Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1067830

57 (2016) 14213–14226
June

Optimized adsorption of 4-chlorophenol onto activated carbon derived from milk vetch utilizing response surface methodology

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Received 15 October 2014; Accepted 7 June 2015

ABSTRACT

In the present study, the adsorption of 4-chlrorophenol (4-CP) from aqueous solutions was investigated using activated carbon prepared from milk vetch. Scanning electron microscopy, Brunauer–Emmett–Teller, and Fourier transform infrared were carried out to characterize as-prepared activated carbon. The adsorption process was optimized by response surface methodology based on central composite design. Accordingly, a 4-CP removal of 89.52% was obtained with a reaction time of 49 min, initial 4-CP concentration of 56 mg/L, adsorbent dosage of 1 g/L, and initial pH of 7. Among various operational parameters, the adsorbent dosage (F-value = 139.5) produced the largest effect on 4-CP removal (%), while initial pH (F-value = 0.620) presented the lowest effect. The pseudo-second-order kinetic equation described the process reasonably well ($R^2 = 0.9996$). The process followed Langmuir isotherm ($R^2 = 0.9969$) with a maximum adsorption capacity of about 87 mg/g. For chemical regeneration, during three-stage regeneration runs, the removal efficiency (%) of 4-CP decreased from 87.45 to 61.15%, while, in the case of thermal regeneration, it decreased from 87.45 to 77.68%, respectively. Overall, activated carbon derived from milk vetch can be applied as an efficient adsorbent for sequestering 4-CP from aqueous phase with relatively high reusability potential.

Keywords: Adsorption; Phenolic compounds; Precursor; Activated carbon; Experimental design

1. Introduction

The presence of refractory organic compounds in aqueous environments can cause adverse effects on aquatic life and human health [1]. Phenolic compounds are widely used in various industries such as pharmaceutical, petroleum refinery, pesticide, herbicide, dye, rubber, wood, cosmetic, paper, and coal conversion industries [2–4]. Discharging phenolic compounds into aqueous environment such as rivers and lakes is of great concerns due to their ecotoxicological and carcinogenic effects. Thus, they are classified as

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priority pollutants. Phenolic compounds can be accumulated in the environment, which can cause unpleasant taste and odor [2,5,6]. Chlorophenols are a group of phenolic compounds with chlorine atoms attached to the phenolic ring, which are widely used to synthesize herbicides, insecticides, and wood preservatives [7]. Many technologies have been applied for the removal of phenolic compounds in aqueous phase, including advanced oxidation processes, biological processes, electrochemical oxidation, reverse osmosis, and adsorption process [3,8]. Comparatively, adsorption is still the most widely used process for removing refractory organic pollutants such as phenolic compounds because of its cost-efficiency, simplicity, and low sensitivity to toxic environments [3,9–12]. A variety of adsorbents have been used for the adsorption of phenolic compounds from aqueous solutions such as activated carbon and clay minerals, namely bentonite and natural zeolites [9]. Among various adsorbents, activated carbon is considered as the most effective material for the adsorption of phenolic compounds from water and wastewater [13,14]. Because of its high cost and the need for regeneration, the application of commercial activated carbon has been limited. Thus, in recent years, activated carbon derived from low-cost agricultural wastes has been considerably used for the adsorption of target pollutants in aqueous solutions [15–19]. In the present study, the application of milk vetch (*Astragalus brachycalyx*) was considered as a new precursor for activated carbon to be used for removing 4-chlorophenol (4-CP) from aqueous phase. *A. brachycalyx* is a species of legume commonly found on rocky mountain slopes in Iran. The application of milk vetch for the preparation of activated carbon would be an economical alternative due to its low cost and availability. To the best of our knowledge, there is no report on the use of milk vetch as precursor of activated carbon and its application for the adsorption of 4-CP in aqueous solutions. To evaluate the efficiency of as-prepared activated carbon for the adsorption of 4-CP, response surface methodology (RSM) on the basis of central composite design (CCD) was applied instead of conventional one-factor-at-a-time statistical approach. The advantages of RSM include possibility of the evaluation of interactive effects of operational parameters and optimization of the operational parameters to attain maximum efficiency. Moreover, it can be performed by reduced number of experiments in comparison with the conventional approach [20–23]. This study focused on the evaluation of the effect of reaction time, initial 4-CP concentration, adsorbent dosage, and initial pH on the adsorption of 4-CP. Afterward, kinetic and isotherm studies were carried out to gain adsorptive data for the full-scale applications.

2. Materials and methods

2.1. Chemicals

All chemicals, which were of analytical grade, were purchased from Merck, Germany, and used as received. Stock solution was prepared by dissolving 1 g of 4-CP (Formula: ClC_6H_4OH; Molecular weight: 128.56 g/mol; Solubility in water (25˚C): 27 g/L; pK_a: 9.41) in 1 L of distilled water and desirable concentrations of 4-CP in experimental reactors were prepared by the dilution of stock solution. Milk vetch was gathered from a hill near city of Ilam (Iran) and used as precursor of activated carbon.

2.2. Preparation of activated carbon

To prepare activated carbon, the milk vetch shrubs were gathered, washed with distilled water, and dried in sunlight for one week. After drying in an oven at 100˚C, they were ground into small pieces. Then, dried shrubs were soaked in concentrated phosphoric acid (95%) for 30 min under string in order to activate the precursor. The weight ratio of milk vetch to phosphoric acid was adjusted to 1:10. The soaked samples were placed in a stainless steel vessel and heated at 600˚C for 1 h in an electric furnace. The resulted activated carbon was washed with distilled water until the pH of washing water reached 6.5. Finally, dried activated carbon was ground, sieved and particles between 60 and 120 mesh size were used for removing 4-CP from aqueous solutions [24].

2.3. Experimental system

100-mL Erlenmeyer flasks were applied as batch flow mode experimental reactors to conduct adsorption study. The pH of solutions was adjusted with 0.1 M HCl and 0.1 M NaOH. They were placed on a shaker (Dragonlab, Model: SK-L330-Pro, China) to agitate the flasks containing 4-CP for an efficient interaction with the adsorbent. The agitation speed and temperature were set to 300 rpm and 25˚C, respectively. The average particle size of as-prepared activated carbon was about 250 μm (see Fig. 1(a)). A control reactor without adsorbent was used to determine the adsorption of 4-CP in the absence of adsorbent. For isotherm and kinetic studies, all experiments were done duplicate and the mean values were written down.

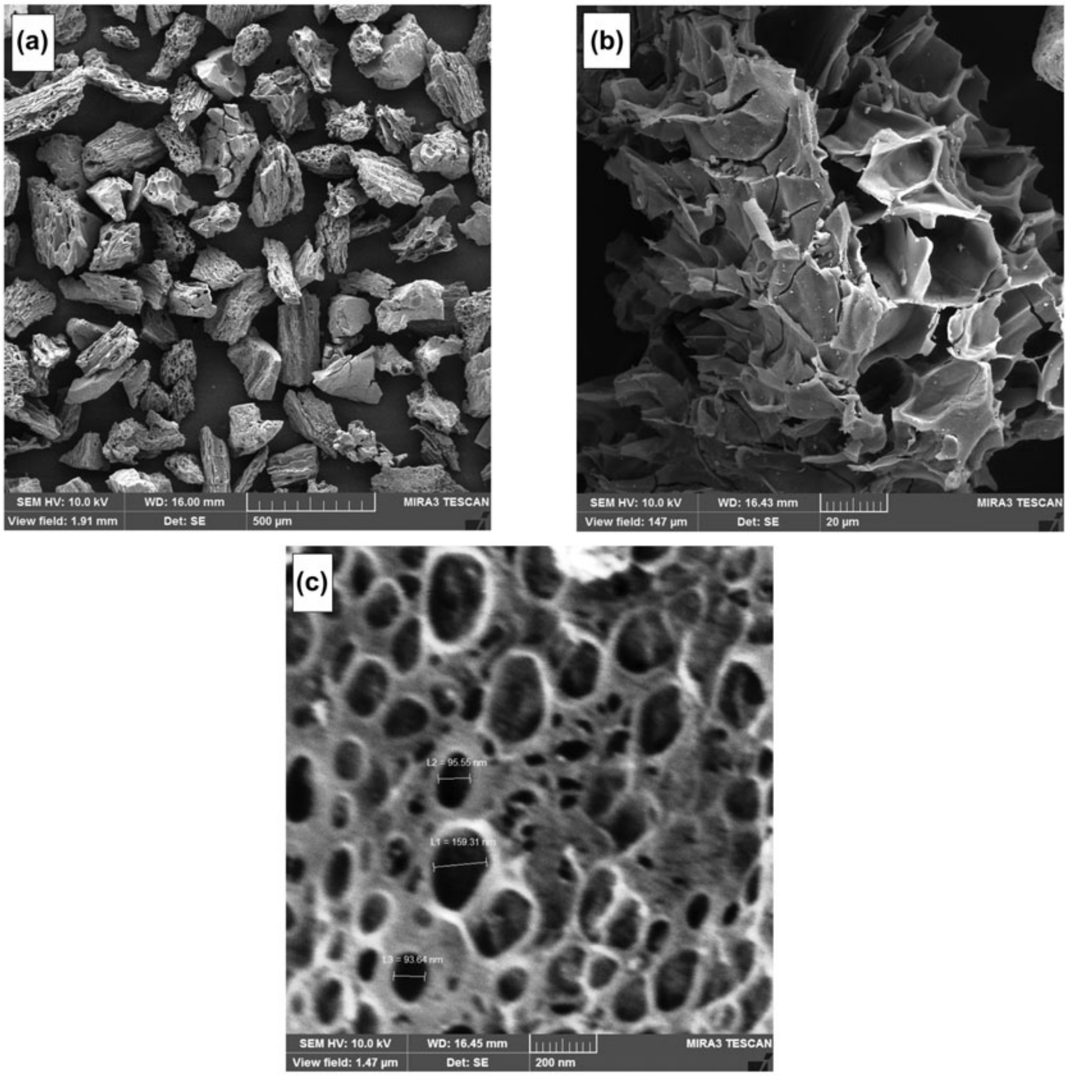

Fig. 1. SEM images of activated carbon derived from milk vetch taken at different magnifications.

2.4. Experimental design

CCD model was used to evaluate the effect of four main operational parameters, including reaction time (min), initial 4-CP concentration (mg/L), adsorbent dosage (g/L), and initial pH on the adsorption of 4-CP onto as-prepared activated carbon. The number of experiments was computed via Eq. (1):

$$N = 2^k + 2k + x_0 \tag{1}$$

where N is the number of experiments, k is the number of studied parameters, and x_0 is the number of replications as central points. Accordingly, the total number of experiments was gained to be 30 ($k = 4$, $x_0 = 6$). The studied parameters (X_i) were coded as x_i as shown in Eq. (2):

$$x_i = (X_i - X_0)/\delta X \tag{2}$$

where X_0 and δX are the values of X_i at the center point and step change, respectively. An empirical second-order polynomial equation was employed to describe the relationship between the dependent parameter (4-CP removal (%)) and the studied operational parameters as shown in Eq. (3):

$$Y = b_0 + \sum_{i=1}^{n} b_i x_i + \left(\sum_{i=1}^{n} b_{ii} x_i\right)^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j \tag{3}$$

where Y is the predicted 4-CP removal (%) and b_0, b_i, b_{ij}, and b_{ii} are constant, linear, interaction, and quadratic coefficients, respectively. Besides, x_i and x_j are the coded values of the experimental parameters. The ranges of the operational parameters are given in Table 1. The reasonable ranges of the operational parameters were determined according to the preliminary experiments.

2.5. Analytical methods

To measure the pH of solution, a Metrohm pH meter was used (Model: E532, Germany). Scanning electron microscopy (SEM) was conducted on a TESCAN microscope (Model: MIRA3, Czech Republic) to assess the surficial structure of as-prepared activated carbon. Fourier transform infrared (FT-IR) analysis was performed using a spectrophotometer (Spectrum RX I, Perkin-Elmer, USA) to determine the surficial functional groups of the adsorbent involved in the adsorption process. The point of zero charge (pH_{pzc}) of as-prepared activated carbon was measured using pH drift method to meaningfully determine the effect of surficial charge and initial pH on the adsorption process [25]. The samples were withdrawn and centrifuged for 5 min at 5,000 rpm. The residual concentration of 4-CP in the samples was measured with a UV–vis spectrophotometer (DR-5000, Hach Co, USA) at maximum wavelength of 280 nm. The removal efficiency (RE (%)) and the amount of adsorbed 4-CP were calculated through $RE\ (\%) = [1 - (C/C_o)] \times 100$ and $q = ((C_o - C) \times V)/M$ equations, respectively, where the amount of adsorbed 4-CP, the initial, and the final concentration of 4-CP in the solution are specified via q (mg/g), C_o (mg/L), and C (mg/L), respectively. In addition, V (L) and M (g) are the volume of colored solution and the weight of adsorbent added to the solution, respectively.

3. Results and discussion

3.1. Structural characteristics

It is advantageous to specify the shape, size distribution, and porosity of the adsorbent. For this, SEM analysis was carried out and its results are depicted in Fig. 1. A relatively uniform particle size distribution can be observed in Fig. 1(a). A sample of the obtained granules was selected and applied to evaluate its surficial characteristics in detail. As depicted in Fig. 1(b), as-prepared activated carbon has a highly porous structure, which is appropriate for the adsorption of 4-CP molecules into the porous network. The diameter size of some of the pores is determined and depicted on Fig. 1(c). According to the results of our previous study, the specific surface area of activated carbon derived from milk vetch was obtained to be about 565 m^2/g [19], which was much higher than rice straw-based activated carbon (5.4 m^2/g) [16] and coal-based activated carbon (331 m^2/g) [26].

The results of FT-IR analysis can be used to determine the role of active surficial functional groups in the adsorption of 4-CP. FT-IR spectra of unloaded and 4-CP-loaded activated carbon were recorded in the range of 400–4,000 cm^{-1} (Fig. 2). As shown in Fig. 2, a broad peak centered at 3,487 cm^{-1} is associated with the O–H groups [27,28]. As shown, an obvious drop in the peak of O–H groups was happened after the adsorption of 4-CP, which may be due to 4-CP bonded to the hydroxyl groups and water adsorbed on the surface of as-prepared activated carbon via hydrogen binding [11,27,29], though the formation of donor–acceptor complex and London dispersion forces (π–π dispersion interaction) cannot be neglected [26]. The London dispersion forces derive from the interactions between the π electrons in the aromatic rings of the phenolic compounds and those in the carbon layers [3]. Similar phenomenon was happened to the peak located at 1,637 cm^{-1} (corresponding to the stretching vibration of

Table 1
Ranges of the experimental parameters for the adsorption of 4-CP onto activated carbon derived from milk vetch

			Studied ranges				
Run no.	Code	Parameter	−2 (α)	−1	0	+1	+2 (α)
1	X_1	Reaction time (min)	10	25	40	55	70
2	X_2	4-CP concentration (mg/L)	30	50	70	90	110
3	X_3	Adsorbent dosage (g/L)	0.4	0.6	0.8	1.0	1.2
4	X_4	Initial pH	3	5	7	9	11

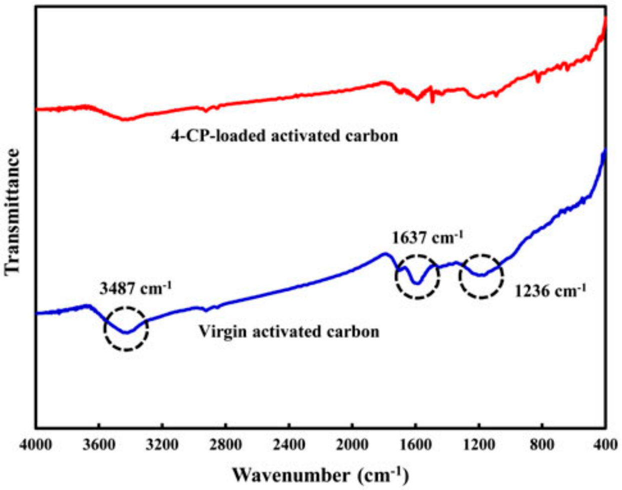

Fig. 2. FT-IR spectra of as-prepared activated carbon before and after the adsorption.

C=C groups) [30–32] and the peak located at 1,236 cm^{-1} (corresponding to the stretching vibration of –CH bonds) [33]. This confirmed the involvement of these bonds in the adsorption of 4-CP onto as-prepared activated carbon. According to the results of FT-IR analysis, it can be pointed out that the surficial functional groups of the adsorbent play significant role in the adsorption of target organic pollutant.

3.2. CCD results

RSM based on CCD was applied for the optimization of operational conditions during the adsorption of 4-CP onto as-prepared activated carbon to achieve maximum RE (%). As a result, a second-order quadratic equation was obtained to relate the relationship between independent parameters (reaction time (x_1), 4-CP concentration (x_2), adsorbent dosage (x_3), and initial pH (x_4)) and dependent parameter (RE (%)) as depicted in Eq. (4):

$$\begin{aligned} Y\ (\text{RE}\ (\%)) = {} & 80.10 + 4.09x_1 - 6.41x_2 + 12.28x_3 - 0.82x_4 \\ & - 0.47x_1x_2 - 0.57x_1x_3 - 0.33x_1x_4 \\ & + 0.60x_2x_3 - 0.72x_2x_4 + 0.42x_3x_4 - 3.52x_1^2 \\ & - 4.77x_2^2 - 5.58x_3^2 - 6.72x_4^2 \end{aligned} \tag{4}$$

The prediction of RE (%) under different operational parameters within the specified ranges can be achieved using Eq. (4). The predicted values of RE (%) were calculated through Eq. (4) and depicted in Table 2 together with the corresponding experimental RE (%). Analysis of variance (ANOVA) was employed as a helpful approach to assess significance of the CCD model for predicting the RE (%) of 4-CP [23,33,34]. The results of ANOVA are shown in Table 3. The results showed that the applied model is significant (*F*-value = 19.98 and *p*-value = 0.0001). The larger *F*-values and smaller *p*-values, the more meaningful is the applied CCD model [21]. The obtained *F*-value (19.98) was clearly larger than the tabulated value (2.352 at 95% significance), which confirmed significance of the applied model [34]. Furthermore, a high correlation coefficient ($R^2 = 0.949$) between the experimental and predicted RE (%) was obtained, indicating the suitability of applied model for describing the adsorption of 4-CP onto activated carbon. This demonstrated that 94.9% of the variations of RE (%) are explained by the model and the model does not elucidate only 5.1% of the variations in RE (%). The good agreement between the experimental and predicted RE (%) is illustrated in Fig. 3(a). Adjusted R^2 modifies R^2 considering the sample size, the number of operational parameters, and statistical conditions. The obtained value of R^2_{adj} (0.902) was close to the value of R^2 (0.949), implying a good fitness between the experimental and predicted RE (%) (Table 3). The signal-to-noise ratio can be determined by the value of "adequate precision." A ratio greater than four is favorable [11,22]. Thus, the obtained "adequate precision" of 13.64 indicates an adequate signal. Inversely, low value of the "coefficient of variation" is preferred. Therefore, low obtained value of "coefficient of variation" (CV = 8.01) indicated suitability of the applied model for the prediction of RE (%). In addition, to evaluate how well the CCD model satisfies the assumptions of ANOVA, the difference between the experimental and predicted RE (%) that is "residual" was calculated [11,34]. The plots of normal probability (%) vs. residuals, residuals vs. run number, and residuals vs. predicted RE (%) are represented in Fig. 3(b)–(d), respectively. As depicted in the plots, the residuals are randomly distributed, suggesting normal distribution of the residuals. Overall, it can be stated that the applied CCD model can be successfully used to navigate the design space. Furthermore, *F*-value of each model term can be employed to compare the significance of model terms [11,23]. As given in Table 4, among individual effects, the adsorbent dosage (*F*-value = 139.5) produced the largest effect on RE (%), while initial pH (*F*-value = 0.620) presented the lowest effect on RE (%).

Table 2
Experimental and predicted results for the adsorption of 4-CP onto as-prepared activated carbon

	Coded parameters				Actual parameters				RE (%)	
Run no.	X_1	X_2	X_3	X_4	X_1	X_2	X_3	X_4	Experimental RE (%)	Predicted RE (%)
1	+1	+1	−1	+1	55	90	0.6	9	42.46	42.11
2	−1	−1	−1	+1	25	50	0.6	9	53.48	48.93
3	0	0	0	0	40	70	0.8	7	80.10	80.10
4	0	+2	0	0	40	110	0.8	7	46.54	48.20
5	+1	−1	−1	−1	55	50	0.6	5	59.22	60.22
6	0	−2	0	0	40	30	0.8	7	74.00	73.84
7	+1	−1	+1	+1	55	50	1.0	9	76.34	81.57
8	+1	+1	−1	−1	55	90	0.6	5	44.52	46.70
9	−1	+1	+1	+1	25	90	1.0	9	64.58	62.15
10	−1	−1	+1	−1	25	50	1.0	5	74.04	72.96
11	−1	+1	−1	−1	25	90	0.6	5	44.31	37.65
12	−1	+1	–1	+1	25	90	0.6	9	37.83	34.40
13	−1	+1	+1	−1	25	90	1.0	5	62.32	63.72
14	0	0	0	0	40	70	0.8	7	80.10	80.10
15	+1	+1	+1	+1	55	90	1.0	9	66.23	67.57
16	0	0	0	0	40	70	0.8	7	80.10	80.10
17	0	0	+2	0	40	70	1.2	7	87.44	82.34
18	0	0	−2	0	40	70	0.4	7	26.62	33.21
19	0	0	0	0	40	70	0.8	7	80.10	80.10
20	0	0	0	−2	40	70	0.8	3	56.57	54.87
21	+1	+1	−1	+1	40	70	0.8	11	48.40	51.60
22	−1	−1	−1	−1	25	50	0.6	5	50.70	49.29
23	+1	−1	+1	−1	55	50	1.0	5	78.24	81.60
24	0	0	0	0	40	70	0.8	7	80.10	80.10
25	−1	−1	+1	+1	25	50	1.0	9	76.52	74.27
26	+1	+1	+1	−1	55	90	1.0	5	67.36	70.48
27	+1	−1	−1	+1	55	50	0.6	9	60.00	58.52
28	0	0	0	0	40	70	0.8	7	80.10	80.10
29	+2	0	0	0	70	70	0.8	7	82.14	74.18
30	−2	0	0	0	10	70	0.8	7	48.38	57.83

Table 3
The results of analysis of variance (ANOVA) for the adsorption of 4-CP onto activated carbon derived from milk vetch

Source	Sum of squares	Degree of freedom	Mean square	*F*-value	*p*-value	
Regression	7,259.50	14	518.54	19.98	0.0001	Significant
Residuals	389.21	15	25.95			
Lack of fit	389.21	10	38.92			
Pure error	0.000	5	0.000			
Total	7,648.71	29				

Notes: R^2 = 0.949, adjusted R^2 = 0.902, adequate precision = 13.64, coefficient of variation (CV) = 8.01 (%).

3.3. Effect of operational parameters

The three-dimensional (3D) response surface plots along with contour plots were used to evaluate the interactive effects of operational parameters. This approach was performed by varying two independent operational parameters, while all other operational parameters were constant. The interactive effect of reaction time and initial 4-CP concentration on 4-CP removal (%) is shown in Fig. 4(a) and (b), while the adsorbent dosage and initial pH were constant at

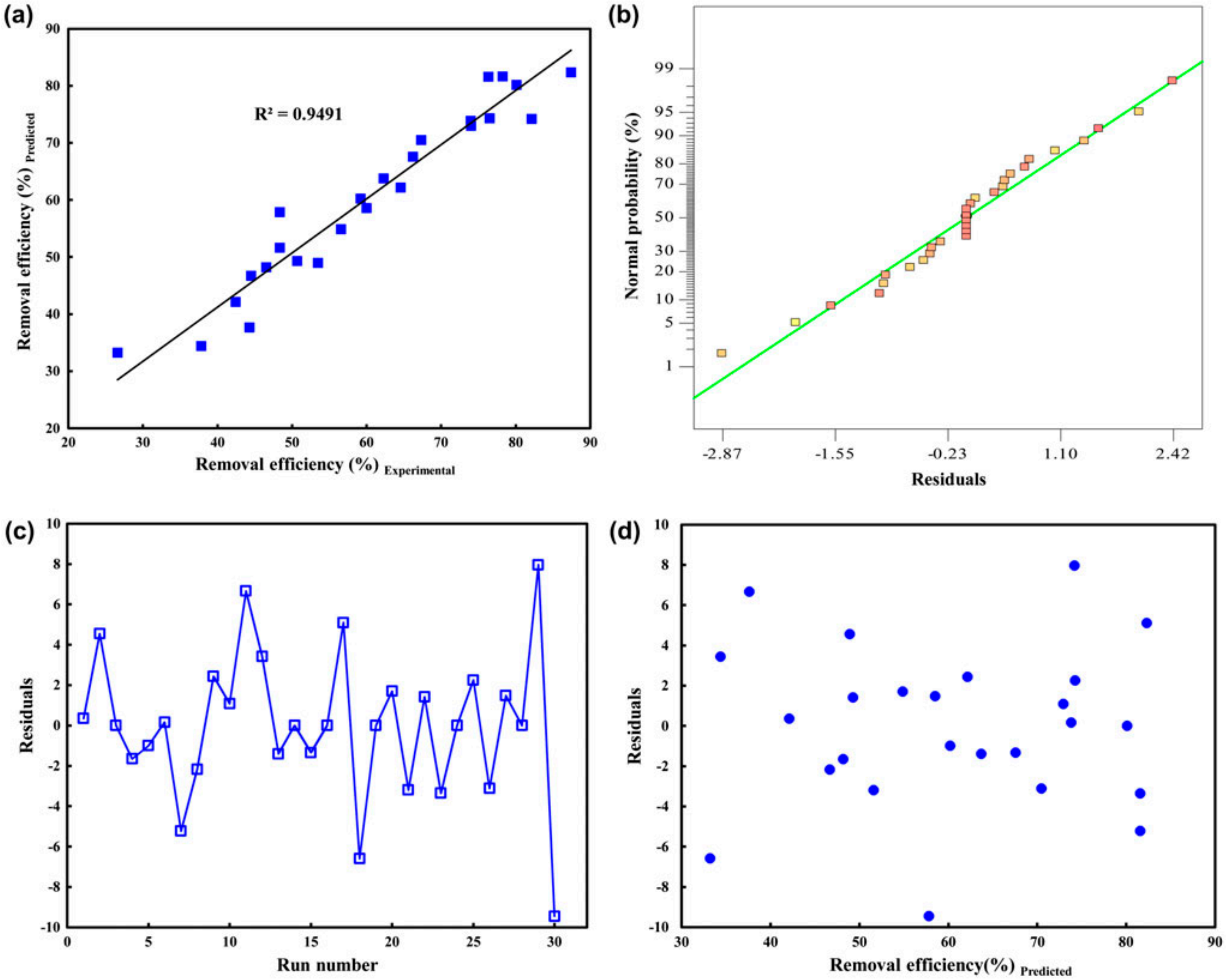

Fig. 3. Plot of predicted 4-CP removal vs. experimental 4-CP removal (%) (a) along with corresponding residual plots (b)–(d).

0.8 g/L and 7, respectively. As shown, decreasing initial 4-CP concentration and increasing reaction time led to increasing 4-CP removal (%). Decreasing 4-CP removal (%) with increasing initial 4-CP concentration is mainly due to the limited adsorption sites available for the adsorption of high concentration of adsorbate molecules [35]. Fig. 4(c) and (d) shows the interactive effect of adsorbent dosage and reaction time where the initial 4-CP concentration and initial pH were constant at 70 mg/L and 7, respectively. Fig. 4(c) and (d) exhibits that increasing adsorbent dosage resulted in increasing 4-CP removal (%). Obviously, increasing the adsorbent dosage results in the increased surface area and active sites leading to an efficient 4-CP removal (%) [5,15]. As shown in Fig. 4(e) and (f), increasing initial pH from acidic value to neutral value caused a gentle increase in 4-CP removal (%), while further increase in pH values led to significant decrease in 4-CP removal (%). The concentration of negatively charged phenoxide ions increases at high pH values. Since the surface charge of as-prepared activated carbon will be negative at pH values higher than pH_{pzc} (2.95), the repulsive force between the negatively charged adsorbate molecules and negative surface charge of the activated carbon will be happened at alkaline conditions [30,36]. From the other point of view, the deprotonation of the functional groups placed on the surface of adsorbent is responsible for the significant decrease in 4-CP removal at high pH values. This leads to the blockage of the surface of activated carbon by water molecules [16]. In agreement with our study, Liu et al., in their study,

Table 4
Estimated regression coefficient and corresponding *F*- and *p*-values obtained during CCD for the adsorption of 4-CP onto as-prepared activated carbon

Coefficient	Coefficient estimate	Standard error	*F*-value	*p*-value
x_0	80.10	2.08	19.98	0.0001
x_1	4.09	1.04	15.46	0.0013
x_2	−6.41	1.04	38.01	0.0001
x_3	12.28	1.04	139.5	0.0001
x_4	−0.82	1.04	0.620	0.4442
x_{12}	−0.47	1.27	0.140	0.7169
x_{13}	−0.57	1.27	0.200	0.6591
x_{14}	−0.33	1.27	0.069	0.7965
x_{23}	0.60	1.27	0.220	0.6433
x_{24}	−0.72	1.27	0.320	0.5792
x_{34}	0.42	1.27	0.110	0.7472
x_{11}	−3.52	0.97	13.12	0.0025
x_{22}	−4.77	0.97	24.05	0.0002
x_{33}	−5.58	0.97	32.92	0.0001
x_{44}	−6.72	0.97	47.69	0.0001

found that high pH values resulted in decreasing the adsorption of 4-CP onto activated carbon fibers [3]. Since 4-CP is a weak acid with a pK_a of 9.41, the 4-CP is present in neutral form at low pH values [13]. This resulted in slightly reduced removal of 4-CP at acidic conditions. Conclusively, acidic and basic pH values resulted in decreasing the adsorption of 4-CP onto as-prepared activated carbon.

3.4. Optimization process

Numerical optimization was carried out to determine the optimum value of each operational parameter for the maximum 4-CP removal (%). In this approach, the RE (%) was set to "maximize," while the studied operational parameters were set to "in range." Accordingly, the maximum 4-CP removal of 89.52% was obtained with a reaction time of 49 min, initial 4-CP concentration of 56 mg/L, adsorbent dosage of 1 g/L, and initial pH of 7. To validate the results of optimization, confirmatory experiments were performed under optimum operational parameters and the results showed a mean 4-CP removal of 87.45 ± 2.35%, which demonstrated that the results of modeling can be reliable to predict 4-CP removal (%) under different operational parameters.

3.5. Reusability of the adsorbent

A three-stage regeneration test was performed using thermal and chemical regeneration under optimum operational parameters (reaction time of 49 min, initial 4-CP concentration of 56 mg/L, adsorbent dosage of 1 g/L, and initial pH of 7) to test reusability potential of the adsorbent. The spent adsorbent was placed in 1-M sulfuric acid for 120 min to attain chemical regeneration, while thermal regeneration was carried out by heating the spent adsorbent for 60 min at 400˚C in an electric furnace. The results of reusability test are shown in Fig. 5. For chemical regeneration, at first, second, and third regeneration runs, the RE (%) of 4-CP was decreased from 87.45% to 76.63, 67.21, and 61.15%, while, in the case of thermal regeneration, it was decreased from 87.45% to 83.04, 79.33, and 77.68%, respectively. These results indicated that activated carbon prepared from milk vetch can be effectively regenerated via thermal regeneration in comparison with chemical regeneration.

3.6. Kinetic study

The effect of reaction time on the adsorption of 4-CP onto activated carbon derived from milk vetch was assessed within reaction time of 50 min, while initial 4-CP concentration, adsorbent dosage, and initial pH were constant at 60 mg/L, 1 g/L, and 7, respectively. Fig. 6 shows that increasing reaction time from 5 to 50 min resulted in increasing the amount of adsorbed 4-CP from 29.33 to 44.07 mg/g, respectively. According to Fig. 6, a reaction time of 50 can be an appropriate timeframe for conducting kinetic study. The time required to reach equilibrium time was relatively short, which can be related to the developed porous structure of the adsorbent prepared from milk vetch [13]. According to the results reported by Wang et al., the equilibrium time obtained in the present

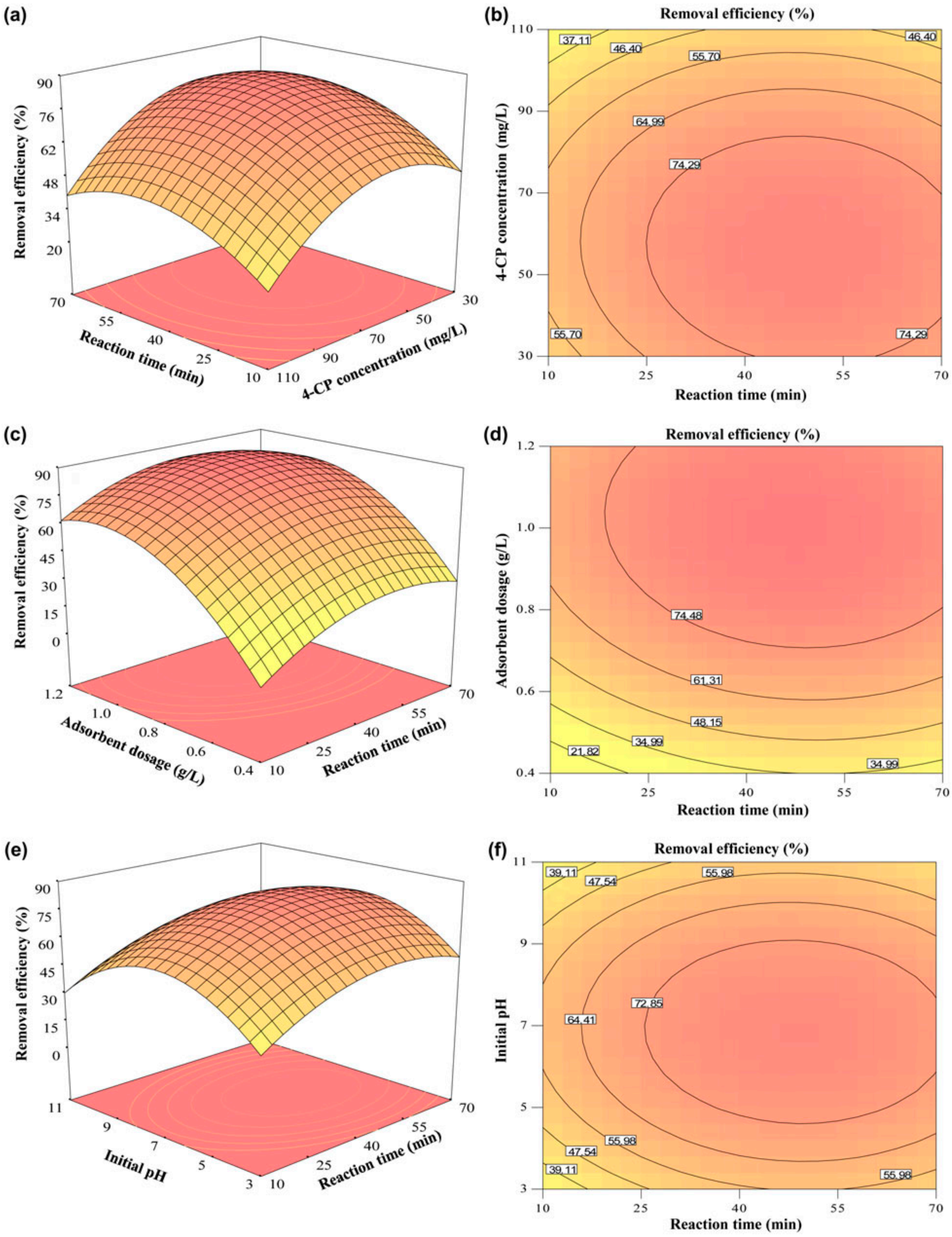

Fig. 4. Interactive effect of initial 4-CP concentration and reaction time (a) and (b), interactive effect of adsorbent dosage and reaction time (c) and (d), and interactive effect of initial pH and reaction time (e) and (f).

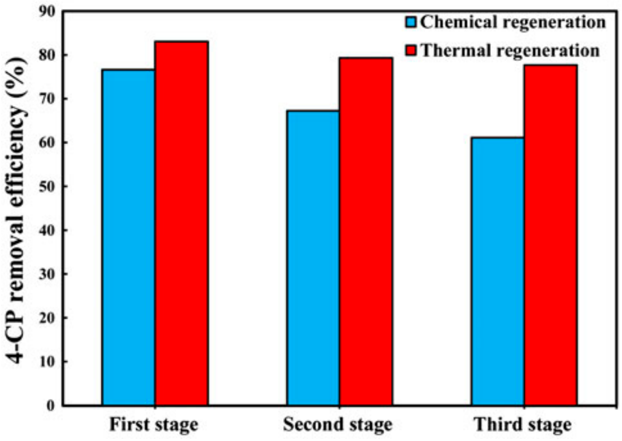

Fig. 5. Reusability of activated carbon prepared from milk vetch within three consecutive regeneration runs.

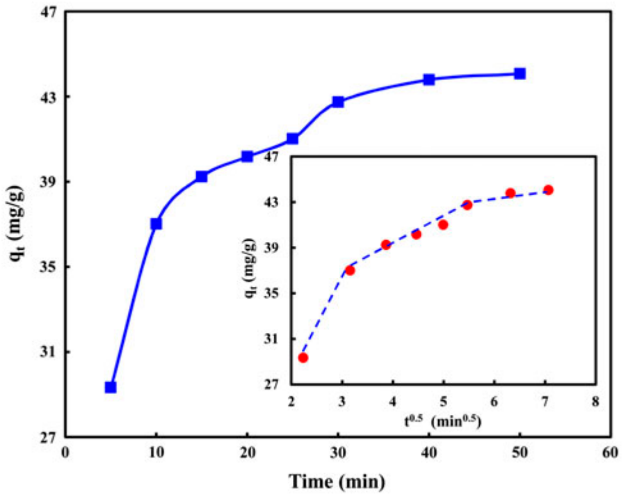

Fig. 6. Effect of reaction time on the adsorption of 4-CP onto as-prepared activated carbon along with intraparticle diffusion plot.

study was much shorter than the time needed for the adsorption of chlorophenol onto activated carbon prepared from rice straw [16]. The pseudo-first-order, pseudo-second-order, and intraparticle diffusion equations were used to conduct kinetic study. Linearized form of the pseudo-first-order equation is represented via Eq. (5):

$$\log(q_e - q) = \log\ q_e - (k_{1,\mathrm{ad}}/2.303)t \tag{5}$$

where q_e (mg/g) and q (mg/g) are the amount of adsorbed 4-CP at equilibrium time and the amount of adsorbed 4-CP at time t, respectively. Moreover, $k_{1,\mathrm{ad}}$ (1/min) is the rate constant of the pseudo-first-order reaction. The values of q_e and $k_{1,\mathrm{ad}}$ can be determined from the intercept and slope of the obtained graph, respectively [3,37,38]. Linearized form of the pseudo-second-order kinetic equation is depicted through Eq. (6):

$$t/q = \left(1/k_{2,\mathrm{ad}}q_e^2\right) + (1/q_e)t \tag{6}$$

where $k_{2,\mathrm{ad}}$ (g/mg min) is the rate constant of the pseudo-second-order reaction. The values of q_e and $k_{2,\mathrm{ad}}$ can be calculated from the slope and intercept of the graph, respectively [15,36]. Linearized form of the intraparticle diffusion equation is exhibited via Eq. (7):

$$q_t = k_p t^{0.5} + C \tag{7}$$

where q_t (mg/g) is the amount of adsorbed 4-CP, k_p is the rate constant of the intraparticle diffusion equation (mg/g min$^{0.5}$), and C is the intercept of the graph. The values of k_p and C were determined from the slope and intercept of the obtained line, respectively. The value of C corresponds to the thickness of the boundary layer [3,25]. The kinetic parameters and correlation coefficients associated with each kinetic equation are given in Table 5. According to the correlation coefficients given in Table 5, the adsorption process can be described by the pseudo-second-order kinetic equation reasonably well ($R^2 = 0.9996$). In agreement with our results, Liu and co-workers, in their study, found that the pseudo-second-order kinetic equation ($R^2 = 0.988$) was more appropriate than the pseudo-first-order kinetic equation ($R^2 = 0.819$) to characterize the adsorption of 4-CP onto commercial activated carbon fibers [3]. In addition, Tseng et al., in their study, reported that the adsorption of 4-CP onto activated carbons derived from pistachio shells follows pseudo-second-order kinetic equation [39]. The value of q_e associated with the pseudo-second-order kinetic equation was obtained to be 46.73 mg/g, which is in accordance with its experimental value (44.07 mg/g). The kinetic data were described by the intraparticle diffusion kinetic equation and the results showed that the process occurred via a three-step mechanism. This trend can be observed via a smaller figure on Fig. 6. The profile of the adsorption process involves rapid external mass transfer (surficial adsorption), intraparticle diffusion into the pores, and adsorption. The final plateau stage is related to the final equilibrium process [3]. Similar trend has been observed by Sze and McKay in the adsorption of *p*-chlorophenol by activated carbon derived from bituminous coal [7]. On

Table 5
Kinetic and isotherm parameters for the adsorption of 4-CP onto as-prepared activated carbon

	Model type	Parameters	Value
Kinetic models	Pseudo-first-order model	$k_{1,ad}$ (1/min)	0.1036
		q_e (mg/g)	25.74
		R^2	0.9504
	Pseudo-second-order model	$k_{2,ad}$ (1/min)	0.0076
		q_e (mg/g)	46.73
		R^2	0.9996
	Intraparticle diffusion model	k_p (mg/g $min^{0.5}$)	2.74
		Intercept	26.772
		R^2	0.8420
Isotherm models	Langmuir model	q_{max} (mg/g)	86.96
		K (L/mg)	0.468
		R^2	0.9969
		R_L	0.019–0.051
	Freundlich model	K_F	9.53
		n	2.056
		R^2	0.9787

the basis of the obtained intercept, the line of intraparticle diffusion plot did not pass through the origin ($y = 2.7433x + 26.772$), suggesting that the intraparticle diffusion or diffusion into the pores was not the sole rate-limiting stage. Besides, the correlation coefficient of the intraparticle diffusion equation exhibited that the intraparticle diffusion equation had the lowest fitness to the experimental data (Table 5). This demonstrated multistep mechanism of the adsorption of 4-CP onto activated carbon and its complicated nature [9]. Moreover, the rate constant of intraparticle diffusion for the adsorption of 4-CP was obtained to be 2.74 mg/g $min^{0.5}$, which was relatively high in comparison with the result of our previous study on the adsorption of azo dye onto biosilica/chitosan composite. It may be due to the porous structure of the activated carbon prepared from milk vetch increasing mass transfer rate [28].

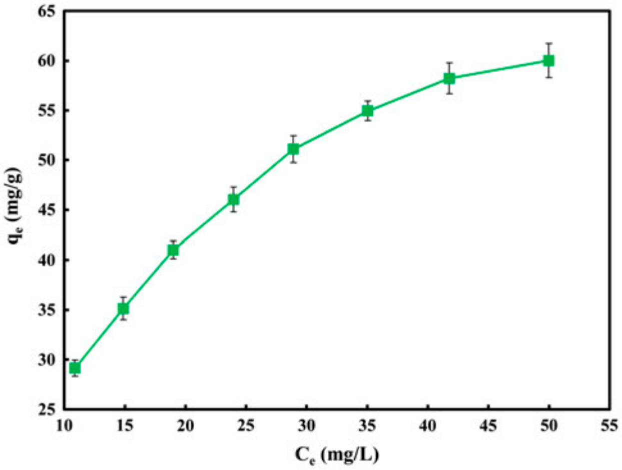

Fig. 7. Isotherm plot of the adsorption of 4-CP onto as-prepared activated carbon depicted at different initial dye concentrations.

3.7. Isotherm study

The adsorption isotherm was investigated by varying initial 4-CP concentration between 40 and 110 mg/L where reaction time, adsorbent dosage, and initial pH were constant at 50 min, 1 g/L, and 7, respectively (Fig. 7). Langmuir and Freundlich isotherm equations, as the most widely used isotherm models, were used to describe the experimental data. Linearized form of the Langmuir equation is illustrated through Eq. (8):

$$C_e/q_e = 1/Kq_m + C_e/q_m \quad (8)$$

where q_m (mg/g), C_e (mg/L), and K (L/mg) are the maximum adsorption capacity of the adsorbent, the residual adsorbate in solution, and the affinity of the active sites for the adsorption of adsorbate molecules (Langmuir constant), respectively [11,28]. Langmuir isotherm could be declared in terms of separation factor (R_L) as shown in Eq. (9):

$$R_L = 1/1 + C_oK \quad (9)$$

Table 6
Maximum adsorption capacities of some carbonaceous adsorbents for the adsorption of 4-CP

Adsorbent material	Maximum adsorption capacity (mg/g)	Ref.
Activated carbon from rattan sawdust	188.7	[37]
Residual coal	82.4	[12]
Rice husk char	36.2	[12]
Activated carbon slurry from fertilizer plants	58.1	[8]
Activated carbons from coal (KOH-activated)	300.9	[42]
Activated carbon from coconut shell	72.8	[39]
Activated carbon cloths	117.0	[6]
Activated carbon fibers (ACFs)	243.1	[3]
Commercial granular activated carbon	112.4	[2]
Activated carbon from cane pith	233.3	[14]
Activated carbon from oil agglomerated bituminous coals	119.0	[37]
Activated carbons from sewage sludge (air-activated)	42.7	[4]
Activated carbons from sewage sludge (KOH-activated)	192.6	[4]
Activated carbon from milk vetch	87.0	Present study

where C_o (mg/L) is the initial 4-CP concentration. On the basis of the value of R_L, the adsorption process can be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), and unfavorable ($R_L > 1$) [36,40,41]. Linear form of the Freundlich equation is represented via Eq. (10):

$$\log\ q_e = \log\ K_F + 1/n\ \log\ C_e \tag{10}$$

where q_e (mg/g) is the amount of adsorbed 4-CP, n is a constant related to the adsorption intensity, and K_F is a constant related to the adsorption capacity for sequestering adsorbate molecules [15,42]. The isotherm parameters are tabulated in Table 5. The values of correlation coefficients obtained for each isotherm equation revealed that the adsorption of 4-CP onto activated carbon derived from milk vetch obeys the Langmuir isotherm equation ($R^2 = 0.9969$). Accordingly, the maximum adsorption capacity (q_m) of as-prepared activated carbon for the adsorption of 4-CP was 86.96 mg/g. In addition, Table 5 shows that the values of R_L were between 0.019 and 0.051, indicating that the adsorption of 4-CP onto as-prepared activated carbon was favorable. Comparatively, maximum adsorption capacities of some carbonaceous adsorbents for the adsorption of 4-CP have been listed in Table 6.

4. Conclusions

Milk vetch shrubs were used as precursor of activated carbon and utilized for the adsorption of a phenolic compound (4-CP) from aqueous media. The adsorption was processed by CCD and the results demonstrated that the maximum 4-CP removal can be achieved at a reaction time of 49 min, initial 4-CP concentration of 56 mg/L, adsorbent dosage of 1 g/L, and initial pH of 7. In the following, kinetic and isotherm studies were carried out and the results showed that the pseudo-first-order kinetic and the Langmuir isotherm equations were found to be as appropriate equations to describe the adsorption of 4-CP. Besides, the intraparticle diffusion plot exhibited that the process has been occurred in three stages and diffusion into the pores was not the sole rate-limiting stage. The results of reusability study demonstrated the capability of as-prepared activated carbon for use in several experimental runs. The results of the present investigation demonstrated that milk vetch can be used as a suitable precursor for the preparation of activated carbon to be used as an efficient adsorbent with high reusability potential to remove organic compounds from aqueous environments.

Acknowledgments

The authors would like to thank Arak University of Medical Sciences and Ilam University of Medical Sciences for their supports.

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