of eutrophication can be different. Most often, it is the mass use of artificial fertilizers and synthetic detergents. These products contribute to the sudden increase of phosphate ions, both in wastewater and in natural waters. One of the possible ways to combat this phenomenon is the treatment of wastewater, which includes the removal of phosphorus (as orthophosphates, polyphosphates and organic phosphates) from this water before it is released into the environment [2]. Orthophosphate forms are mostly represented in wastewater, in addition to smaller amounts of organic phosphate. About 4 to 15 mg/L of phosphorus is usually present in municipal wastewater. In contrast, phosphate levels significantly higher than 10 mg/L can be found in industrial wastewater, especially in the production of detergents or metal coating processes [3,4].

Numerous processes and methods have been developed to remove dissolved phosphorus from aqueous solutions, like biological [5], physical (reverse osmosis, electrodialysis) [6], and chemical treatments (precipitation, ion exchange, adsorption) [3]. Biological treatment is characterized by a limited ability to remove phosphate (10-30%). Enhanced biological treatment is cheap and removes up to 97% of total phosphorus, but due to specific conditions, it is not feasible in practice. Physical methods are too expensive and less efficient (remove only 10% of total phosphorus). Chemical methods of phosphate removal have proven to be the most effective.

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The most common conventional techniques of physicochemical treatment include phosphate precipitation using Fe, Ca or Al salts [7], and phosphate removal by fly ash in adsorption or dissolution-precipitation processes [3]. However, expensive precipitants, neutralization of the effluent, and the accumulation of chemical sludge as a secondary pollutant limit the wider application of these techniques. The fact is that some chemical treatment methods are not sustainable.

Numerous studies have shown that adsorption and ion exchange are the most reliable and effective alternative physicochemical methods of phosphate removal [8]. Adsorption methods are easy to handle, allow adsorbent regeneration and generate relatively small amounts of by-products. The selected adsorbent should be cheap, easily available, and above all effective for phosphate removal. Various materials like modified biochar [8], zeolite [9], activated carbon [10], fly ash [11], and pumice (a porous type of igneous volcanic rock) [12], were tested to remove phosphate from aqueous solutions. These materials have attracted considerable attention due to their characteristics: low production cost, availability, and surface properties (surface area, pore diameter and volume, surface charge, and functional groups on the surface).

However, special attention is paid to natural biodegradable (green) sorbents, which together with sorbed phosphates can be used in agriculture as fertilizer [1], even in calcareous soils [13]. Interest in the application of agricultural residues (biomasses) as biosorbents of various anionic pollutants has increased recently due to their advantages: low price, high availability, biodegradability, sorption capacity, and easy handling. Extensive research into the process of phosphate biosorption (chemisorptions, anion exchange) has been carried out, which is aimed at the preparation of biosorbents using agricultural waste or residues. Namely, these agricultural by-products must be modified before application, which implies activation of their surface (most often with quaternary ammonium reagents) in order to increase biosorption capacity and chemical stability [14]. Among the numerous biosorbents of phosphate species, the bottle gourd shell (*Lagenaria vulgaris*) stands out.

Similar to other lignocellulosic biomasses, the bottle gourd shell was modified into a cationic biosorbent and applied to the phosphate sorption process [15,16]. Batch biosorption experiments showed that quaternary ammonium *Lagenaria vulgaris* shell (QALS) is a valuable sorbent of anionic species, primarily phosphate [17-19]. However, these experiments were mostly conducted using a conventional approach to analysis. Similar to the "One-Variable-At-a-Time" (OVAT) methodology, here one parameter is changed during the optimization of the sorption conditions, while the other conditions are kept constant. In such cases, the optimization of sorption conditions requires the implementation of numerous and time-consuming experiments, which can certainly affect the outcome (process efficiency) due to the lack of important information about the complete process. Therefore, implementing a factorial design to fill the gaps in sorption studies can be very useful if the whole picture of sorption is to be seen.

Although it has been studied a lot, the phosphate sorption process is still a challenge and constantly requires innovation in the development of water purification technology to increase the sorption capacity and maximize the use of the applied sorbent under optimal conditions. In this sense, assessment and prediction of sorption conditions, using the design of experiments methodology, are of particular importance [10]. The OVAT methodology is a univariate experimental approach, which is based on the multiple process analysis while varying only one factor at constant values of other sorption parameters. This approach often involves guesswork and relying on luck and successful implementation depends on the intuition and experience of the researcher. The experimental technique itself requires larger amounts of chemicals and a longer time while obtaining a limited amount of information about the process. Besides, OVAT approach experiments can often be inefficient, unreliable, and point to false optimum conditions of process [20]. On the other hand, the Design of Experiments (DoE) is a multivariate experimental approach. This is a more powerful experimental technique for exploring new processes. It is most often used to gain more insight into existing processes, as well as to optimize these processes in order to achieve the most efficient performance [20].

Integrated design methodologies enable first the determination of critical process factors (through OVAT) and then the optimization of the sorption process in the next phase. One of the powerful approaches in the optimization process is the statistical technique of experiment design, which is based on the response surface methodology (RSM). After determining the important factors (by the method of factorial or screening design), the model can be successfully refined using RSM. The central composite design (CCD) is one of the two main types of RSM (in addition to the Box-Behnken design), which is most often used when information from a factorial experiment needs to be taken into account. Using this empirical technique, the multiple effects of several process input variables (independent factors) can be simultaneously evaluated, as well as the relationship between the predicted response and independent factors. The advantages of RSM as a statistical method for process optimization and modeling are cost savings of experiments and significant prediction of the factors' optimal trend [21].

The application of experiment design in phosphate sorption studies using various sorbents is known in the literature. Various design methodologies (OVAT, Box–Behnken, and CCD) have been reported for numerous sorbents: dolochar (a by-product of the sponge iron industry) [22], activated carbon from cork [23], leftover coal [24], etc. However, no information is available so far about the experiment design of the phosphate sorption process on the bottle gourd biosorbent.

In the aforementioned studies, the influence of sorption parameters such as sorbent dose, particle size, solution concentration, temperature, and pH on the phosphate sorption process was most often considered. However, since the complex interactions of several factors (significant and insignificant) are involved in the efficiency of phosphate sorption, it is often useful to combine OVAT with the CCD statistical approach to model the process. In addition, this integrated OVAT-RSM approach to process analysis enables consideration of the incremental factor of phosphate sorption efficiency, based on experimentally determined limit values of sorption parameters.

Therefore, this integrated study aims to provide a research contribution to the establishment of an adequate mathematical model for the development of a batch process for the treatment of phosphate-contaminated waters. For this purpose, the CCD-RSM methodology used enables finding connections between sorption parameters and their effects on the studied sorption process, with a minimal number of experiments series to be performed. DoE methodologies were designed and implemented to fill gaps in previous conventional studies of phosphate sorption processes using a chemically modified bottle gourd sorbent, the quaternary ammonium *Lagenaria vulgaris* shell (QALS).

## Experimental

### Materials and methods

Previously prepared and characterized, the quaternary ammonium *Lagenaria vulgaris* shell (QALS) was used as a sorbent in all phosphate sorption experiments [15]. Modification of alkaline-treated lignocellulosic biomass to cationic form was achieved by surface functionalization using trimethylammonium groups (CHMAC agent). The morphological characteristics of the porous sorbent are particle size between 400 and 600 μm, micropore volume $4.96 \times 10^{-4}$ mL/g, specific surface area 1.07 $m^2/g$, $pH_{ZPC}$ value 7.05, with 1.4 mmolN/g of $NR_4^+Cl^-$ active groups on the sorbent surface [15,19]. Aqueous phosphate solutions (simulated working solutions) were obtained by diluting a stock solution (1000 mg/L $PO_4^{3-}$) of $KH_2PO_4$ (purity of 99.9%, Merck) to concentrations ranging from 5 to 100 mg/L. Batch sorption experiments were monitored after adding QALS sorbent to the working solution (50 mL) at fixed sorption parameters (sorbent dose 2 g, stirring speed 150 rpm) and changeable reaction conditions (initial phosphate concentrations 5-100 mg/L, pH 3-9, temperature 20-40 °C, during 60 min of sorbent-sorbate contact time). The content of the remaining phosphate in the solution after sorption (expressed as phosphorus) was determined using an ICP-OES spectrometer (Spectro ARCOS FHE12, Germany), axially at 213,618 nm. Phosphate removal efficiency (RE, %) and equilibrium phosphate concentration ($Q_e$) were calculated using the equations as given below:

$$\mathrm{RE}\ (\%) = \frac{C_o - C_t}{C_o} \cdot 100 \qquad (1)$$

$$Q_e = \frac{V \cdot (C_o - C_e)}{m} \qquad (2)$$

where: $C_o$, $C_e$ and $C_t$ are initial, equilibrium and final phosphate solution concentrations (mg/L) at time $t$, m is the dry mass of the sorbent (g), and $V$ is solution volume (L).

### Sorption kinetics

To investigate the kinetics of phosphate sorption, the linear kinetic equations of the Lagergren model (pseudo-first-order, Eq. 3) and the Ho model (pseudo-second-order, Eq. 4) were applied.

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \qquad (3)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \qquad (4)$$

where: $k_1$ ($min^{-1}$) and $k_2$ (g/mg min) are rate constants, $Q_e$ (mgP/g) is sorbed phosphate amount in equilibrium, and $Q_t$ (mgP/g) is sorbed phosphate amount at time $t$ (min).

### Sorption isotherm

For equilibrium tests and to determine the constants of the sorption isotherm, the experimental results were analyzed using two non-linear isotherms, the Langmuir model (Eq. 5) and the Freundlich model (Eq. 6).

$$Q_e = \frac{Q_{max} K_L C_e}{1 + K_L C_e} \qquad (5)$$

$$Q_e = K_F \cdot C_e^{1/n} \qquad (6)$$

where: $K_L$ is Langmuir constant related to the energy of sorption (L/mg), $K_F$ is Freundlich constant characterizing sorption capacity $((mg/g)(mg/L)^{1/n}$, $n_F$ is Freundlich parameter related to energy or intensity ($1/n_F$) of sorption, $C_e$ is equilibrium concentration (mg/L), $Q_{max}$ is maximum sorption capacity (mg/g).

### Statistical analysis and data validation

Determination of critical sorption conditions was performed using the OVAT approach. Experimental conditions' effect on the sorption process was evaluated by the multivariate mathematical model (RSM). Four factors were selected for the CCD design: initial concentration (A), solution pH (B), temperature (C) and sorbent-sorbate contact time (D). In this case, the number of necessary experimental runs (N) for the selected factors ($k$) and the number of replicates at the central point ($z$) according to the CCD was assessed based on the following equation:

$$N = 2^k + 2k + z \qquad (7)$$

An empirical model based on a second-order polynomial equation was used to evaluate the relationship between independent factors and their influence on the predicted response (Y):

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i<j} \cdot \sum \beta_{ij} X_i X_j + \sum_{i=1}^{k} \beta_{ii} X_i^2 + e_i \quad \text{..............(8)}$$

where: $X_i$ and $X_j$ – are the coded values of independent factors, $\beta_o$, $\beta_i$, $\beta_{ii}$, $\beta_{ij}$ – are the model constant, linear, quadratic and interaction coefficients (respectively), $k$ – is the number of independent factors, $e_i$ – is the error.

A statistical software package (JMP Pro16, SAS) including analysis of variance (ANOVA) was applied for the planning of experiments, data processing and statistical analysis of the obtained results and model validation.

## Results and discussion

Various phosphate sorption experiments in the batch mode were performed for two reasons. First of all, in the direction of the conventional approach, which together with the OVAT methodology, aims to fill the gaps of previous studies regarding the identification of critical sorption conditions and the clarification of the sorption mechanism under these conditions. The second reason is to reveal the interaction effects of independent factors on a measured response (phosphate removal efficiency), to optimize the sorption process (prediction of optimal experimental conditions for maximum phosphate sorption) according to CCD under RSM. According to the first reason, studies of the sorption process were performed from the aspect of understanding the sorption mechanism. Namely, the chemical and physical interactions between the sorbent and the phosphate ions are responsible for the phosphate removal from the aqueous solution [8]. Given that various mechanisms are possible (ion exchange, electrostatic interaction, hydrogen bonding, complexation of the outer or inner sphere), clarification of the phosphate sorption mechanism is of particular importance. Considering that the sorption mechanism is interconnected to the kinetics, sorption isotherms, thermodynamics and sorption capacity, these conventional tests were first carried out. For this purpose, the concentration range of the simulated aqueous solutions was chosen considering the possible phosphate concentrations in typical wastewaters [3].

### Batch sorption study

The phosphate removal efficiency using the QALS sorbent was monitored as a function of the sorbent-sorbate contact time (0-90 min) and the initial phosphate concentration (10-100 mg/L), under constant values of the other sorption conditions (ambient temperature 20 °C, pH value 6, sorbent dose 2 g/L, and stirring at 150 rpm) (Figure 1).

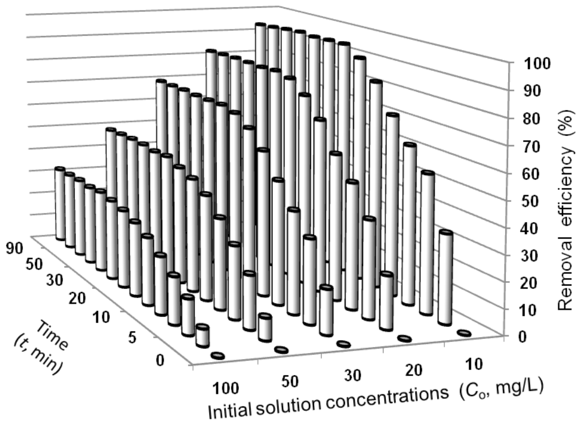


**Figure 1.** Effects of initial solution concentration and sorbent-sorbate contact time on phosphate removal efficiency.

In all observed cases of initial solution concentrations, the efficiency of phosphate removal increases sharply up to 15 min, probably due to the higher mass transfer driving force. After this period, a slower process follows due to the decrease in the driving force over time, until the equilibrium is established in the system. As shown in Figure 1, the removal efficiency of phosphate gradually decreases (from 93% to 30%) with increasing solution initial concentration (from 10 mg/L to 100 mg/L). The reason for this is that the active sorption centers become saturated quickly at higher initial concentrations. However, it is understood that the amount of sorbed phosphate increases (from 4.5 to 16.7 mg/g) with an increase in initial concentration (from 10 mg/L to 100 mg/L). This is understandable given that at higher initial concentrations the driving forces (diffusion gradient) are greater, while the barriers of mass transfer between the solid interfaces and solution are overcome. Conducted batch sorption experiments suggest that the optimal sorption time is between 40-50 min (depending on the initial concentration) when the equilibrium of the process is achieved. Similar findings have been reported in the literature [17-19].

### Sorption kinetics

Sorption kinetics is important for clarification of the reaction pathway, the rate constant, and the process control mechanism [17-19]. The kinetics of phosphate sorption was analyzed through batch experiments involving monitoring the concentrations of phosphate solutions during the sorption time. To define the kinetics of sorption in the fluid-solid system, typical kinetic models (Eqs. 3 and 4) were selected. The linear regression analysis method was applied to the experimental results obtained under the following conditions: initial concentrations 10-50 mg/L, pH 6, contact time 0-50 min, sorbent dose 2 g/L, temperature 20 °C, and stirring at 150 rpm. The corresponding kinetic parameters of the applied models are shown in Table 1. The Lagergren model can be applied to describe the sorption process up to 30 min (before reaching equilibrium), while the Ho model describes the entire (0–50 min) sorption process [17]. Based on the increase in the $k_1$ constant, it is evident that the removal of phosphate from the solution with a higher initial concentration takes place significantly faster, which can be explained by a higher driving force. For both applied models, the experimental values ($Q_{e\ exp}$) were comparable to the calculated values of equilibrium capacity (Qe cal). However, a significantly better agreement achieved using the Ho model ($R^2$> 0.99) suggests that the pseudo-second-order equation better describes the kinetics of the phosphate sorption by QALS sorbent.

**Table 1.** Sorption kinetics parameters

| Parameters / Models | | Pseudo-1st-order linear model | | | Pseudo-2nd-order linear model | | |
|---|---|---|---|---|---|---|---|
| Initial concentrations (mg P / L) | $Q_{e\ exp}$ (mg/g) | $Q_{e\ cal}$ (mg/g) | $k_1$ ($min^{-1}$) | $R^2$ | $Q_{e\ cal}$ (mg/g) | $k_2$ (g/mg min) | $R^2$ |
| 10 | 4.72 | 4.48 | - 0.146 | 0.988 | 4.78 | 0.109 | 0.998 |
| 20 | 8.21 | 8.29 | - 0.128 | 0.994 | 8.55 | 0.036 | 0.996 |
| 30 | 10.35 | 10.53 | - 0.129 | 0.994 | 10.87 | 0.028 | 0.996 |
| 50 | 12.24 | 13.01 | - 0.134 | 0.999 | 12.82 | 0.021 | 0.994 |

Similar reported results for phosphate sorption indicate a possible mechanism of chemisorption on the sorbent surface as the rate-limiting step [12]. However, this statement should be accepted conditionally, given that phosphate diffusion in the interior of the porous sorbent is also possible (depending on the structure and size of the pores). Thus, intraparticle diffusion may be an important rate-limiting step in phosphate sorption. Additionally, literature data related to the intraparticle diffusion model (Weber-Morris model) contribute to clarifying the sorption mechanism [17-19]. Consequently, the phosphate sorption by QALS sorbent takes place by a more complex mechanism for which a certain degree of control at the boundary layer is characterized. This indicates that surface sorption is not the only control step of the sorption rate, but that an intraparticle diffusion mechanism is also included.

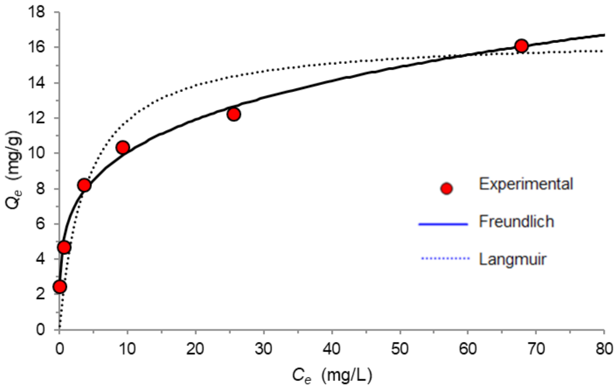


**Figure 2.** The plot of Langmuir and Freundlich sorption isotherm ($C_o$ = 10-100 mg/L, $m_{sorbent}$ = 2 g/L, pH = 6.0, $T$ = 20 °C; $t$ = 60 min; mixing speed = 150 rpm)

### Sorption isotherm

The Langmuir model is based on the assumption that the surface of the sorbent during sorption is covered by only one layer of sorbate (asymptotic approach). In contrast, the Freundlich model describes sorption on a heterogeneous surface, where multi-layer sorption occurs with the observation that the sorbent amount increases with increasing equilibrium concentration [17-19]. Langmuir and Freundlich sorption isotherm for phosphate sorption process and agreement with experimental results are presented in Figure 2.

The corresponding parameters of the sorption isotherm models are summarized in Table 2. Based on the data obtained by non-linear regression, it is clear that the Freundlich model better describes the system ($R^2$ = 0.995, $\chi^2$ = 0.169) compared to the Langmuir model ($R^2$ = 0.889). The favorability of the sorption process was evaluated based on the Freundlich constant $n_F$ (). The $n_F$ value (4.09 > 1), as a measure of deviation from linearity, indicates favorable sorption of phosphate, whereby sorption is significantly more favorable at higher initial concentrations of the solution. The 1/n value (0.244 < 1) suggests that chemisorption is the dominant process, but not the only one [17-19]. Based on the Freundlich constant $K_F$ (5.728) the sorption capacity of the sorbent was estimated (at 17.85 mg/g), which compared to the experimental value (17.77 mg/g) gives an acceptable relative deviation (0.46%).

**Table 2.** Freundlich and Langmuir isotherm constants obtained by non-linear regression

| Isotherm | Constants | | Statistical parameters | |
|---|---|---|---|---|
| Langmuir | $Q_{max}$ (mg/g) | 16.608 | $R^2$ | 0.8899 |
| | $K_L$ (L/mg) | 0.249 | $\chi^2$ | 4.1923 |
| Freundlich | $K_F$ (mg/g)(mg/L)$^{1/n}$ | 5.728 | $R^2$ | 0.9955 |
| | 1/$n$ | 0.244 | $\chi^2$ | 0.1693 |
| | $n_F$ | 4.090 | $Q_{estimated}$ (mg/g) = 17.85 | |

### OVAT monothetic analysis

The OVAT methodology, as a monothetic analysis, is an experimental design method that involves testing one factor at a time (sorption conditions) instead of several factors simultaneously. Although the RSM design method is more favored in the case of multifactorial analysis, the OVAT approach may have an advantage over fractional factorial analysis under certain conditions, such as a limited number of cycles, achieving improvement in the system under investigation, and when the experimental error is not large in comparison with the value of factor effects (in case the factors are independent of each other).

The univariate OVAT experimental approach was used to investigate the sorption of phosphate ions from the solution using the QALS sorbent. The choice of input variables for the study and optimization of the phosphate sorption process was made in accordance with literature data on the most influential sorption parameters, which indicate that the dose of sorbent and the speed of mixing have the least influence in relation to other more significant parameters [17-19]. For the OVAT approach, four input variables were selected and studied (initial solution concentration, pH value, time, and temperature), while the mixing (150 rpm) and sorbent dose (2 g/L) were used as fixed parameters in all experiments. The primary screening of the phosphate sorption process using OVAT analysis showed that positive and sometimes minimal effects on phosphate removal efficiency were achieved among the conducted experiments. The experimental combinations of various effects used in this OVAT analysis are detailed below.

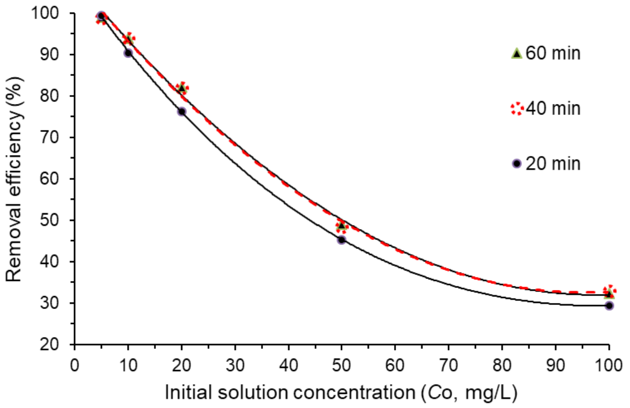


**Figure 3.** Effect of the initial solution concentration ($C_o$) on the phosphate removal efficiency (%) using QALS sorbent at different contact times (20, 40 and 60 min), constant parameters (pH = 6.0, $T$ = 20 °C), and fixed sorption conditions (sorbent dose = 2 g/L, mixing speed = 150 rpm).

### Effect of initial solution concentration

In this experiment, one variable ($C_o$ = 5, 10, 20, 50, 100 mgP/L) was varied as a function of phosphate removal efficiency (%), at three selected sorbent-sorbate contact times (20, 40 and 60 min), while other sorption parameters (pH = 6.0, $T$ = 20 °C, sorbent dose = 2 g/L, mixing speed = 150 rpm) were maintained constant. The obtained results are presented in Figure 3. This experiment showed that the removal efficiency of phosphate decreases in all cases with increasing initial solution concentrations. On the other hand, it can be observed that with a longer sorbent-sorbate contact time, the removal efficiency is significantly better. The rate of phosphate uptake in the beginning (up to 20 min) is higher, probably due to the greater free sorption surface of the sorbent (available to the sorbate), after which the rate of sorption decreases. It was found that the process reaches a plateau in the time range of 40-60 min when the equilibrium of the process is established (the available sorbent surface reaches the maximum of the sorption capacity). A further increase in contact time as an input variable does not affect the sorption process. The maximum removal efficiency (95-100%) is achieved in the case of an initial concentration below 10 mg/L (typical for municipal wastewater), while the removal efficiency decreases to 50% if the initial concentration is lower than 50 mg/L during 40-60 min (typical for industrial wastewater).

### The influence of contact time

For the OVAT analysis of this effect, one variable (sorbent-sorbate contact time, $t$ = 0, 2, 5, 7, 10, 15, 20, 25, 30, 40, 50, 60 min) was varied as a function of phosphate removal efficiency (%), at three selected initial solution concentrations (10, 30 and 50 mg/L), while the other sorption parameters (pH = 6.0, $T$ = 20 °C, sorbent dose = 2 g/L, mixing speed = 150 rpm) were kept constant. In the case of considering the influence of the sorbent-sorbate contact time on phosphate removal, it is evident that the sorption process is characterized by a fast and a slow phase (Figure 4). In the first phase, sorption takes place very quickly during the first period (15-20 min). This indicates that in the initial period, the more available active sites on the sorbent surface are rapidly filled at a high phosphate concentration (due to higher diffusion of the boundary layer). The slower stage of sorption (20-40 min) is a consequence of the corresponding phosphate mass transfer to the sorbent particle and intraparticle diffusion [18,19]. Equilibrium is typically established within 40-50 minutes.

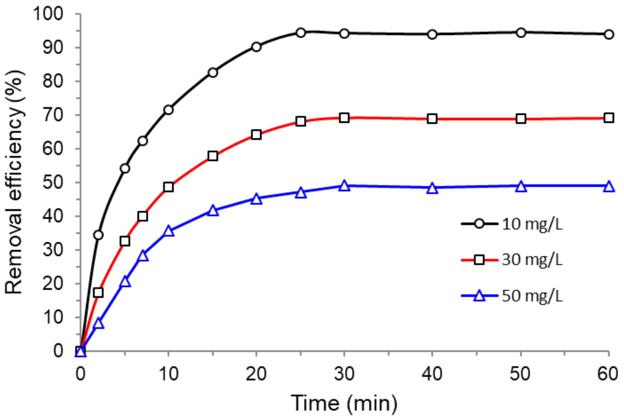


**Figure 4.** Effect of the contact time on the phosphate removal efficiency (%) using QALS sorbent at different initial solution concentrations (10, 30 and 50 mg/L), constant parameters (pH = 6.0, $T$ = 20 °C), and fixed sorption conditions (sorbent dose = 2 g/L, mixing speed = 150 rpm).

### Effect of initial pH

The pH value can be a critical factor affecting the sorption process when it comes to the removal of various phosphate anions ($H_2PO_4$-, $HPO_4^{2-}$, $PO_4^{3-}$) [19]. Given that the pH zero point of charge ($pH_{zpc}$) for the sorbent used is 7.05, it is expected that the sorption of phosphate anions at pH < 7.05 will be increased (positively charged sorbent surface). Also, phosphate sorption at pH > 7.05 should be lower due to electrostatic repulsion with competing OH- ions (negatively charged surface) [19]. In the chemical sense, the region for pH<3 should be avoided, considering that phosphate anions protonate into $H_3PO_4$ molecules, which do not have sorption ability. The efficiency of phosphate removal (%) as a function of pH value (3, 6 and 9), at the two typical initial concentrations of the solution (30 and 50 mg/L) and the constant values of other parameters ($t$ = 40 min, $T$ = 20 °C, sorbent dose = 2 g/L, mixing speed = 150 rpm), is presented in Figure 5.

The obtained results revealed that the QALS sorbent could sorb phosphate ions over a wide pH range (from 3 to 9). The maximum phosphate removal efficiency (about 70%) is achieved at a pH between 6.0 and 6.5 when the initial concentration of the solution is 30 mg/L. In the first case ($pH > pH_{zpc}$), phosphate removal efficiency decreases (from 70% to 58%) with increasing solution pH (from 6 to 9), indicating that phosphate sorption is likely based on physical (electrostatic) interactions between the sorbent surface and sorbate. At high pH values (in alkaline conditions), phosphate sorption decreases due to increased competition with $OH^-$ ions. In the second case ($pH < pH_{zpc}$), the phosphate removal efficiency decreases significantly more (from 70% to 40%) with decreasing solution pH (from 6 to 3), which is contrary to expectation. Namely, the lower efficiency of the process is a consequence of the more pronounced protonation of anions (increase in $H^+$ concentration at pH<5) and the appearance of various ionic species in the phosphate solution. It is characteristic that the more protonated ions have a smaller sorption effect ($H_3PO_4 < H_2PO_4^- < HPO_4^{2-} < PO_4^{3-}$) [19]. On the other hand, the significant values of phosphate removal at $pH > pH_{ZPC}$ suggest that in addition to electrostatic interaction, there is another sorption mechanism, probably ion exchange. Other studies report similar observations [8]. The electrostatic mechanism, which exists in both physical and chemical sorption processes, represents a reversible and easier way of sorption compared to other mechanisms. Ion exchange is also a reversible process. Similar sorption behavior was observed in solutions with a higher phosphate concentration (50 mg/L). Also, with more concentrated solutions, there is a significant decrease in phosphate removal efficiency (Figure 5). In general, it can be stated that the pH value has a significant influence on phosphate sorption, and that the sorption process is controlled by two mechanisms: electrostatic interaction and ion exchange.

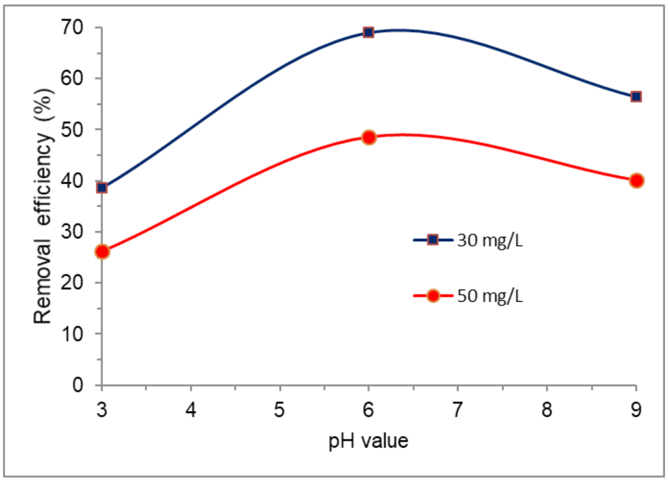


**Figure 5.** Effect of the pH value on the phosphate removal efficiency (%) using QALS sorbent at different initial solution concentrations (30 and 50 mg/L), constant parameters ($t$ = 40 min, $T$ = 20 °C), and fixed sorption conditions (sorbent dose = 2 g/L, mixing speed = 150 rpm).

### The influence of temperature

The temperature of the process can significantly affect the phosphate removal efficiency, considering the exothermic or endothermic type of sorption. In this sense, the sorption process was analyzed at different temperatures (20, 30 and 40 °C), for the two selected initial phosphate concentrations (30 and 100 mg/L) and the constant values of other parameters *($t$ = 40 min, pH = 6.0). The obtained results are presented in Figure 6. The maximum phosphate removal efficiency (about 70%) is achieved at 20 °C from a phosphate solution with an initial concentration of 30 mg/L. Research has shown that in the case of an increase in process temperature (from 20 to 40 °C), the efficiency of sorption decreases, which indicates that phosphate sorption is a spontaneous process (higher thermal energy of the system). This leads to a higher mobility of phosphate ions, which encourages enhanced desorption from the surface of the sorbent. Consequently, there is a decrease in total phosphate sorption. Similar sorption behavior was observed in solutions with a higher phosphate concentration (100 mg/L). Also, with more concentrated solutions, there is a significant decrease in phosphate removal efficiency (Figure 6).

### Thermodynamics

Thermodynamic studies provide more detailed insight into the nature and probability of sorption occurring [8,17]. The values of the characteristic thermodynamic parameters ($\Delta G$, $\Delta H$ and $\Delta S$), based on the equilibrium constant ($K_e$), characterize energetic and other possible changes during the process [18]. Thermodynamic parameters of the phosphate sorption process at different temperatures (20, 30 and 40 °C) are shown in Table 3. As previously stated, decreasing the efficiency of phosphate removal with increasing temperature (due to desorption) indicates that the sorption process is favored at lower temperatures. The exothermic nature of the process is indicated by the negative values of Δ*H* [17]. The spontaneity and feasibility of phosphate removal in the temperature range of 20-30 °C are confirmed by the values of Δ*G*<0. Namely, Δ*G* values up to –20 kJ/mol indicate electrostatic interaction between phosphate ions and active sorption centers of the sorbent. Bearing in mind that the value of Δ*H* can indicate the main sorption mechanism (multilayer physisorption up to -20 kJ/mol, ion exchange - electrostatic interaction up to -80 kJ/mol, or single-layer chemisorption up to -800 kJ/mol), it is possible to assume that phosphate sorption takes place by an ion exchange mechanism in this particular case [18]. A negative Δ*S* value indicates a stable process and that there are no structural changes on the surface of the sorbent, which is characteristic of the random behavior of the system.

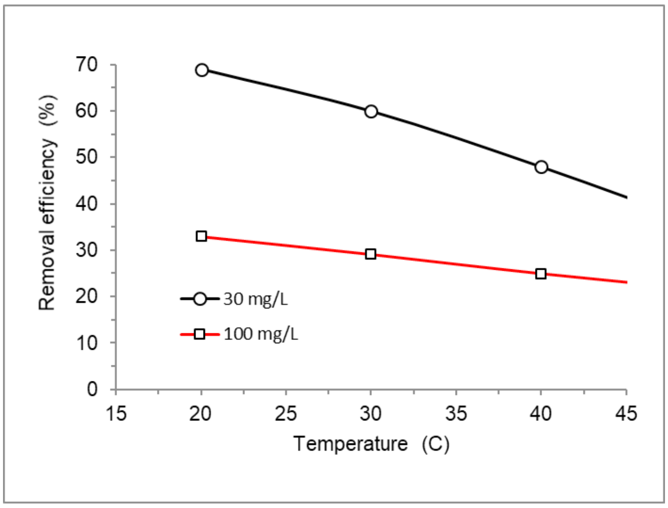


**Figure 6.** Effect of the temperature on the phosphate removal efficiency (%) using QALS sorbent at different initial solution concentrations (30 and 100 mg/L), constant parameters (*t* = 40 min, pH = 6.0), and fixed sorption conditions (sorbent dose = 2 g/L, mixing speed = 150 rpm).

**Table 3.** Thermodynamic parameters for the phosphate sorption process.

| Constants | Temperature (°C) | | |
|---|---|---|---|
| | 20 | 30 | 40 |
| $K_e$ | 2.25 | 1.51 | 0.90 |
| Δ*G* (kJ/mol) | -1.97 | -1.04 | 0.26 |
| Δ*H* (kJ/mol) | | -37.52 | |
| Δ*S* (J/molK) | | -120.8 | |
| $R^2$ | | 0.992 | |

### The outcome of the OVAT approach

During the conventional investigation of the phosphate sorption process in this study, the following facts were established. According to the equilibrium tests, the Freundlich model fits best with the experimental data, which confirms assumptions that the sorption process is reversible and takes place on two layers. The kinetics of the phosphate sorption process is best represented by the Ho model, which more closely predicts the equilibrium sorption capacity. OVAT studies applied to evaluate important experimental conditions as input variables for the phosphate sorption process ended up revealing their individual trends, as well as how these variables individually affect the final outcome (phosphate removal efficiency). Based on the OVAT analysis, the basic experimental conditions of phosphate sorption were evaluated (as central points for experimental design) as follows: there are 4 critical variables that significantly affect the sorption process (pH, $C_o$, *T* and *t*); the equilibrium of the process is achieved in a time interval of 40-50 min; maximum removal of phosphate occurs in the temperature range of 20-25 °C; a significant range of pH value is between 5 and 7; the optimal values of these studied variables depend on the phosphate initial concentration. Bearing in mind that the maximum phosphate removal efficiency (95-100%) has already been achieved in solutions typical of naturally polluted waters (phosphate content below 10 mg/L), it is more interesting to study the sorption processes in solutions simulated for municipal and industrial wastewater (initial phosphate concentrations above 30 mg/L).

However, for complete optimization of the phosphate sorption process, it is necessary to include the design of experiments (DoE). With this multivariate experimental technique, more insight can be gained into the manipulation of numerous input variables. In this sense, an RSM-CCD design was developed to fill the gaps of the previous sorption study, which was not achieved by the OVAT methodology. In accordance with the individual trend of important input variables (detected by the OVAT method), three levels (-1, 0, +1) were selected for each critical factor. The estimated values of the critical variables from the OVAT analysis were taken as the coded values for the CCD design.

### Design of sorption study

Design of experiments (DoE) is a preferable method to the OVAT approach given that it better addresses some important concerns such as achieving the same precision in effect estimation with fewer runs, the ability to estimate interactions and achieving the optimal settings of factors that OVAT may miss. Also, greater precision in estimating the effect can be achieved when all factors vary simultaneously [21]. In this study, the CCD methodology was used to reveal the interaction effects of input process factors on response. Given that increasing the initial solution concentration decreases the phosphate removal efficiency (expressed in %), while the sorbent sorption capacity rises during the sorption process, the sorbed phosphate amount per sorbent mass (Q) is chosen as the response for the CCD design. The JMP Pro16 software package (by SAS) was used for planning the experiments, and how one or more experiments should be run. Its implementation in this research is focused on the screening of the main effects, as well as the effects of two-factor interaction, which is necessary to optimize the performance of the sorption process. The CCD methodology was implemented with four input variables selected for study: A – initial concentration, B – pH value, C – temperature, and D – contact time, at three levels (Table 4).

**Table 4.** Selected values of input variables (factors) for the CCD matrix.

| Input parameters | Factors | Levels<br>low<br>-1 | center<br>0 | high<br>1 |
|---|---|---|---|---|
| Initial phosphate concentration, $C_o$ (mg/L) | A | 30 | 50 | 70 |
| pH value of the solution | B | 4 | 6 | 8 |
| Sorption temperature, *T* (°C) | C | 20 | 25 | 30 |
| Sorbent-sorbate contact time, *t* (min) | D | 20 | 40 | 60 |

In this case, for four input variables (factors) at three levels, the number of necessary experimental runs (N) was estimated based on Eq. 7, as follows: N = $2^4$ + 2x4 + 2 = 26. Of the planned 26 experiments, two replicates at the central point are intended to determine the experimental error. Thereof, 16-factor points refer to the assessing main effects and two-way interactions, 8 axial points are used to evaluate square terms, and 2 central points to evaluate the model adequacy. The corresponding CCD matrix for the four factors, randomly generated by the software, is shown in Table 5. Additionally, the influence of the combined variables on the outcome, in the form of response (Y) and predicted values of the sorbed phosphate amount (*Q*) subsequently performed by CCD, are presented in the same Table 5 for better clarity.

**Table 5.** The experimental CCD matrix with the response (Y) and predicted values of sorbed phosphate amount (*Q*).

| Runs | Pattern | A<br>$C_o$<br>(mg/L) | B<br>pH<br>value | C<br>*T*<br>(°C) | D<br>*t*<br>(min) | Response Y<br>*Q*<br>(mg P) | Predicted Y<br>*Q*<br>(mg P) | Predicted<br>Std Err |
|---|---|---|---|---|---|---|---|---|
| 1 | ---- | 30 | 4 | 20 | 20 | 15.25 | 16.05 | 0.5925 |
| 2 | +--- | 70 | 4 | 20 | 20 | 31.30 | 29.95 | 0.5925 |
| 3 | -+-- | 30 | 8 | 20 | 20 | 18.34 | 18.01 | 0.5925 |
| 4 | --+- | 30 | 4 | 30 | 20 | 11.60 | 10.28 | 0.5925 |
| 5 | ---+ | 30 | 4 | 20 | 60 | 14.60 | 16.05 | 0.5925 |
| 6 | ++-- | 70 | 8 | 20 | 20 | 28.92 | 28.01 | 0.5925 |
| 7 | +-+- | 70 | 4 | 30 | 20 | 23.97 | 24.18 | 0.5925 |
| 8 | +--+ | 70 | 4 | 20 | 60 | 30.04 | 29.95 | 0.5925 |
| 9 | -++- | 30 | 8 | 30 | 20 | 12.46 | 12.23 | 0.5925 |
| 10 | -+-+ | 30 | 8 | 20 | 60 | 17.62 | 17.99 | 0.5925 |
| 11 | --++ | 30 | 4 | 30 | 60 | 11.13 | 10.29 | 0.5925 |
| 12 | +++- | 70 | 8 | 30 | 20 | 22.90 | 22.24 | 0.5925 |
| 13 | ++-+ | 70 | 8 | 20 | 60 | 27.29 | 28.01 | 0.5925 |
| 14 | +-++ | 70 | 4 | 30 | 60 | 23.07 | 24.18 | 0.5925 |
| 15 | -+++ | 30 | 8 | 30 | 60 | 11.77 | 12.23 | 0.5925 |
| 16 | ++++ | 70 | 8 | 30 | 60 | 21.31 | 22.24 | 0.5925 |
| 17 | 0a00 | 50 | 4 | 25 | 40 | 16.17 | 17.39 | 0.6686 |
| 18 | 0A00 | 50 | 8 | 25 | 40 | 19.02 | 17.39 | 0.6686 |
| 19 | 00a0 | 50 | 6 | 20 | 40 | 25.63 | 26.41 | 0.5485 |
| 20 | 00A0 | 50 | 6 | 30 | 40 | 18.86 | 20.64 | 0.5485 |
| 21 | 000a | 50 | 6 | 25 | 20 | 21.57 | 23.52 | 0.4659 |
| 22 | 000A | 50 | 6 | 25 | 60 | 24.07 | 23.52 | 0.4659 |
| 23 | 0000 | 50 | 6 | 25 | 40 | 25.57 | 23.52 | 0.4659 |
| 24 | 0000 | 50 | 6 | 25 | 40 | 25.03 | 23.52 | 0.4659 |
| 25 | a000 | 30 | 6 | 25 | 40 | 20.69 | 20.28 | 0.7285 |
| 26 | A000 | 70 | 6 | 25 | 40 | 32.24 | 32.23 | 0.7285 |

### Development and validation of the mathematical model

In order to develop an adequate mathematical model with interaction terms, an empirical relationship was fitted between the input variables and the results obtained by CCD. The empirical relationship is based on a quadratic equation (Eq. 8). Namely, by the data multiple regression analysis for each run (Table 5), regression polynomial model coefficients were calculated and replaced in Eq. 8 to obtain an adequate model. After omitting the insignificant factors, the developed second-order polynomial model which presents the influence of significant factors on the response (Y), can be expressed in terms of coded factors (Eq. 10). In the proposed mathematical model (Eq. 10), which reveals the influence of the combined process parameters on the sorption capacity, the positive sign of the model coefficients refers to synergism and the negative sign to the antagonism of the influence.

$$Y = 23.52 + 5.98\times A - 2.88\times C - 0.97\times AB + 2.74\times A^2 - 6.13\times B^2 \quad \ldots\ldots\ldots(9)$$

### Comparison of actual and predicted values

The experimental results (response Y, Table 5) indicate a wide range of phosphate sorption (11 to 33 mg, with a mean value of 21.17) depending on the process parameters. Similar behavior is shown by the predicted values (a mean value of 21.16, SD=0.0038), with a standard error in the range of 0.46 to 0.72 (predicted Y, Table 5). The correlation diagram of the predicted and actual values of the sorbed phosphate amount is shown in Figure 7. The comparison of predicted and actual values confirms that the results evaluated by the second-order polynomial model are significantly consistent with the experimental ones ($R^2$ = 0.985) at different combinations of sorption process parameters.

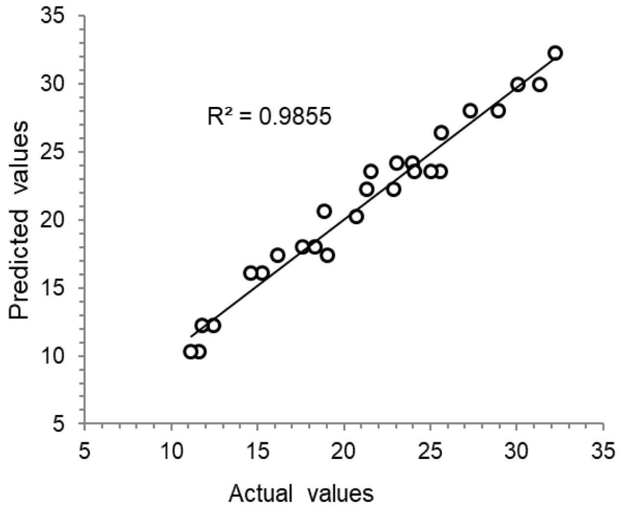


**Figure 7.** The correlation plot of the actual vs. predicted sorbed phosphate amount.

### Analytical validation

The significance of the variables, their main effects on the response, as well as the model itself, were assessed using the statistical ANOVA method (Table 6). Considering that four independent factors ($C_o$, pH, $T$, $t$) and one dependent factor (sorbed phosphate amount) were considered in this study, a two-way interaction was chosen in the multiway ANOVA to avoid possible complications associated with higher-order ANOVA [21].

**Table 6.** ANOVA test.

| | Source | DF | Sum of Squares | F Ratio | Prob > F |
|---|---|---|---|---|---|
| | Effect Tests | (* statistically significant values) | | | |
| A | $C_o$ (30,70 mg/L) | 1 | 642.96980 | 350.6550 | **< 0.0001 *** |
| B | pH (4,8) | 1 | 0.34722 | 0.1894 | 0.6719 |
| C | $T$ (20,30 $^{o}$C) | 1 | 149.76036 | 81.6745 | **< 0.0001 *** |
| D | $t$ (20,60 min) | 1 | 1.62601 | 0.8868 | 0.3666 |
| A·B | $C_o \cdot$ pH | 1 | 15.15156 | 8.2632 | **0.0151 *** |
| A·C | $C_o \cdot T$ | 1 | 3.46891 | 1.8918 | 0.1964 |
| B·C | pH $\cdot T$ | 1 | 0.33351 | 0.1819 | 0.6780 |
| A·D | $C_o \cdot t$ | 1 | 0.50766 | 0.2769 | 0.6092 |
| B·D | pH $\cdot t$ | 1 | 0.11391 | 0.0621 | 0.8078 |
| C·D | $T \cdot t$ | 1 | 0.02326 | 0.0127 | 0.9124 |
| $A^2$ | $C_o \cdot C_o$ | 1 | 27.21146 | 14.8403 | **0.0027 *** |
| $B^2$ | pH · pH | 1 | 80.60886 | 43.9615 | **< 0.0001 *** |
| $C^2$ | $T \cdot T$ | 1 | 2.36183 | 1.2881 | 0.2805 |
| $D^2$ | $t \cdot t$ | 1 | 0.38026 | 0.2074 | 0.6577 |
| | | | Lack of Fit | | |
| Lack of Fit | | 9 | 16.11215 | 1.4035 | 0.2935 |
| Pure Error | | 11 | 14.03145 | | Max $R^2$ |
| Total Error | | 20 | 30.14360 | | 0.9855 |
| | | | Analysis of Variance | | |
| Model | | 5 | 939.01800 | 124.6059 | < 0.0001 |
| Error | | 20 | 30.14360 | | |
| Cor. Total | | 25 | 969.16160 | | |
| | | | Summary of Fit | | |
| | $R^2$ | | 0.9855 | | |
| | $R^2_{pred.}$ | | 0.9688 | | |
| | $R^2_{act.}$ | | 0.9611 | | |
| | Root Mean Square Error | | 1.2276 | | |
| | Mean of Response | | 21.17 | | |
| | Observations (Sum Wgts) | | 26 | | |

### Significant variables

The significance of the factors (used parameters) and the proposed quadratic model were analyzed using ANOVA, based on combinations of F-value and probability (p-value). The significance of each variable was assessed through the analysis of variance via the Fisher statistical test. Based on the calculated high F-values (“F-ratio > 4”, Table 6) it is evident that the developed model indicates five significant variations in the response. Also, the associated “Prob>F” indicates that the model terms A, A2, B2, AB and C are statistically significant ($p<0.05$). Based on the “Effect Tests” (Table 6), it can be stated which are the most significant effects and in which order their influence decreases: A (initial concentration) > C (temperature) > BB (quadratic effect for pH) > AA (quadratic effect for initial concentration) > AB (interaction initial concentration × pH). For other values that are not statistically significant, the main effects and their interactions are excluded from further data processing. In addition, the non-significant "Lack of Fit" (Table 6), based on the F-ratio (1.4035<4), confirms that the presented second-order polynomial model (Eq. 10) describes well the influence of factors on the response, given that the p-value of 0.2935 is greater than 0.05.

### Pareto analysis

The most significant factors can also be evaluated using a Pareto plot. The results of the ANOVA analysis, presented in the form of a Pareto chart (Figure 8), show the significance of each studied variable effect based on the probability (p-value) and LogWorth value (defined as $-\log_{10}p$). The factor with the highest LogWorth value has the largest effect, and a value exceeding 2.0 means that the effect is significant at the 0.01 level. In this sense, the ANOVA analysis showed that the initial concentration (A) and the temperature (C), as well as BB, AA, and AB interactions, were significant within the confidence interval of 95% ($p \leq 0.05$).

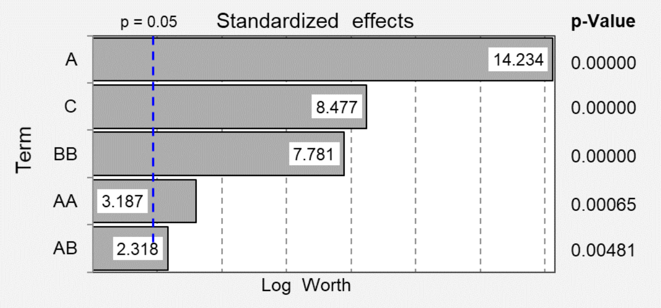


**Figure 8.** Pareto plot for CCD design experiments, showing the standardized effect of independent variables and their interaction on the response.

The parameter estimates are particularly important because of the regression model. A high significant regression at the confidence level of 95% is indicated by values of $p<0.05$. The 95% confidence intervals for each coefficient in the model are given in Table 7. This report provides an estimate of the model parameters (the regression coefficients in the quadratic model and the coefficients of linear effects), providing a t-test for each parameter under the hypothesis that it equals zero. It was observed that the initial concentration (A) offered the largest effect on phosphate sorption, with a percent contribution (PC) of about 40%.

### Model validation

The model correctness (accuracy and adequacy) was checked using an analysis of variance. Based on the determination coefficient ($R^2$) of 0.9855, the ANOVA indicated that the model is correct (Table 6). Also, the comparison of actual ($R^2_{act.}$ = 0.9611) and predicted ($R^2_{pred.}$ = 0.9688) determination coefficients confirmed that the model and experimental data fit well. Based on the statistically significant p-value of the model, which is less

**Table 7.** Parameter estimates.

| Term | Coefficient | Std Error | t Ratio | Prob > \|t\| | Lower 95% | Upper 95% | PC* (%) |
|---|---|---|---|---|---|---|---|
| Intercept | 23.523729 | 0.465979 | 50.48 | < 0.0001 | 22.551714 | 24.495743 | - |
| A | 5.9766667 | 0.289365 | 20.65 | < 0.0001 | 5.373061 | 6.580272 | 39.54 |
| C | -2.8844440 | 0.289365 | -9.97 | < 0.0001 | -3.488050 | -2.280839 | 23.55 |
| $B^2$ | -6.1349150 | 0.678099 | -9.05 | < 0.0001 | -7.549404 | -4.720426 | 21.62 |
| $A^2$ | 2.7350847 | 0.678099 | 4.03 | 0.0007 | 1.320596 | 4.149574 | 8.85 |
| A·B | -0.9731250 | 0.306918 | -3.17 | 0.0048 | -1.613345 | -0.332905 | 6.44 |

* PC – percent contribution of term

than any level of significance (<0.0001), it can be concluded that at least one term in the model explains a significant part of the variability in the amount of sorbed phosphate (Table 6). The stated statistical parameters, which confirm the statistical validity of the model, suggest that the proposed model can reasonably be used to construct a 3D response surface diagram (RSM spatial design).

### Main effects

The fact is that the separation and consideration of each input variable separately in the four input trends of the OVAT methodology did not show the entire sorption situation by which the significance of the input variable in interaction with other variables can be quantified. Unlike the OVAT approach, the special importance of the DoE methodology is that it can indicate the main effects of all studied input variables. In this sense, the main effects of the sorption process parameters studied in this research are shown in Figure 9. In the case of applying the DoE methodology, it can be seen that the $C_o$ variable shows a high positive effect on sorption (A = 5.9766), while the *T* variable has a negative effect on the sorption of phosphate by QALS (C = -2.8844). Additionally, the sorbent-sorbate contact time (D) has a very weak effect.

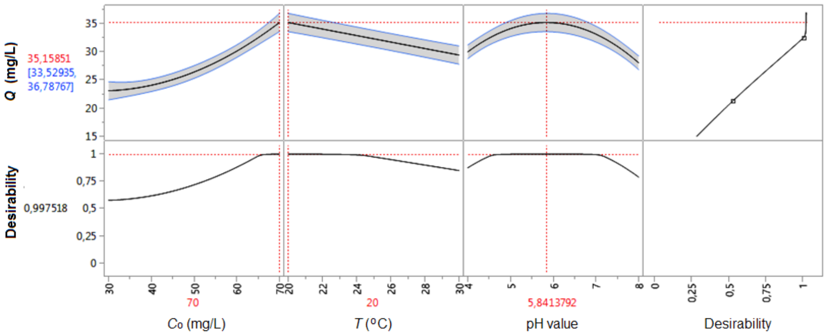


**Figure 9.** Prediction profiles, showing the sorbed phosphate amount (*Q*) as a function of initial phosphate concentration, sorption temperature and pH value.

Based on the full ANOVA analysis (Figure 9), it is evident that the sorbed phosphate amount (*Q*) increases with increasing initial phosphate concentration ($C_o$). A sudden increase of *Q* was observed in the initial solution concentrations range of 50-70 mg/L. It is expected that at a temperature of 20 °C and a pH value of 6, at an initial concentration above 65 mg/L, there will be a gradual establishment of the sorption process equilibrium. Conversely, the sorbed phosphate amount decreases with increasing temperature. The maximum value for *Q* is expected at a temperature in the range of 20–25 °C, at a pH value of 6 and at an initial concentration of 70 mg/L. In addition, the sorbed phosphate amount increases in the pH range from 4 to 6, while it decreases in the range from 6 to 8. The maximum sorbed phosphate amount is reached at pH 6. Optimum sorption is expected for a pH value in the range from 4.7 to 7, at a temperature of 20 °C and an initial concentration of 70 mg/L. In this case, the contact time factor was not analyzed, because it is not statistically significant either as a main effect or in interaction with other factors. Experiments have shown that after 30-40 minutes, the sorption equilibrium is slowly reached and there are no significant changes.

### Interaction effects of variables on the response

It is clear that in the sorption process, the input variables do not behave independently, but they interact mutually, thus creating a better presentation of the overall performance. As already mentioned, in addition to identifying the main effects, the DoE methodology is also characterized by the detection of interactions between the studied input variables. Therefore, in this multivariate approach, the interaction effects were considered according to the main effects in order to obtain a more complete picture of the sorption process.

The effects of A, B and C factors on Y response are shown in Figure 10, where non-parallel segments provide visual evidence of possible interactions. The interaction plots show that most of the two-parameter interaction effects are insignificant, except for the AB interaction (significant changes in behavior). Also, the ANOVA analysis of the CCD design (Tables 6 and 7) confirmed that the interaction between pH value (B) and initial concentration (A) was significant within the 95% confidence interval (p<0.05). The identified interaction encourages further research into the optimal sorption process using the Response Surface Methodology (RSM) design.

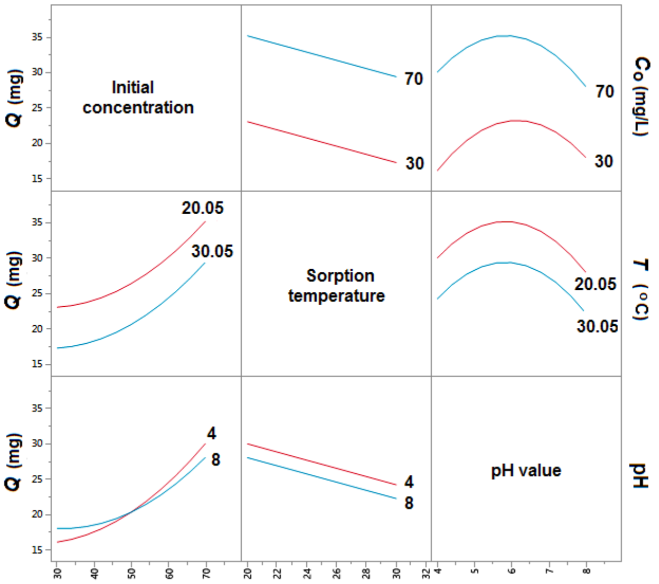
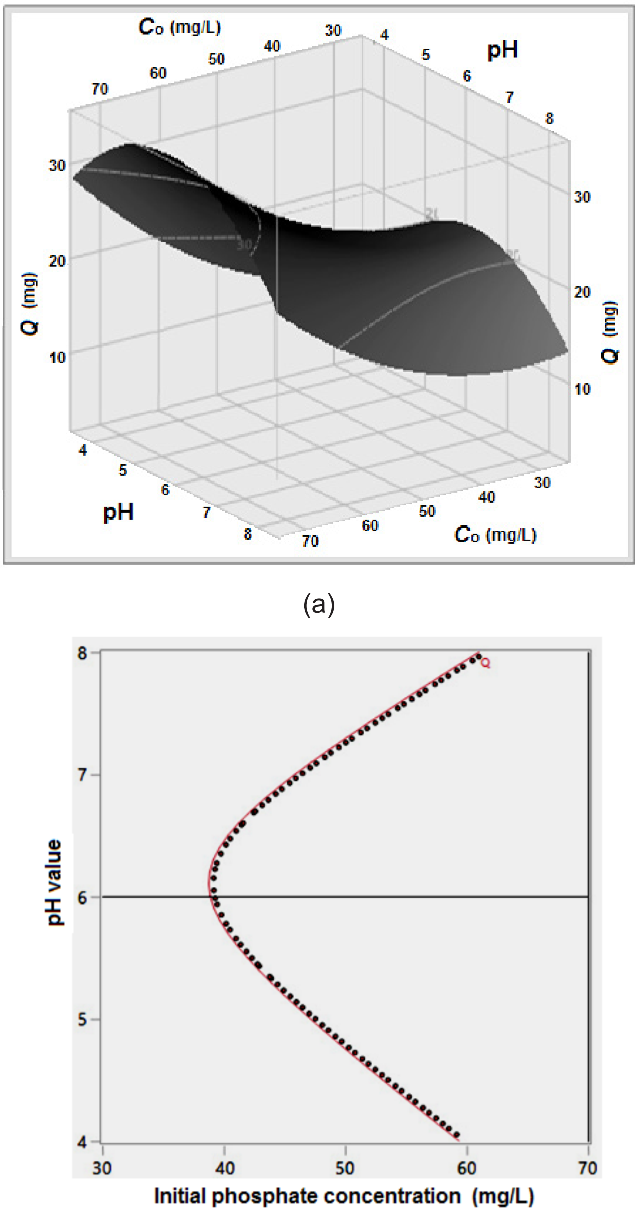


**Figure 10.** Interaction profiles, representing the interaction of the row effect with the column effect.

To further investigate the interactive effects, 3D surface plots based on RSM were analyzed. As previously determined, factor D (sorbent-sorbate contact time) and its interaction with other input variables was a non-significant model term at the 0.05 level. For this reason, the remaining AB, BC and AC interactions were included in the RSM design. From the developed model equation (Eq. 10), 3D response plots were constructed in order to visualize the relationship between variables and response.

Given that only one statistically significant two-parameter interaction effect (AB) was identified, the 3D response surface curve and the corresponding contour plot for variation of initial concentration and pH are shown in Figure 11. In this RSM set, the responses ($Q$) are represented on the Z-axis depending on the remaining two factors ($C_o$ and pH), while the other factors were maintained at their adequate level ($T$ = 20 °C, $t$ = 40 min). In the constructed 3D interaction diagram, which represents a significant interaction between initial concentration and pH, a region of higher Q values can be observed for higher values of initial concentration (≈70 mg/L) and pH value around 6. This behavior is understandable, given that a basic solution (pH>8) favors the sorption of competing OH- ions instead of target phosphates, while a more acidic solution (pH<4) favors less sorbable forms of phosphate. Hence, it follows that AB combined effect is significant in the model.



(a)

(b)

**Figure 11.** 3D Response surface graph (a) for phosphate sorption (effect of initial concentration and pH) and the corresponding contour plot (b).

To determine the maximum amount of sorbed phosphate, it is necessary to optimize the Desirability function (Prediction profiles, Figure 9). It was determined with 95% confidence that the mean value of the population for $Q$ would fall between 33.53 and 36.79 mg, for the following optimal conditions: initial solution concentration of 70 mg/L, solution pH of 5.84, and temperature of 20 °C. The value for contact time is not taken into account here (it is not a statistically significant factor), but it is assumed to be 40 min (when equilibrium is established). In accordance with that, the predicted value of $Q$ was found to be 35.16 mg. Given that 2 g of sorbent was used in all experiments, the predicted sorption capacity of the QALS sorbent is 17.58 mgP/g.

To check the practical applicability of the model, the phosphate sorption experiment was conducted again under the estimated experimental conditions of the optimal sorption process. In this validation procedure, the sorbed phosphate amount of 34.96 mg was obtained, which represents the sorbent sorption capacity of 17.48 mgP/g. This result is in very good agreement with the model's predicted response of 35.16 mg (Figure 9). The validation results show a good coincidence with the response in the RSM-CCD design, confirming the capability and applicability of the regression model.

## Conclusion

The conducted batch experiments showed that varying the sorption conditions has a different effect on the phosphate sorption efficiency of the QALS sorbents. This required an integrated study of the sorption process optimization. This sorption study successfully integrated conventional kinetic and OVAT experimental research methodologies with a DoE central composite design. The integration made a remarkable contribution in filling the gaps of all previous studies and revealing a major part of the hidden phosphate sorption process.

Primarily, conventional kinetic and equilibrium studies revealed that the pseudo-second-order kinetic model adequately describes the sorption kinetics with the ability to predict experimental equilibrium uptake and that the sorption process follows the Freundlich sorption model very well. The research using the OVAT approach managed to reveal the trends of four important input variables ($C_o$, pH, $T$ and $t$) that significantly affect the sorption process. Based on testing the minimum and maximum values of the studied variables it was found that a greater amount of sorbed phosphate from more concentrated solutions (>30 mg/L) is achieved at a lower temperature range (20-25 $^{o}$C). According to the OVAT analysis, the pH value was an important factor for optimizing the removal of phosphate in different forms from the aqueous solution. The RSM-CCD design was useful in identifying the main process factors, testing their significance, and determining the effects of factor interactions on response. A statistical quadratic model was developed and validated to predict the response in the form of sorption capacity. The adequacy of the second-order polynomial model was evaluated using regression analysis and analysis of variance. The calculated F-value (>4) and low probability ($p<0.05$) for the response demonstrate that the model is significant ($R^2$ = 0.985) and can be used to predict the amount of phosphate sorbed. RSM methodology completed the picture of the sorption process by revealing significant effects of variables: initial phosphate concentration (positive) and temperature (negative). The sorbent-sorbate contact time is not a statistically significant factor, considering that the equilibrium of the process is established at 40 min. The interaction between pH and initial phosphate concentration had a significant effect on the predicted response. With 95% confidence, it was determined that the mean value of the population for the amount of sorbed phosphate is between 33.53 and 36.79 mg under optimal sorption conditions ($C_o$ = 70 mg/L, pH = 5.84, $T$ = 20 $^{o}$C, $t$ = 40 min). In a repeated validation experiment at the predicted optimal sorption conditions, the obtained value of sorption capacity (17.48 mgP/g) was very close to the value predicted by RSM-CCD (17.58 mgP/g), which confirms the applicability of the regression model.

In general, although the efficiency levels of key process factors and the effects of their interactions are more easily observed using a multifactor DoE analysis, this study showed that the applied mathematical tools OVAT and CCD are complementary and extremely useful in improving the optimization of the phosphate sorption process, with a minimum of experiments to achieve the goal. The applied integrated research opens the door to future studies on the optimization of sorption processes, both batch and flow type, which will be directed to the removal of various anionic pollutants from real wastewaters, including a better insight into the effect of coexisting ions in solution in order to design a practical solution for the treatment of industrial wastewater.

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**Izvod**

# INTEGRISANI OVAT-RSM DIZAJN ZA POPUNJAVANJE PRAZNINA STUDIJE PROCESA SORPCIJE FOSFATA NA KATJONSKI MODIFIKOVANOJ KORI TIKVICE SUDOVNJAČE

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Studija koja uključuje konvencionalne (ravnotežu, kinetiku, termodinamiku) i OVAT eksperimentalne pristupe integrisane sa “Design of Experiments” (DoE) metodologijom sprovedena je u cilju popunjavanja praznina dosadašnjih istraživanja procesa uklanjanja fosfata iz vodenog rastvora korišćenjem hemijski modifikovane kore tikvice sudovnjače, kvaternarnog amonijum *Lagenaria vulgaris* biosorbenta. Integrisani eksperimentalni dizajn je implementiran u optimizaciji procesa sorpcije sa ciljem: predviđanja optimalnih faktora (eksperimentalnih uslova sorpcije), procene interakcijskih efekata nezavisnih varijabli na efikasnost sorpcije, određivanja maksimalnog sorpcionog kapaciteta sorbenta i pojašnjenja mehanizma sorpcija fosfata korišćenjem kinetičkih i izotermnih modela. Kritični faktori procesa sorpcije fosfata su određivani pomoću "One-Variable-At-a-Time" (OVAT) metode. Evaluacija i optimizacija interakcionih efekata faktora izvršena je korišćenjem “Central Composite Design” (CCD) u okviru “Response Surface Methodology” (RSM) analize. Za planiranje eksperimenata, obradu podataka i statističku analizu dobijenih rezultata primenjen je statistički softver (JMP Pro16), koji je nasumično generisao CCD matricu sa 4 faktora ($C_o$, pH, $T$ i vreme) na tri nivoa (-1, 0, +1). Predviđeni polinomski model drugog reda za proces sorpcije fosfata pokazao se visoko značajnim (p<0,0001). Statistički značajan efekat interakcije faktora na odgovor pokazala je interakcija između početne koncentracije fosfata ($C_o$) i pH rastvora. Maksimalni kapacitet sorpcije predviđen modelom (17,58 mg/g) u poređenju sa eksperimentalnom vrednošću (17,48 mg/g) ukazuje da se eksperiment i model veoma dobro uklapaju. Razvijen i validiran model može naći potencijalnu primenu u optimizaciji procesa prečišćavanja otpadnih voda kontaminiranih fosfatima korišćenjem ekološki prihvatljive kore tikvice sudovnjače.

**Ključne reči:** Dizajn eksperimenta, RSM-CCD, OVAT, sorpcija fosfata, *Lagenaria vulgaris.*