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Optimization of phosphate removal from drinking water with activated carbon using response surface methodology (RSM)

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ABSTRACT

The presence of phosphate in water has become a worldwide problem because of improving eutrophication and decreasing the quality of water. In this work, phosphate (PO_4^{3-}) removal from water using activated carbon was studied and main process parameters such as initial phosphate concentration (C_0), adsorbent dosage, and pH of solution have been optimized to obtain maximum removal. Central composite design in response surface methodology (RSM) package has been used to perform the experimental design according to RSM analysis, the phosphate removal model proved to be highly significant with very low probability value (<0.0001). Based on the developed predictive model, the optimum conditions were 0.53 (g/50 mL) adsorbent dosage, pH 4, and $C_0 = 11.62$ (mg/L) for having 95.41% of phosphate removal. This optimum predicted result was investigated by performing the corresponding experiment, and it was observed that the experiment and model result were fitted well. Kinetic data were analyzed using pseudo-first-order, pseudo-second-order, and intraparticle diffusion equations. According to the results, adsorption of phosphate onto activated carbon is an effective approach and economical alternative process in comparison with common applications.

Keywords: Phosphate removal; Response surface; Activated carbon; Optimization

1. Introduction

Water is the vital matter for most of the known forms of life and its quality is major concern worldwide. Increasing industrial and agricultural activities pollute water resources, so water treatment and purification are becoming more important nowadays [1,2]. Phosphate is an inorganic compound which is considered as an agricultural fertilizer. Phosphate has not been considered toxic, but has been proven to be responsible for eutrophication. Eutrophication increases algal growth, which consumes the dissolved oxygen in water. Phosphate comes to water resources from agricultural fertilizers, detergents which contain sodium tripolyphosphates, erosion of soils, and discharge from sewage treatment plants [2,3]. The US Environmental Protection Agency (US EPA) has

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determined a maximum contaminant level (MCL) of 1 (mg PO_4^{3-}) in drinking water [2,4].

Different technologies have been performed to remove phosphate such as biological treatment [5–7], chemical treatment [7], ion exchange [8,9], membrane [10], and adsorption [3,11,12]. Among these processes, adsorption was considered as an economical and efficient alternative for removing trace ions. Moreover, adsorption has simple design and operation, and post-treatment is not required [1,3,12]. Therefore, in this work, adsorption has been selected to remove phosphate from drinking water to meet the phosphate standard in drinking water. Adsorbents play a very significant role for having economical and efficient removal. A good adsorbent should have high specific surface area and provide high selectivity toward adsorbed material. Activated carbon is considered as a comprehensive adsorbent for water treatment, which shows a good adsorption of inorganic removal [1,13,14].

Accordingly, in this study, activated carbon has been used as an adsorbent for removing phosphate and operating parameters have been optimized for having maximum removal percentage. Firstly, the efficiency of activated carbon was assessed for phosphate removal. Secondly, using Design Expert software, a model was developed for predicting removal percentage with respect to the important operating parameters. Thirdly, the parameters values for having the maximum removal percentage were determined. Finally, adsorption kinetics have been studied.

2. Material and methods

2.1. Reagents

Commercial activated carbon with specific surface area, about 922 (m^2/g) was used as an adsorbent. Activated carbon was sieved to 16–35 mesh size. KH_2PO_4 was used to make phosphate solution. NaOH and HCl were used for pH adjustments. All the solutions were made using deionized water that was produced by milli-Q deionized water package.

2.2. Analytical procedure for analyzing phosphate concentration

In order to measure phosphate concentration more accurately, Lovibond package was used. After the adsorption time, phosphate solution was 10 mL of filtered through Whatman filter paper. First of all, 10 mL of filtered phosphate solution was poured in the Lovibond's cell, then put in the Lovibond device and set as zero, and after that Lovibond's tablets were added to cell and crushed, respectively. This procedure converts phosphate to molybdenum blue complex and determines phosphate concentration. The solution was then mixed until the tablets dissolved. After 10 minutes of reaction time, the concentration was measured [15].

2.3. Experimental procedures

Activated carbon was dried at 120℃ and kept in a desiccator for removal experiments. All the experiments were carried out at room temperature (25℃). For better contact, samples were shaken with constant speed of 100 rpm for 1 h with a shaker (FINEPCR, model SH30). The pH was measured and set using a pH meter (GenWay, model 3345). Removal of phosphate was carried out at different ranges of pH, concentration and adsorbent dosages in 50 mL solution based on designed experiments. All tests and analyses were performed twice to confirm the repeatability.

The removal percentages of phosphate were obtained using Eq. (1).

$$\text{Phosphate Removal }\% = \frac{C_i - C_f}{C_i} \times 100 \qquad (1)$$

where C_i and C_f are the initial and final phosphate concentration (mg/L) in solution.

2.4. Kinetic studies

In order to study the kinetic of adsorption, adsorbent was suspended in 10 mL of phosphate solution and concentration was measured at different contact times 10–60 min and shaking speed of 100 rpm. Initial concentration of solution, pH, and amount of adsorbent were set in their optimum amounts based on the Design expert optimization.

The amount of adsorbed phosphate by adsorbent after elapsing t min, q_t, was obtained from Eq. (2).

$$q_t = \frac{V(C_i - C_t)}{m} \qquad (2)$$

where V is the volume of the solution of phosphate in L, C_i and C_t are initial concentration and concentration at time t in (mg/L), and m is the amount of adsorbents in g.

3. Experimental design

Experimental design was carried out using central composite design (CCD) model in response surface methodology (RSM) package. The model was used to find a relation between response (phosphate removal percentage) and parameters. Final model which was reduced by removing unimportant factors was used to optimize the process parameters. Design expert (version 7.0.0) software was applied to analyze experimental data [16,17].

Three main parameters, including pH (X_1), initial concentration (X_2), and adsorbent dosage (X_3) were selected and introduced to Design expert. Totally 20 experiments were obtained for these three factors (using $(2^k + 2k + 6)$ which k is the number of factors). In CCD method, each factor has five levels and is coded as $-\alpha$, −1, 0, 1, $+\alpha$, where α is equal to 1.68179. The actual and coded form of variables from RSM studies have been listed in Table 1.

4. Results and discussions

Experiments have been done according to the lay out presented in Table 2. Based on the results, removal percentages of phosphate varied between 25.66 and 85.00.

4.1. Analysis of variance

The analysis of variance (ANOVA) of regression parameters of the predicted response surface model was performed and results have been reported in Table 3. According to the table, the model F-value of 241.43 and very low probability value (<0.0001) indicate that the model is significant and can be used for accurate prediction of phosphate removal. Moreover, adequate precision of the model was 56.982, which is an adequate signal for the model (adequate precision > 4). The model R-squared is 0.9893, which shows the model is able to explain 98.93%, indicating just 1.07% of total dissimilarity might not be explained by the empirical model. Also, adjusted and predicted R-squared are very close to 1, which shows the model is adjusted well with the experimental data. For variables, p-value less than 0.0500 indicate that the model terms are significant, while values greater than 0.1000 indicate that the model terms are not significant [18,19]. Therefore, X_1, X_2, X_3, X_2^2, X_3^2 are significant model terms. Based on these results, it can be concluded that this suggested model is reasonable for predicting phosphate removal percentage.

In order to determine the optimum values of variables, regression model was developed against the significant model terms. Based on the available models in RSM package, the data were fitted with quadratic model.

According to the ANOVA Table, an empirical relation between phosphate removal and important parameters can be explained by the following polynomial:

$$\text{Removal}\ \% = 56.14 - 7.64X_1 - 8.93X_2 + 11.75X_3 + 1.97X_2^2 - 2.92X_3^2 \tag{3}$$

where X_1, X_2, and X_3 were pH, initial concentration, and adsorbent dosage, respectively.

Using normal probability studentized residuals plot (Fig. 1) and predicted vs. actual plot (Fig. 2) better judgment about model adequacy can be provided. The data points in normal probability plot follow a straight line, which indicates that residuals follow a normal distribution. Moreover, the predicted vs. actual plot also follow a straight line, which indicates that this model can be used for having an accurate prediction.

RSM was performed to optimize the process. The goal of optimization was set as maximum removal, while the process parameters were set as "within the range." Based on RSM analysis, 95.41% phosphate would be removed in the case of optimum conditions of (0.53 (g/50 mL) adsorbent dosage, pH 4, and C_0 = 11.62 (mg/L)). In order to assess this prediction, an experiment was performed under these conditions, and results indicated that there is a good agreement between experimental data and model prediction (1.5% of relative error).

Table 1
Actual and coded form of selected parameters

	Actual form of coded levels				
Independent variables	$-\alpha$	−1	0	+1	$+\alpha$
X_1 (pH)	3.00	4.00	5.50	7.00	8.00
X_2 (initial concentration, mg/L)	11.48	20.00	32.50	45.00	53.52
X_3 (adsorbent dosage, g/50 mL)	0.115	0.200	0.325	0.450	0.535

Table 2
Response values for experimental conditions

Run	pH	C_0 (mg/L)	Adsorbent dosage (g/50 mL)	% Removal
1	5.50	32.50	0.325	56.00
2	8.00	32.50	0.325	39.39
3	5.50	32.50	0.325	56.92
4	7.00	45.00	0.450	51.89
5	5.50	32.50	0.115	28.00
6	7.00	45.00	0.200	30.00
7	7.00	20.00	0.450	68.00
8	5.50	32.50	0.325	56.80
9	5.50	11.48	0.325	77.35
10	7.00	20.00	0.200	45.00
11	4.00	20.00	0.450	85.00
12	4.00	45.00	0.200	41.56
13	4.00	45.00	0.450	64.87
14	5.50	53.52	0.325	45.07
15	5.50	32.50	0.535	66.77
16	3.00	32.50	0.325	25.66
17	5.50	32.50	0.325	56.81
18	5.50	32.50	0.325	56.55
19	4.00	20.00	0.200	58.00
20	5.50	32.50	0.325	56.81

Table 3
ANOVA and adequacy of the model

	Coded level				
Source	Sum of squares	D.f.	Mean square	*F*-value	*p*-value
Model	3,775.78	5	755.16	241.43	<0.0001
X_1	609.27	1	609.27	194.79	<0.0001
X_2	1,089.53	1	1,089.53	348.34	<0.0001
X_3	1,884.01	1	1,884.01	602.34	<0.0001
X_2^2	53.43	1	53.43	17.08	0.0012
X_3^2	117.32	1	117.32	37.51	<0.0001
Residuals	40.66	13	3.13	–	–
Lack of fit	40.08	8	5.01	43.12	0.0003
Pure error	0.58	5	0.12	–	–

Notes: SD = 1.77, PRESS = 100.46, $R^2 = 0.9893$, $R^2_{\text{adj}} = 0.9852$.

4.2. Adsorption kinetics

Kinetic models were carried out to discover the controlling mechanism of phosphate adsorption such as mass transfer and chemical reaction. Three general kinetic models namely pseudo-first-order, pseudo-second-order, and intraparticle diffusion were applied to study the experimental data. The pseudo-first-order, pseudo-second-order, and intraparticle diffusion are given in Eqs. (4)–(6), respectively [20].

$$\log(q_\text{e} - q_t) = \log q_\text{e} - \frac{k_1 \times t}{2.303} \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_\text{e}^2} + \frac{t}{q_\text{e}} \tag{5}$$

$$q_t = k_\text{p} t^{0.5} \tag{6}$$

where q_e (mg/g) and q_t (mg/g) are the amounts of phosphate adsorbed at equilibrium and time t, respectively. k_1 (1/min), k_2 (g/mg min) are the rate constant of pseudo-first-order and pseudo-second-order adsorption, and k_p (mg/g min$^{0.5}$) is the intraparticle diffusion rate constant. The experimental and calculated parameters of the above kinetic models are

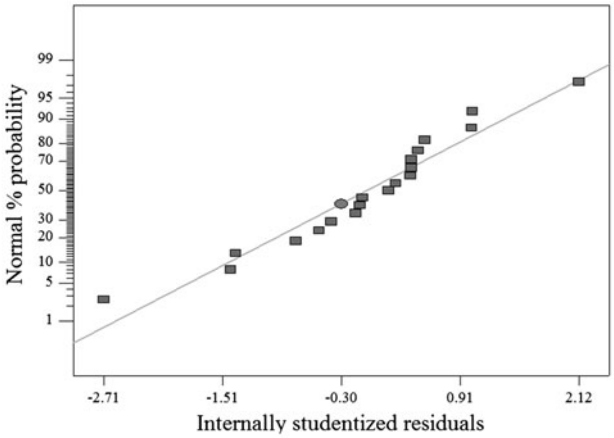

Fig. 1. Normal probability plot of studentized residual.

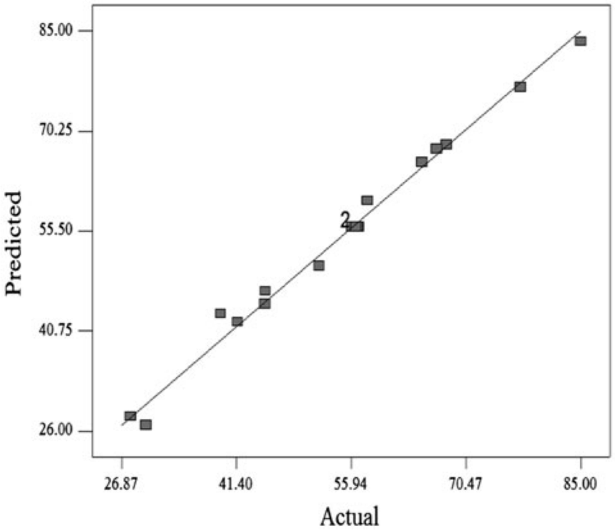

Fig. 2. Predicted values vs. actual values.

Table 4
Kinetics model parameters

Pseudo-first order	k_1 (1/min)	0.0044
	q_e (mg/g)	2.6528
	R^2	0.9669
Pseudo-second order	k_2 (g/mg min)	0.8385
	q_e (mg/g)	1.0508
	R^2	0.9999
Intraparticle diffusion	K_p (mg/g min$^{0.5}$)	0.0129
	R^2	0.9683

summarized in Table 4. As it can be seen, pseudo-second-order kinetic model shows the best fit with experimental data because of the highest amount of R^2 and closest experimental and calculated amount of adsorption.

5. Conclusion

In the present study, optimization of phosphate removal from drinking water was investigated with adsorption onto activated carbon. Process optimization concentrated on the influence of operating variables such as adsorbent dosage, initial concentration, and pH using CCD in RSM package. Furthermore, interaction between parameters was investigated, and it was indicated there is no interaction. The adjusted and predicted R^2 were 0.9852 and 0.9737, respectively, showing that the actual and predicted data fitted well. The optimum results indicated that 0.53 (g/50 mL) of adsorbent dosage was required to achieve 95.41% of phosphate removal when the phosphate concentration and pH were 11.62 (mg/L) and 4, respectively. This predicted value was obtained with 1.5% error by carrying out experiment in optimum conditions that shows a good agreement of experimental and model. Adsorption kinetics data fitted well with pseudo-second-order equation.

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