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Removal of phosphate from aqueous solutions using granular ferric hydroxide process optimization by response surface methodology

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ABSTRACT

Granular ferric hydroxide was used in the present study to evaluate the efficiency of phosphate removal from aqueous solutions using central composite design and optimization by response surface methodology (RSM). The interaction of important parameters including pH, contact time, adsorbent dose and initial concentration of phosphate was used on the phosphate removal process and optimization of the removal process. The design of this research was based on central composite, which is one of the methods of RSM. The number of standard samples in this study was 35. The results of optimization of the variables derived by solver command in the initial phosphate concentration were 1.78 mg L^{-1}, pH = 5.81, contact time = 82 min, and adsorbent dosage = 4.03 g, maximum removal efficiency of 92.14%. Experimental results of phosphate removal with three repetitions indicated that maximum removal efficiency of phosphate in optimal conditions was 91.6%. Also, the experimental adsorption data indicated that the data follow the pseudo-second-order kinetic model ($R^2 = 0.979$) and Freundlich isotherm model ($R^2 = 0.997$). Based on the Langmuir model, the maximum phosphate adsorption (Q_{max}) was 6.541 mg g^{-1}. In general, it can be concluded that granular ferric hydroxide with a good quality and low operating cost has high efficiency in removal of phosphate from various aqueous solutions.

Keywords: Adsorption; Phosphate; Aqueous solutions; Granular ferric hydroxide; RSM

1. Introduction

Phosphate is one of the most important materials for many industries, which is used extensively in the production of fertilizers, detergents, water softeners, and food and drink products [1,2]. Most countries in the world use phosphate as an essential material in their industrial processes [2]. Mineral phosphate salts are widely used in the pharmaceutical industry, detergents, chemical fertilizers, textiles, semiconductor components, foodstuffs, fire extinguishers and water refinery [3–5]. Urban wastewater is one of the main sources of phosphorus entry into receiving waters. Phosphorus is available in urban sewage, usually in the concentration of 4–16 mg L^{-1} and phosphorus per capita in urban areas is typically about 2–3 g d^{-1} per person [6–8]. Phosphorus plays an important role in the growth

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of plants in soil and as a limiting element in the growth of algae and in occurrence of eutrophication in surface water bodies [2]. To create the phenomenon of eutrophication, a concentration of 0.005–0.05 mg L^{-1} of phosphate is required in terms of phosphorus [9]. The standard of phosphate in drinking water is 0.2 mg L^{-1} and the standard for discharge of effluent to surface water is 6 mg L^{-1} [3,10]. The excessive biological proliferation will age the lake and reduce its quality as a result of the excessive growth of algae and plants, and the entry of toxic compounds that produces flavours and odours, reduces oxygen and changes the ecological system of the streams and rivers [11–13]. Preventing algae growth is the best possible solution to prevent water quality loss and this is possible by controlling the discharge of nutrient compounds of nitrogen and especially phosphorus [14–16]. The removal of phosphorus can be done in the form of sequestration, adsorption or by biological methods. The development of these techniques began in the 1950s following the emergence of the eutrophication phenomenon and the need to reduce phosphorus input to surface water [2,17–19]. While biological phosphorus removal methods may include disadvantages such as high sludge production, design complexity, and the need for exploitation skills, microorganism sensitivity to environmental factors and the need for a carbon source and high cost of investment and exploitation and sequestration methods has the disadvantages of high cost of chemicals and the high sludge volume and non-specificity of the process, adsorption by advanced adsorbents can be a very promising process for controlling nutrients in aquatic resources, by eliminating these limitations [20,21]. The adsorption process is a suitable method for removing phosphate from aqueous media, which increases the adsorption capacity of the materials by activating the surface [3,21]. Nowadays, the use of chelating resins is increasing and because of their high adsorption capacity, stability and selectivity, they are used in the removal of elements [22]. These resins have a polymer structure and form complexes with operating groups that have the power to select ions [22,23]. Iron oxy hydroxides are in the form of fry hydrate and are naturally available in three-capacity forms, such as hematite, magnetite and goethite [24]. The response surface methodology (RSM) is much more efficient than the old single parameter optimization methods, since it prevents time and additional material wasting. In this research, central composite design (CCD) was used to obtain the maximum information with the least number of experiments (in terms of implementation) by distributing test points in the optimal range [2,3]. This statistical method has the ability to analyze the effects of variables simultaneously. For the optimization of the four variables (pH, contact time, initial concentration of phosphate, adsorbent dose) in the present study, 35 experiments were considered.

According to the searches conducted, there was no study investigating the efficiency of the granular ferric hydroxide shell with this model. Since this material, as a cheap adsorbent, has appropriate adsorption ability, the researchers decided to implement this study. In this study, the effective variables in the adsorption process, including pH, contact time, initial concentration of phosphate, adsorbent dose were investigated for the first time using RSM.

2. Material and methods

2.1. Chemicals

The chemicals used in this study, such Sodium hydroxide, hydrochloric acid, were purchased from Sigma-Aldrich Company (USA) and potassium dihydrogen phosphate (KH_2PO_4) was purchased from Kimia Pars Shayankar Co. in Iran. All of the chemicals used were of laboratory grade.

2.2. Characteristics of adsorbent

In this study, the performance of a type of adsorbent resin of granular ferric hydroxide (GFH) from the crystallized-FeOH compound is weak which is mainly composed of mineral organite investigated in the removal of phosphate from aqueous solution. This resin is a new type of adsorbent containing a combination of anionic polymer resin and iron oxide with a zeolite structure (α-FeOOH). The pores of this adsorbent have been coated with specific processes by iron oxides on a nanometer scale. This thin and highly active iron oxide layer acts selectively and removes phosphate from the aqueous solution. The structure of polystyrene resin provides high mechanical strength and ductility. SEM image and schematic of GFH is shown in Fig. 1. Due to the uniformity of the particle size of the resin, when it is used as a filter, liquid flows uniformly through the resin and the amount of pump energy decreases for the same operation due to the homogeneous particle shape. The physical and chemical characteristics of materials purchased from the Wasserchemie German company are listed in the Table1. Initially, in order to remove moisture, GFH was placed in the oven for 90 min at 105°C and then cooled down in the desiccator.

2.3. Adsorption experiments

First, a soluble salt of potassium dihydrogen phosphate (KH_2PO_4) was used to prepare the stock phosphate solution. As based on the method of 4,500 books, the standard method consumes 0.2195 g of salt of potassium hydrogen phosphate in distilled water and it is diluted to 1,000 mL volume to make a stock solution, then concentrations of 1–9 mg L^{-1} of phosphate were prepared from the stock solution [24].

The variables used in this study were initial phosphate concentrations 1–9 mg L^{-1}, contact time 15–120 min, pH 3–11 and adsorbent dosage 1–9 g. In order to completely mix the adsorbent and absorbent material, the samples were placed on a shaker (GLF 3018 model) at a speed of 250 rpm for a specified period of time. After a certain contact time, the samples were filtered with filter paper with a pore size of 0.45 microns and residual phosphate concentrations in solution were determined using the UV/VIS spectrophotometer (PerkinElmer, Lambda 25) at the wavelength of 420 nm.

Then the phosphate removal efficiency was determined by the adsorbent (granular ferric hydroxide) using the following equation:

$$\%\mathrm{RE} = \frac{\left(C_i - C_t\right)}{C_i} \times 100 \quad (1)$$

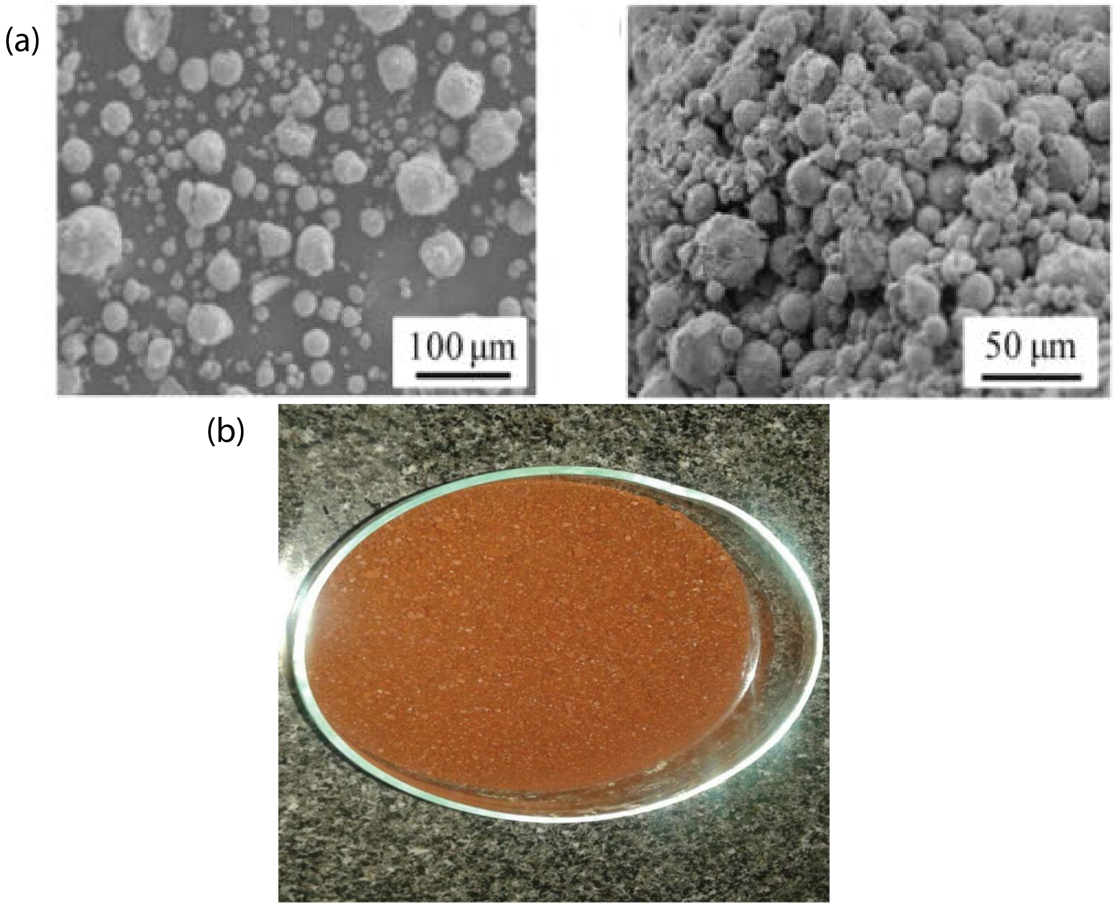


Fig. 1. SEM image (a) and schematic (b) of GFH.

Table 1
GFH properties used in the experiments

Property	Unit	Value
Saturation	Percentage	43–48
Porosity	Percentage	72–77
pH	Na	7.5–8.2
Specific surface	m^2/m^3	280
Effective size	mm	0.32–1
Uniformity coefficient	Na	About 3

Na = not available.

where C_i and C_t are the initial concentrations and concentrations at time t, respectively.

2.4. Statistical design of adsorption experiments

The central composite design was used to determine the interaction properties of pH parameters, contact time, adsorbent dosage and initial concentration of phosphate on the phosphate removal process and optimization of the removal process. Also, in different stages of determining the number of empirical tests, the RSM was used for modeling and optimization. Data analysis was performed using the software R, version 3-3-2 (2016-10-31) and Microsoft Excel version 2016 for plotting calibration curves and basic mathematical calculations. The Solver add-in program in Microsoft Excel software was used to determine the optimal values for the study variables. Table 2 shows the experimental ranges and the level of independent variables in CCD in this study. For phosphate pollutant, our preliminary guess in order to optimize the same central points of 5, 3, 67.5 and 7 was. respectively, for the concentration of phosphate, the adsorbent content, contact time and pH, according to Y was calculated. Limits are also the range of axial points that should be used in the solver command. As it is known, when all the points are equal to the central value, efficiency is equal to 80%.

Considering the above assumptions, the following results are obtained after applying the solver command.

2.5. Isotherms and kinetic studies

The adsorption isotherm equations for an adsorbent indicate the adsorption properties of the adsorbent and are very important for the design of adsorption processes. The equilibrium relationship between the amount of absorbent to the adsorbent unit (q_e) and the final concentration of solution (C_e) at constant temperature is considered as the adsorption isotherm. Various isothermal models have been described

Table 2
Experimental ranges used in CCD design for phosphate adsorption

Parameter	Limiting range		Minimum	Maximum	Average	Range
Phosphate concentration (X_1)	–1	1	1	9	5	4
pH (X_2)	–1	1	3	11	7	4
Contact time (X_3)	–1	1	15	120	67.5	52.5
Adsorbent dosage (X_4)	–1	1	1	5	3	2

for measuring the adsorption equation of the compounds in the solution. Of these, the Langmuir and Freundlich models are the most commonly used models. The experimental results of this study are based on these two models. The linear isotherm model of Langmuir assumes that single-layer adsorption on an adsorbent surface and is expressed as follows [3,8,17]:

$$\frac{C_e}{q} = \frac{1}{q_{\max}} C_e + \frac{1}{bq_{\max}} \quad (2)$$

where $q_{\max}$ (mg g^{-1}) is the surface concentration in the one-layer coating and represents the maximum q_e values that can be obtained by increasing C_e. The K_L parameter is a coefficient of adsorption energy and increases with increasing power of adsorption layers. The values of $q_{\max}$ and K_L are obtained by linear regression (C_e/q_e) vs. C_e. The Freundlich equation is expressed as follows [3,8]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

where K_F and n are the constants of the Freundlich equation. The K_F constant represents the adsorbent capacity for the absorbent material and $1/n$ is the reverse reaction degree, which indicates the performance of the adsorption power. The values of K_F and n can be obtained by plotting linear regression of log q_e vs. log C_e [2,3].

Experiments on the estimation of phosphate adsorption isotherms on the surface of granular ferric hydroxide was performed by adding different amounts of the adsorbent (from 1 to 10 g) into a series of Erlenmeyer assays with a volume of 100 mL solution each containing 1.78 mg L^{-1} of phosphorus solution. The pH of the solution was set at 5.81 (optimal value obtained from the experiment) to determine the isotherm. The samples were then contacted with the adsorbent for 82 h on a laboratory shaker at 250 rpm and at constant temperature (25°C). After passing the predetermined time and passing the samples through the filter, the concentration of residual phosphorus was read by spectrophotometer at the wavelength of 420 nm. The phosphorus content adsorbed on the adsorbent particles was determined based on the following equilibrium mass equation [3]:

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (4)$$

where q_e is the adsorption capacity (mg of phosphorus metal adsorbed per the adsorbent unit – mg g^{-1}), V represents solution volume (L), C_0 and C_e, respectively, denote the initial and secondary concentrations of phosphorus metal (mg L^{-1}) and m is the adsorbent mass added (g).

Adsorption kinetics is among the most important factors for the design of adsorption systems and determination of adsorbent residence time in the adsorption process. The adsorption kinetics depend on the physical and chemical properties of the adsorbent and somewhat determines the type of mechanism of the adsorption system. The most commonly used adsorption kinetics is pseudo-first and second-order models. The pseudo-first-order model has been presented by the Lagergren. The general form of the equation of the quasi-first-order model is as follows [2,4]:

$$q_t = q_e\left(1 - e^{-k_1 t}\right); \quad h_0 = k_1 q_e \quad (5)$$

where q_e and q_t are the adsorption capacity, respectively, at equilibrium time and at time t (mg g^{-1}), t is the time (min), k_1 is the first-rate adsorption rate constant (min^{-1}) and h_0 denotes the initial adsorption rate in the pseudo-first-order kinetics (mg g^{-1} min^{-1}).

The pseudo-second-order model has been presented by h_0. The general form of the pseudo-second-order equation is as follows [3]:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}; \quad h_0 = k_2 q_e^2 \quad (6)$$

where k_2 is a pseudo-second-order kinetic constant (mg g^{-1} min^{-1}) and h_0 is the initial adsorption rate in the pseudo-second-order kinetics (mg g^{-1} min^{-1}).

3. Results and discussion

3.1. RSM model analysis for phosphate removal

When our aim is to find the optimal point or points in problem solving, or if we are suspecting to a higher-level model, the use of the RSM seems necessary. The observed values for phosphate removal efficiency (percentages) are shown in Table 3.

Also, the results of analysis of variance and regression for the RSM are provided in Tables 4 and 5. Based on the results obtained from the analysis of variance, the values of adjusted R^2 = 0.9686 were close to multiple R^2 = 0.9815. Therefore, the quadratic model can well predict the effect of independent parameters on the phosphate adsorption process. Also, the insignificant values of lack of fit = 0.3409875 (>0.05) and the significant value of p-value = 3.39e-14 (<0.05) showed that this model is significant and can estimate the appropriate phosphate removal. In the regression analysis of

Table 3
Observed values for phosphate removal

Run No.	Phosphate concentration (mg L^{-1})	pH	Contact time (min)	Adsorbent (g L^{-1})	Observed values (%)
1	3	7	67.5	3	20
2	3	5	93.75	4	65
3	3	7	67.5	3	35
4	3	9	41.25	2	74
5	3	5	93.75	2	84
6	3	5	93.75	2	58
7	3	7	67.5	3	76
8	3	7	67.5	3	67
9	7	9	93.75	4	59
10	7	7	67.5	3	39
11	7	9	93.75	2	62
12	7	9	93.75	2	50
13	7	5	93.75	4	24
14	7	9	41.25	4	32
15	7	9	93.75	4	65
16	7	7	67.5	3	67
17	5	5	41.25	2	74
18	5	5	41.25	4	70
19	5	5	41.25	2	31
20	5	9	41.25	4	63
21	1	9	41.25	2	79
22	5	7	67.5	3	74
23	5	5	41.25	4	11.9
24	5	3	67.5	3	79
25	5	7	67.5	1	81
26	5	7	67.5	3	83
27	5	7	67.5	3	80
28	5	7	67.5	3	78
29	5	7	67.5	3	80
30	5	7	15	3	83
31	5	7	67.5	3	82
32	5	7	67.5	3	77
33	9	11	67.5	3	59
34	5	7	120	3	83
35	5	7	67.5	5	82

phosphate removal, the values of significance can be detected according to the coefficients of Pr(>|*t*|) and *p*-value. The results of regression analysis showed that all the models of the variables studied were significant, except the interaction between pH parameters and initial concentration of phosphate, adsorbent dose and phosphate concentration, pH and dose of adsorbent, contact time and adsorbent dose, which were not significant. In addition, the maximum *t*-value was related to the contact time parameter (11.7074).

The final equation of the second-order regression model of phosphate removal was obtained by multiple regression analysis on the coded data as follows:

$$\begin{aligned} Y = {} & 80.0000 - 10.0833X_1 - 29.2667X_2 + 17.4167X_3 + \\ & 8.9167X_4 + 2.7500X_1 \times X_2 - 10.7500X_1 \times X_3 - \\ & 5.2500X_1 \times X_4 + 18.75X_2 \times X_3 + 4.2500X_2 \times X_4 - \\ & 1.2500X_3 \times X_4 - 13.6167X_1^2 - 39.6667X_2^2 - \\ & 32.1167X_3^2 - 10.1167X_4^2 \end{aligned} \tag{7}$$

where Y = removal efficiency; X_1 = phosphate concentration (mg L^{-1}); X_2 = pH value; X_3 = contact time (min); X_4 = dsorbent dosage (g L^{-1}).

The results of optimization of the solver variables in the initial concentration of phosphate were 1.78 mg L^{-1}, pH = 5.81, contact time equal to 82 min and adsorbent consumption of 4.03 g, maximum removal efficiency of 92.14%. Experimental results of phosphate removal with three repetitions indicated that maximum removal efficiency of phosphate was 91.6% in optimal conditions. Therefore, the experimental results confirm optimization conditions for phosphate removal by the RSM. Figs. 1 and 2, respectively, illustrate the contour diagrams and three-dimensional diagrams related to the interactions of different parameters in phosphate removal.

The results of this study showed that by increasing the adsorbent dosage, contact time and decreasing pH, the phosphorus removal efficiency increased. Reducing the phosphorus concentration will increase efficiency; this is due to the presence of more vacant spaces for the phosphate adsorption process on the granular ferric hydroxide.

3.2. Effect of pH on the phosphate removal process

The effect of pH and initial concentration of phosphate on the adsorption process is shown in Figs. 2a and 3a. At this stage, the contact time and adsorbent dose are 67.5 min and 3 g L^{-1}, respectively. The highest amount of phosphate removal is observed at pH of 5.81 and low initial concentration of phosphate. Therefore, increasing the removal of phosphate in low pH can be due to the competition between H$^+$ ions and negative phosphate ions in the solution [2,21].

In a study conducted by Shams et al. [25], using GFH adsorbent, they removed the fluoride ion from aqueous solution. The results showed that by increasing pH from 4 to 12, the fluoride removal rate decreased. In this study, the optimal pH for removing the pollutant was 4–8 [25]. In another study, where GFH adsorbent was used to remove sulphate, the results showed that by reducing pH, the sulphate removal efficiency increases and the optimal pH was in the range of 2–7, which is consistent with the result of our study [26].

3.3. Effect of the initial concentration of phosphate on the removal process

Figs. 2b and 3b show the interaction effects of the parameters of contact time and initial concentration of phosphate at pH of 7 and adsorbent dose of 3 g L^{-1}. As observed, the highest phosphate removal efficiency is at low concentrations of phosphate and high contact time. Because at low concentrations of phosphate, there are more binding sites for reaction of adsorption of pollutant [2].

Table 4
Regression analysis for phosphate removal

Term of model	Coefficient estimate	Standard error	*t*-value	Pr (>|*t*|)	*p*-value
Intercept	80.0000	1.098	72.8122	<2.2e-16	***
X_1	–10.0833	1.487	–6.7779	1.365E-06	***
X_2	–29.2667	1.487	–19.6728	1.479E-14	***
X_3	17.4167	1.487	11.7074	2.101E-10	***
X_4	8.9167	1.487	5.9937	7.344E-6	***
$X_1 \times X_2$	2.7500	3.644	0.7547	0.4592484	
$X_1 \times X_3$	–10.7500	3.644	–2.9200	0.0079165	**
$X_1 \times X_4$	5.2500	3.644	–1.4407	0.1651390	
$X_2 \times X_3$	18.7500	3.644	5.1454	4.925E-05	***
$X_2 \times X_4$	4.2500	3.644	1.1663	0.2572166	
$X_3 \times X_4$	–1.2500	3.644	–0.3430	0.7351576	
X_1^2	–13.6167	2.596	–5.2449	3.924E-05	***
X_2^2	–39.6667	2.596	–15.2789	1.712E-12	***
X_3^2	–32.1167	2.596	–12.3708	7.926E-11	***
X_4^2	–10.1167	2.596	–3.8968	0.0008955	***

Code of significance: ***$P < 0.001$, **$P < 0.01$, *$P < 0.05$

Table 5
Analysis of variance (ANOVA) for phosphate removal

Model formula in RSM X_1, X_2, X_3, X_4	DF	Sum of squares	Mean square	*F*-value	Probability (>*F*)
First-order response	4	8,046.4	2,011.59	151.4869	1.184e-14
Two-way interaction	6	521.9	86.98	6.5501	0.0006052
Pure quadratic response	4	5,524.7	1,381.18	104.0123	4.344E-13
Residuals	20	265.6	13.28	–	–
Lack of fit	10	183.6	18.36	2.2388	–
Pure error	10	82.0	8.20	–	–

Lack of fit = 0.3409875, multiple R^2 = 0.9815, adjusted R^2 = 0.9686, *F*-statistic = 75.81 on 14 and 29 DF.

3.4. Effect of contact time on the removal process

Contact time is one of the most important parameters affecting the removal rate, and also economically affects the fabrication cost of purification units [27].

Figs. 2c and 3c show the interaction effect of the parameters of contact time and pH on the phosphate adsorption process. The results indicate that at low pH and high contact time, the efficiency of phosphate removal by granular ferric hydroxide increases. At high contact time, due to sufficient time for contact and adsorption of the pollutant, the removal efficiency is also increased. So that more than 50% of the removal occurs during the first 15 min of contact of adsorbent with the pollutant.

Also, the effect of two variables of the adsorption dose and contact time on the phosphate removal process has been shown in Figs. 2f and 3f. In these figures, it has been determined that at high contact time and high initial adsorbent dose, the efficiency of phosphate removal is increased to a large extent and then decreases, and this is due to the completing adsorption levels in the granular ferric hydroxide. In a study conducted by Kumar et al. [28] using this adsorbent, it was reported that the maximum removal rate occurred in the first 10 min and the time to reach the equilibrium was about 60 min. According to another study in which GFH adsorbent was used to remove bromate, the results showed that the highest removal rate was in the first 5 min and the time to reach equilibrium is 20 [29].

3.5. Effect of adsorbent dose on phosphate removal process

The effect of parameters of adsorbent dose and initial concentration of phosphate at pH of 7 and the contact time of 67.5 min is shown in Figs. 2d and 3d. The results indicate that by increasing the adsorbent content at low initial concentrations of phosphate, the phosphate removal efficiency in the adsorption process by GFH is maximum. Since at low concentrations of phosphate, it is related with high levels of adsorbent therefore, the spaces needed to adsorb phosphate are far higher and the removal process can be easily accomplished [27].

In addition, as shown in Figs. 2e and 3e, the effect of pH and adsorbent dose parameters in the phosphate adsorption process on GFH reflects the fact that at low pH and high adsorbent dose, the efficiency of the phosphate adsorption process is higher.

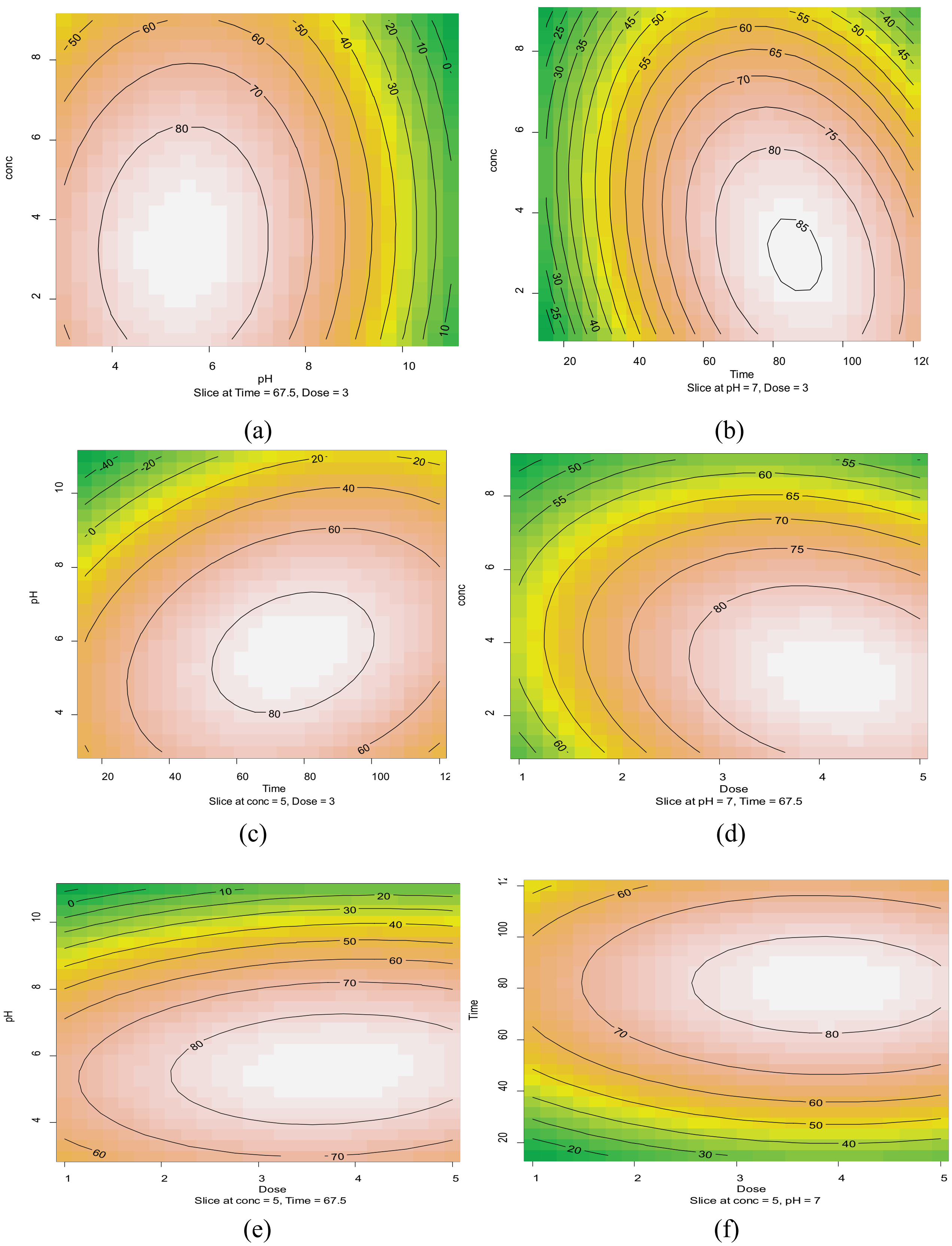
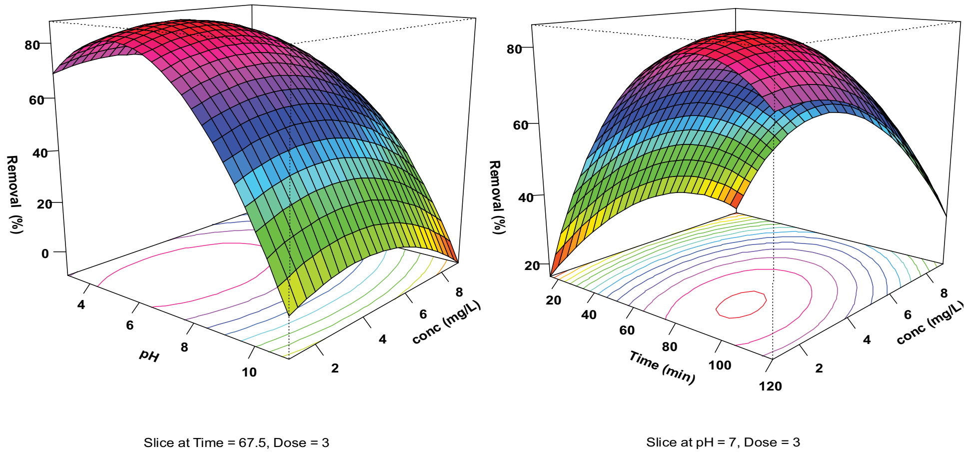
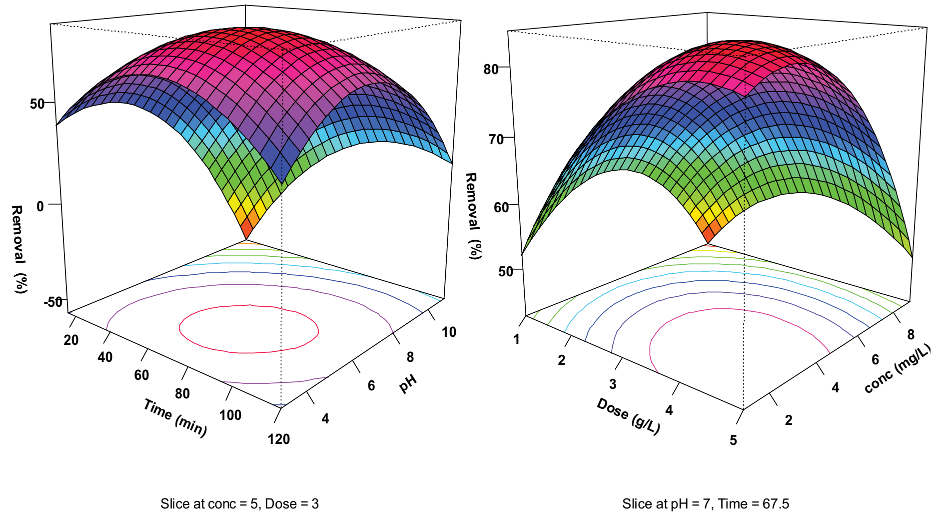


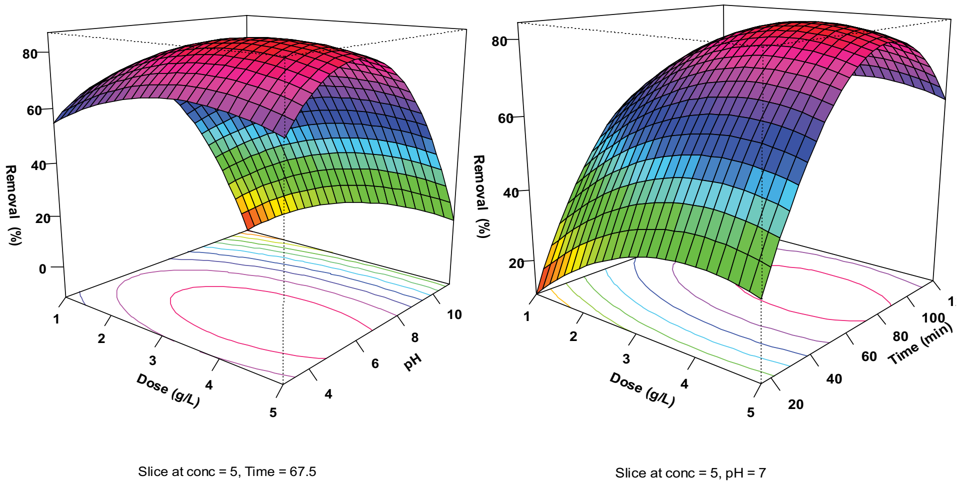
Fig. 2. Contour plots for the interaction effect of variables on the phosphate removal. (a) Phosphate concentration and pH, (b) phosphate concentration (mg L^{-1}) and contact time (min), (c) pH and contact time (min), (d) phosphate concentration (mg L^{-1}) and adsorbent dose (g L^{-1}), (e) pH and adsorbent dose (g L^{-1}), and (f) contact time (min) and adsorbent dose (g L^{-1}).



(a) (b)



(c) (d)



(e) (f)

Fig. 3. 3D plots for the interaction effect of variables on the phosphate removal. (a) phosphate concentration and pH (b) phosphate concentration (mg L^{-1}) and contact time (min), (c) pH and contact time (min), (d) phosphate concentration (mg L^{-1}) and adsorbent dose (g L^{-1}), (e) pH and adsorbent dose (g L^{-1}), and (f) contact time (min) and adsorbent dose (g L^{-1}).

3.6. Study of isotherm and adsorption kinetics

Langmuir and Freundlich models were used to study the phosphate adsorption isotherms from granular ferric hydroxide. Table 6 shows the calculated isotherm parameters of the phosphate adsorption process.

The isothermic model of the reaction indicated that the adsorption of phosphate was investigated in multi-layer form on GFH adsorbent and the maximum adsorption was 6.541 mg phosphate per gram of adsorbent and the isotherm is Freundlich type with $R^2 = 0.997$. Zhao et al. [30] in a study on the process of granular ferric hydroxide adsorbent for phosphate removal showed that the Langmuir maximum adsorption capacities of powder and granular ferric hydroxides were 74.07 and 56.18 mg g^{-1} at pH 7.0 ± 0.2, respectively, which is consistent with our study [30]. In another study using three different inorganic materials to remove phosphate from aqueous solutions, the maximum sorption capacities at 25°C was found to be 244.58 mg g^{-1} for calcined hydrotalcite at 500°C, 192.9 for calcined hydrotalcite at 400°C, 144 mg g^{-1} for goethite, 60 mg g^{-1} for hydrotalcite and 34.57 mg g^{-1} for aluminumoxid S. Also results showed that kinetic data followed a pseudo-second-order kinetic model [31].

Pseudo-first and pseudo-second-order kinetics models were used to study the kinetics of phosphate adsorption from granular ferric hydroxide. Table 7 provides the calculated kinetic parameters of the phosphate adsorption process.

According to the table, the regression coefficient (R^2) for removing phosphate in a pseudo-second-order kinetic model is higher than the pseudo-first-order model; therefore, the adsorption process for phosphate follows a pseudo-second-order model. In a study by Shams et al. [26] with granular ferric hydroxide on sulphate removal, the adsorption process followed a pseudo-second-order model which is consistent with our study. And also Xie et al. [32] examined the removal of phosphate by two lanthanum hydroxides (LHs), a commercial LH and a synthesized LH from waste alkaline solution and concluded that the phosphate adsorption data agreed well with the Langmuir model with the calculated maximum capacity of 107.53 mg g^{-1} (dry weight) for synthesized LH and 55.56 mg g^{-1} (dry weight) for commercial LH, respectively. A comparison of adsorption efficiency of different adsorbents for phosphate removal is given in Table 8.

Table 6
Isotherm and their parameters for phosphate adsorption onto GFH

Isotherm	Parameters	Values
Langmuir	K_L	1.342
	q_m (mg g^{-1})	6.541
	R^2	0.961
	R_L	0.026933–0.142418
Freundlich	K_F	3.300
	n	3.019
	R^2	0.997

Table 7
Kinetic model and their parameters for phosphate adsorption onto GFH

Kinetic model	Parameters	Value
Pseudo-first-order	K_1	–0.05
	q_e (mg g^{-1})	0.59
	R^2	0.975
Pseudo-second-order	K_2	0.04
	q_e	0.64
	R^2	0.979

Table 8
Comparison of adsorption efficiency of adsorbents for phosphate removal

Adsorbent	Adsorption capacity (mg P g^{-1})	Reference
Goethite	6.7	[33]
Hematite	5.3	[33]
Dry tailings (30% iron oxide)	8	[33]
Magnetic Fe–Zr binary oxide	13.6	[34]
Magnetite	3.2	[35]
Magnetic iron oxide	5.03	[36]
ACF-LaO	11	[37]
Red mud	0.6	[38]
Pseudo-boehmite (pseudo-γ-Al_2O_3)	13.6	[39]
Granular ferric hydroxide	6.5	This study

4. Conclusions

In this study, the application of adsorption process to remove phosphate from aqueous solutions using granular ferric hydroxide was investigated in a batch experiment with central composite design by RSM. The effect of key parameters including pH, contact time, initial concentration of phosphate and adsorbent dose on phosphate removal efficiency was evaluated. The results showed that granular ferric hydroxide with a desirable quality have low cost of operation (compared with traditional methods), the efficiency of removal of 92.1% phosphate from aqueous solutions under optimal contact time of 82 min, adsorption dose of 4.03 g L^{-1} and initial phosphate concentration of 1.78 mg L^{-1} at ambient temperature of 25°C. In general, it can be concluded that granular ferric hydroxide has a high potential for phosphate removal from aqueous solution.

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Conflict of interest

The authors of this article declare that they have no conflict of interests.

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