



Facile synthesis of mesoporous carbon aerogel for the removal of ibuprofen from aqueous solution by central composite experimental design (CCD)

Sara Abolhasani^a, Ali Ahmadpour^{a,*}, Tahereh Rohani Bastami^b, Alireza Yaqubzadeh^a

^a Department of Chemical Engineering, Faculty of Engineering, Ferdowsi University of Mashhad, Mashhad, Iran

^b Department of Chemical Engineering, Faculty of Engineering, Quchan University of Technology, Quchan, P.O. Box 94771-67335, Iran

ARTICLE INFO

Article history:

Received 1 November 2018

Received in revised form 6 February 2019

Accepted 17 February 2019

Available online 18 February 2019

Keywords:

Carbon aerogel

Mesopore

Ibuprofen

Adsorption

Experimental design

ABSTRACT

In this paper, carbon aerogel as a nanostructure adsorbent was prepared from mixed resorcinol and formaldehyde precursors by the ambient pressure drying. Synthesis of carbon aerogel is performed in four main steps: preparation of wet gel, aging, wet gel drying and pyrolysis. The cheap precursors in this synthesis were significant and economical for the mass production. The prepared carbon aerogel was characterized by surface area measurement, field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), energy dispersive X-ray (EDX) mapping analysis and Fourier transform infrared (FTIR) spectroscopy. According to the surface area analysis, the carbon aerogel has a high surface area of $790 \text{ m}^2 \text{ g}^{-1}$, a total pore volume of $1.47 \text{ cm}^3 \text{ g}^{-1}$ and a mean pore diameter of 7.48 nm. According to the FESEM images, a uniform particle size distribution with a diameter of <50 nm was observed. Adsorption investigation of ibuprofen from aqueous solution was performed by the carbon aerogel. Design Expert with a coherent program was used for the adsorption process optimization. The main objective of this study was to evaluate operational variables such as contact time, adsorbent dosage, pH, and interaction of these variables in the adsorption process. According to the kinetic study, the compatibility of experimental data with the pseudo-second-order model represents the heterogeneous chemical adsorption on the adsorbent surface. The results of Freundlich isotherm demonstrate the multilayer adsorption with a heterogeneous system for adsorption process.

© 2019 Elsevier B.V. All rights reserved.

1. Introduction

Recently, the discovery of pharmaceutical contaminants in water media has aroused the global concern. Hospital wastewaters need to be monitored for the release of pharmaceuticals and non-observance of hygiene standards [1–3]. There are several technologies such as advanced oxidative processes [4], adsorption [5], microbial degradation [6] and membrane technology [7], which are used to remove these contaminants. Among these technologies, adsorption has attracted growing attention due to its affordability, high efficiency, potential for regeneration and eco-friendly nature [8,9]. A number of adsorbents with distinct properties are used for water and wastewater treatment such as activated carbon, clays, minerals and fly ash [10–12]. Aerogels are also effective for the removal of various concentrations of hazardous water pollutants which are considered as favorable adsorbents [13,14]. Carbon aerogels (CA) are nanostructured sponge-like carbon materials with unique properties like well-proportioned porosity, high surface area, low density and the ability to adsorb multiple times their own weight

[15–17]. Generally, carbon aerogels are derived from various precursors such as organic precursors, carbon-based materials and biomass [18,19]. Ibuprofen (IBP), which is used for analgesic, antipyretic and swelling reduction, belongs to the class of nonsteroidal anti-inflammatory (NSAID) and analgesic agent [20,21]. Ibuprofen dissolves in water with a solubility of about 21 mg L^{-1} (298 K) and its reported concentration in surface water is in the range of ng L^{-1} to mg L^{-1} [22–24]. In recent years, the removal of ibuprofen, as a pharmaceutical contaminant, from aqueous solutions has been considered. The molecular size of the ibuprofen is $1.3 \times 0.6 \text{ nm}^2$. This can give information about the accessibility of these molecules to the pore channels of the mesoporous materials [25]. New adsorbents such as graphene oxide, activated carbon and zeolite were applied for the removal of IBP from water media [26–28]. Recently, carbon aerogels, as adsorbents, have been utilized to remove different contaminants. Ren et al. employed carbon aerogel to remove methylene blue with an adsorption capacity of 819.67 mg g^{-1} . They chose the glucose as a precursor under the hydrothermal process to produce the adsorbent [29]. Han et al. synthesized eco-friendly and hydrophobic carbon aerogel from affordable materials (cellulose-based waste newspaper), which are used to adsorb organic materials such as pump oil, ethanol and gasoline with an adsorption capacity of up to

* Corresponding author.

E-mail address: ahmadpour@um.ac.ir (A. Ahmadpour).

100% [30]. Heavy metals removal from aqueous media using carbon aerogel have also been studied [31,32]. Huan et al. explored the use of Fe nanoparticles/carbon aerogel for H₂S removal as a sulfur compounds and gained high adsorption percentage [33]. Also, carbon aerogel has potentials for the IBP adsorption due to its specific texture and properties [34]. In order to attain the optimal response, statistical methods with a coherent program are required. Response surface methodology (RSM) is a well-known method based on a statistical approach in which modeling the relationship between input parameters and response can provide optimal conditions [35,36]. Besides, the central composite design (CCD) as a subset of surface response methods consists of three groups of design points (factorial, axial and center points) that can estimate the curvature of system using a second-order equation [37]. This is the first paper to use carbon aerogel to investigate the IBP removal from aqueous solutions. The use of cheap precursors and simple drying at ambient pressure in this synthesis makes it significant and affordable for the mass production. The main objectives of this study are as follows: (i) synthesis of mesoporous carbon aerogel based on optimal operating conditions (973 K, 2 h) under ambient pressure drying; (ii) investigation of the ibuprofen removal as a pharmaceutical model from aqueous solutions using the proposed adsorbent; and (iii) evaluation of operating variables such as contact time, adsorbent amount, pH, and interaction of these variables in the adsorption process. To this end, the response surface (central composite design) is especially effective. Kinetic studies are also carried out to determine the rate of adsorption reaction.

2. Materials and methods

2.1. Materials

Resorcinol (C₆H₆O), Formaldehyde (CH₂O, 37%) and CTAB (C₁₉H₄₂BrN) were all provided by Merck Company. Mili-Q water was used with a minimum resistivity of 18.2 MΩ cm⁻¹. Ibuprofen (C₁₃H₁₈O₂) was also supplied by Sigma-Aldrich Corporation.

2.2. Preparation of carbon aerogel

The mesoporous carbon aerogel was prepared by sol-gel polycondensation method and the ambient pressure drying process [38,39]. Initially, 5 g (0.045 mol) of resorcinol and 7.223 g (0.240 mol) of formaldehyde with a ratio of R/F = 1/2 were added to 7.2 mL of distilled water. Then, 0.13 g of CTAB, as a catalyst, by a ratio of R/CTAB = 125 was added to that solution and stirred for 15 min to mix thoroughly. Homogeneous solution with a pH of 5.8 was poured into a glass container and sealed. Finally, the solution was placed in an oil bath (353 K) for 7 days to polymerize and prepare the Resorcinol-Formaldehyde (RF) gel. The container lid was opened after a week and it was set under the hood at ambient temperature (298 K) for 2 days in order to release its volatile compounds. Finally, a dry gel was obtained in the oven after two curing steps: at a temperature of 333 K for 24 h and then at a temperature of 378 K for 24 h. Consequently, a reddish-orange dry gel of RF was produced. For the purpose of pyrolysis and carbonization, RF aerogel was placed in a tubular furnace at a temperature of 973 K and thermal gradient of 278 K min⁻¹ under nitrogen flow (150 mL min⁻¹) for 120 min.

2.3. Characterization

Morphology and the formation of microstructures were determined by Field Emission Scanning Electron Microscope (FESEM, Tescan Mira3 FEG) equipped with an energy dispersive X-ray (EDX) mapping detector. EDX and MAP techniques were used to demonstrate a semi-quantitative view and frequency distribution of elements on a nano-structure surface respectively. The surface area was determined by Brunauer-Emmett-Teller (BET, BELSORP MINI II) analysis in the relative

Table 1

Operating variables and functional range of the CCD method for removing ibuprofen from the aqueous environment.

Variable	Unit	Code	-α	+α	Central point
Time	s	A	300	5400	47.5
pH	-	B	3	9	6
Adsorbent dosage	g L ⁻¹	C	0.5	1.5	1

pressure range of 0–0.99 at 77 K. Also, the Barrett-Joyner-Halenda (BJH) method was used to determine the Porosity measure. Functional groups and existing bonds were determined by Fourier-transform Infrared spectroscopy between 400 and 4000 cm⁻¹ (FTIR, Thermo Nicolet Avatar 360, USA). The carbon aerogel crystalline structure was determined by the analysis of X-ray Diffraction spectroscopy (XRD, D8-Advance Bruker Cu Kα1 λ = 0.15406 nm).

2.4. Zero point charge measurement

The zero point charge (pHpzc) of carbon aerogel was measured by the analysis of zeta potential at pH = 5. The pH adjustment was carried out by HCl (1 and 0.1 mol m⁻³) aqueous solutions. A sample of 0.02 g carbon aerogel in an aqueous solution of 50 mL IBP (10 mg L⁻¹) was used for this purpose.

2.5. Liquid phase adsorption

Initially, an aqueous solution with a concentration of 10 mg L⁻¹ was provided in order to study the adsorption of ibuprofen. The adsorption experiments were carried out based on a batch system at ambient temperature (298 K) in beaker containing 50 mL of specimen. The residuals

Table 2

The points and results obtained from the experimental design.

No. of experiment	Type of experiment	Time (s)	pH	Adsorbent dosage (g L ⁻¹)	Removal amount (mg L ⁻¹)	Removal efficiency (%)
1	Factorial	1150	4	0.67	8.04	80.48
2	Factorial	4549	4	1.33	8.90	89.19
3	Central	2850	6	1.00	9.34	93.47
4	Axial	2850	3	1.00	9.74	97.40
5	Axial	5400	6	1.00	9.67	96.79
6	Axial	2850	6	1.50	9.76	97.62
7	Factorial	1150	4	1.33	9.97	99.78
8	Axial	300	6	1.00	8.61	86.14
9	Axial	2850	6	1.50	9.89	98.95
10	Factorial	4549	4	0.67	10.00	100.00
11	Factorial	4549	8	1.33	9.93	99.35
12	Factorial	4549	8	0.67	8.72	87.21
13	Central	2850	6	1.00	9.78	97.88
14	Factorial	1150	8	1.33	9.00	90.02
15	Factorial	4549	4	0.67	10.00	100.00
16	Axial	2850	3	1.00	10.00	100.00
17	Axial	2850	9	1.00	9.48	94.89
18	Axial	2850	6	0.50	8.26	82.62
19	Central	2850	6	1.00	10.00	100.00
20	Central	2850	6	1.00	9.90	99.03
21	Axial	5400	6	1.00	9.37	93.74
22	Central	2850	6	1.00	9.94	99.43
23	Axial	300	6	1.00	8.12	81.22
24	Axial	2850	9	1.00	9.25	92.51
25	Factorial	1150	8	0.67	8.98	89.83
26	Factorial	1150	8	0.67	8.73	87.35
27	Central	2850	6	1.00	8.67	86.76
28	Factorial	4549	8	0.67	8.47	84.73
29	Axial	2850	6	0.50	8.60	86.09
30	Factorial	1150	4	0.67	9.71	97.11
31	Factorial	4549	8	1.33	9.47	94.70
32	Factorial	4549	4	1.33	9.14	91.49
33	Factorial	1150	8	1.33	9.70	97.19
34	Factorial	1150	4	1.33	10.00	100.00

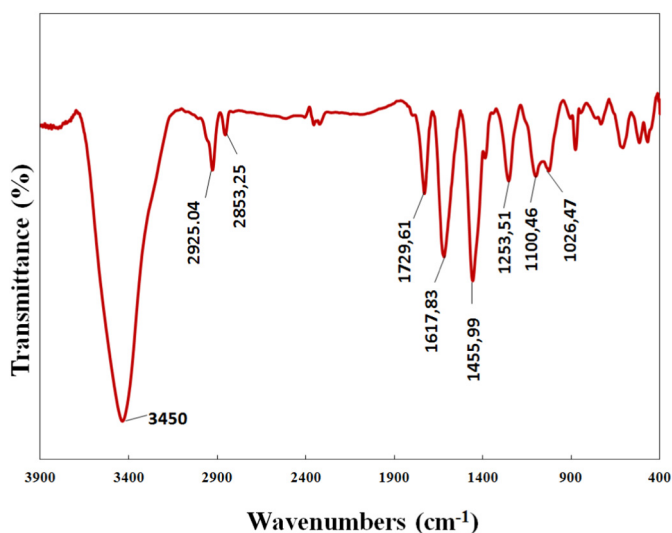


Fig. 1. FTIR spectrum of carbon aerogel.

of ibuprofen adsorption in specimens were measured by UV-Vis spectrophotometer (AnalyticJena-Spekol 1300.1) with a maximum wavelength of 224 nm [40,41]. The concentration of unknown specimens was determined by the calibration curve. The equilibrium adsorption capacity, q_e (mg g⁻¹), was determined by the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_e and C_0 are the concentration of remaining ibuprofen at the equilibrium and the initial concentration of ibuprofen based on mg L⁻¹, respectively. It should be borne in mind that V is the volume of solution in terms of L and W is the adsorbent dosage in g.

2.6. Experimental design

The Design-Expert 7 software was employed to perform the experimental design, investigate the effects of different parameters and determine the final model; furthermore, the central composite design (CCD) method was used to designate the surface response. The influence of operating parameters like pH, time, adsorption dosage and their interaction on the removal of ibuprofen from the aqueous environment were examined. The range and level of these parameters are shown in Table 1.

All 34 runs were performed. The results of experiments based on the CCD method are shown in Table 2. Considering the arbitrariness of alpha value, this parameter was considered equal to 1.5. All experiments were performed in the volume of 50 mL of ibuprofen solution, with an initial ibuprofen concentration of 10 mg L⁻¹ at room temperature. The HCl and NaOH (1 and 0.1 mol m⁻³) solutions were used to adjust pH.

The relation between responses and independent variables can be obtained using the following second-order polynomial equation:

$$Y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i=1}^k \sum_{j=1}^k \beta_{ij} x_i x_j + \varepsilon_0 \quad (2)$$

In Eq. (2), Y is the sign of responses, k is the number of independent factors, β_0 is the sign of crossing and β_i , β_{ii} , β_{ij} and β_{ij} are linear coefficients, second-order and interactive effects, respectively. Also, x_i and x_j indicate the encoded levels for independent variables [42,43].

3. Results and discussion

3.1. Characterization of carbon aerogel

The FTIR spectrum of carbon aerogel in a 400 to 4000 cm⁻¹ is shown in Fig. 1. The peak at a wavenumber of 3450 cm⁻¹ is related to the hydroxide (-OH) groups on the surface, which represents the hydrophilicity of carbon aerogel. Furthermore, the wavenumber of 1617.83 cm⁻¹ indicates the double bond of C=C in resin resole aromatic rings [44]. The peaks at a wavenumber of 1100- and 1253 cm⁻¹ confirm the remaining C-N amine groups caused by the presence of CTAB in the initial composition. The vibration caused by the peak at a wavenumber of 1455.99 cm⁻¹ illustrates the functional group (C-O); Moreover, the wavenumber of 1729.61 cm⁻¹, which is associated with the extant carbonyl group (C=O) in the organic aldehyde compound, is related to resorcinol-formaldehyde aerogel.

The elemental composition of carbon aerogel is shown in Fig. 2 using EDX map micrograph. Carbon element, as a major component with a percentage of 73.87 wt%, confirms the structure of constructed carbon. The amounts of N, Br and O in the adsorbent structure are 4.98, 0.36 and 20.79 wt%, respectively.

The XRD pattern of as-prepared adsorbent is illustrated in Fig. 3. Strong C (0 0 2) and weak C (1 0 1) diffraction peaks are placed at $2\theta = 25^\circ$ and $2\theta = 43^\circ$ respectively. The wide peaks reveal that the synthesized carbon aerogel is an amorphous compound [45]. The high intensity of peaks indicates a high percentage of graphitizing the carbon-aerogel structure [46].

The observed pores in carbon-aerogel SEM images confirm the pore fluid exit during drying process; moreover, the compound consists of

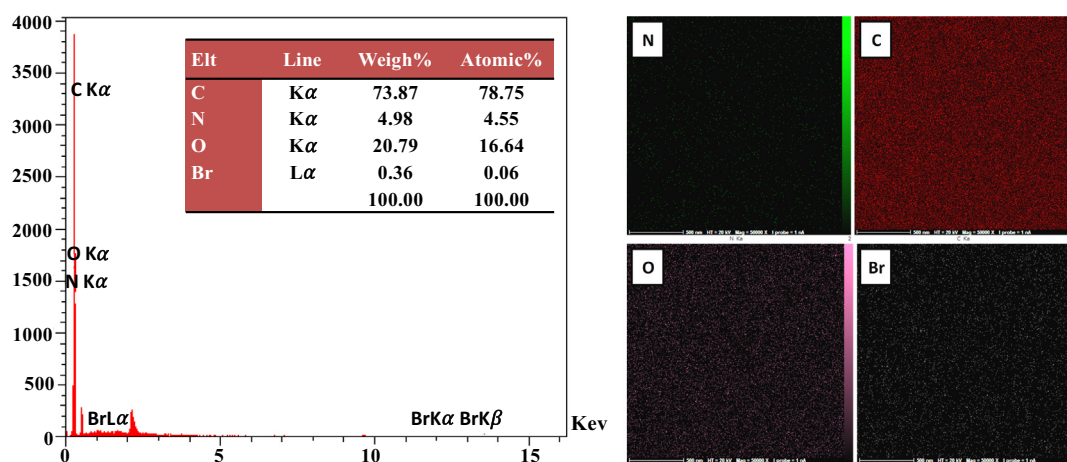


Fig. 2. EDX analysis and element map on carbon aerogel.

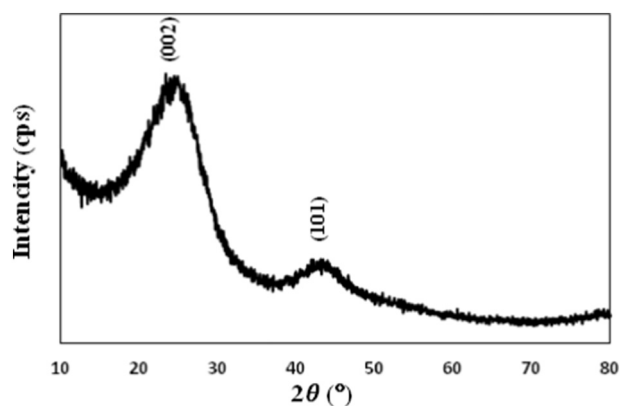


Fig. 3. XRD spectrum of carbon aerogel.

relatively uniform and regular particles with a diameter of <50 nm (Fig. 4a, b).

Nitrogen adsorption-desorption isotherm and pore size distribution of prepared carbon aerogel are shown in Fig. 5. Adsorption and desorption isotherm is of type (IV), which can be considered as an example of mesoporous (from 2 to 50 nm) structure. The observed hysteresis is of H1 type (based on IUPAC denomination) and it represents the cylindrical geometry of pores [47]. The BET surface area, the total volume of pores and their average pore diameter are $790 \text{ m}^2 \text{ g}^{-1}$, $1.47 \text{ cm}^3 \text{ g}^{-1}$ and 7.48 nm , respectively.

3.2. Statistical analysis

The results of variance analysis (ANOVA) with backward removal for improving the quality of the predicted model are presented in Table 3. The effects of various parameters and the final model can be predicted based on the data presented in this table. The important and effective parameters of the model are specified by P-value and F-value. P-value has a significance level of $\alpha = 0.05$ so that parameters whose value is less than this value are considered as significant. On the other hand, higher F-value indicates accurate prediction for experimental data. Moreover, low P-value of the presented model indicates its validity and significance. The adsorbent dosage, the square of adsorbent dosage and time are considered as the most important parameters in ibuprofen adsorption by carbon aerogel. The adequate precision reveals the ratio of predicted values to the average predicted errors (signal to noise

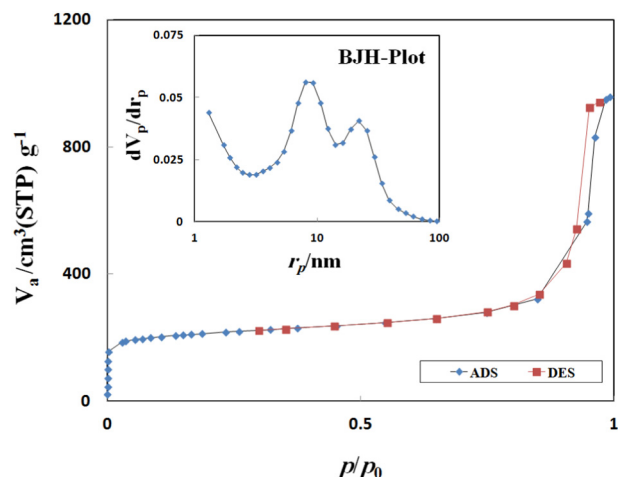


Fig. 5. Nitrogen adsorption and desorption isotherm at a temperature of 77 K and the pore size distribution of carbon aerogel.

ratio). Accordingly, values higher than 4 are acceptable. It is worth mentioning that the proposed model will be useless if the coefficient of variance is <10 [48]. The coefficient of variance and adequate precision are 6.17 and 32.63, respectively. The quality of curve fitting is determined by the coefficient of determination (R^2) and the adjusted coefficient of determination (R^2_{adj}). The fitting of the model will be important if these parameters are close to 1 [49]. As such, R^2 (0.966) and R^2_{adj} (0.958) show that values predicted by the response surface model are close to the experimental values. In the absence of a fit parameter, high-values indicate the accuracy of the predicted model. The final model of the ibuprofen adsorption by carbon aerogel based on the adsorption capacity (mg g^{-1}) and coded variables is as follows:

$$\text{Removal amount} = 9.69 + 0.23A - 0.29B - 3.31C - 0.27AC + 0.31BC - 0.28A^2 + 0.94C^2 \quad (3)$$

The diagram of normal probability percentage is shown in Fig. 6. The linear distribution of data suggests that error values are distributed normally without a specific variance [50]. The random dispersion of data in the curve of internally studentized residuals versus predicted values (Fig. 7) indicates that the variance is constant.

The simultaneous effect of two variables of time and adsorbent dosage on the amount of ibuprofen removal by adsorbent is illustrated in

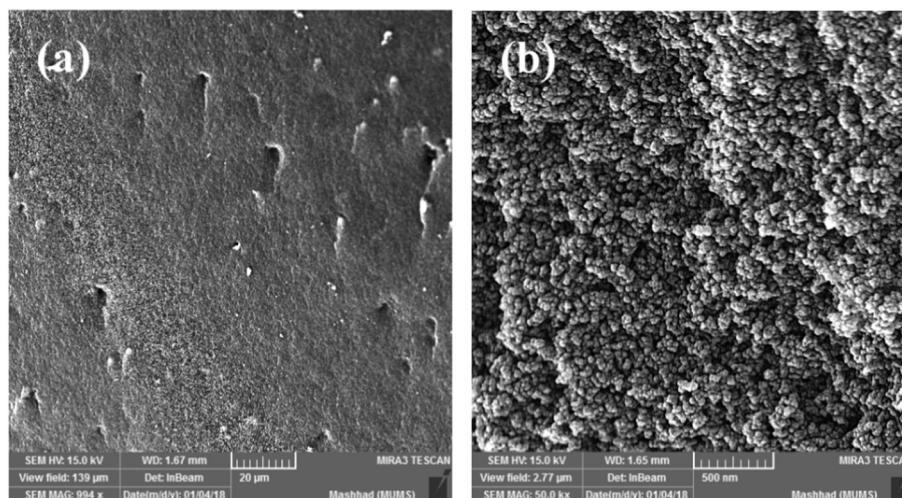


Fig. 4. Carbon-aerogel FESEM images a) $20 \mu\text{m}$ scale and b) 500 nm .

Table 3
ANOVA for response surface reduced quadratic model.

Source	Sum of squares	df	Mean square	F-value	P-value	
Model	298.71	7	42.67	108.46	<0.0001	Significant
A (time)	1.31	1	1.31	3.32	0.0799	
B (pH)	2.17	1	2.17	5.51	0.0267	
C (adsorbent dosage)	273.90	1	273.90	696.18	<0.0001	
AC	1.18	1	1.18	3.01	0.0948	
BC	1.52	1	1.52	3.86	0.0602	
A ²	1.42	1	1.42	3.60	0.0688	
C ²	15.63	1	15.63	39.72	<0.0001	
Residual	10.23	26	0.39			
Lack of fit	4.29	7	0.61	1.96	0.1146	Insignificant
Pure error	5.93	19	0.31			
Cor total	308.94	33				

Fig. 8. The pH has been considered constant and equal to 6. The results reveal that the amount of carbon aerogel can be the most effective parameter in ibuprofen removal. The maximum removal efficiency is reached in the highest adsorbent dosage (1.33 g L^{-1}) and the highest time (4549.8 s). The IBP molecules was removed in a short time (<300 s), and they reached equilibrium gradually. Accessibility of the more active sites of the adsorbent for IBP molecules at the initial stage was credited to the fast adsorption rate. The contact time has a direct effect on the removal efficiency of IBP by carbon aerogel. The active sites and the surface areas available for adsorbing contaminants increase with an increase in adsorbent dosage [37,42]. For this reason, the amount of the adsorbed IBP has grown up by increasing the adsorbent dosage of carbon aerogel.

The simultaneous effects of two variables of pH and adsorbent dosage on the amount of ibuprofen removal by adsorbent are illustrated in the 3D diagram of Fig. 9. The maximum removal is reached at the highest adsorbent dosage (1.33 g L^{-1}) in pH = 4. As mentioned earlier, the increase of the carbon aerogel dose led to the increase of the adsorbed IBP because of greater contact between the adsorbent surface and IBP molecules. Ibuprofen is a weak acid with PK_a of 4.92. The surface charge of ibuprofen is cationic and positive in $\text{pH} < 4.92$ due to the protonation of carboxyl groups. Moreover, the ibuprofen is converted into the anionic form with a negative surface charge in $\text{pH} > 4.92$ due to the loss of proton from the carboxyl group in its structure [24]. Since pH_{pzc} of the synthesized carbon aerogel is equal to 2.1, according to the analysis of zeta potential, the surface charge of adsorbent

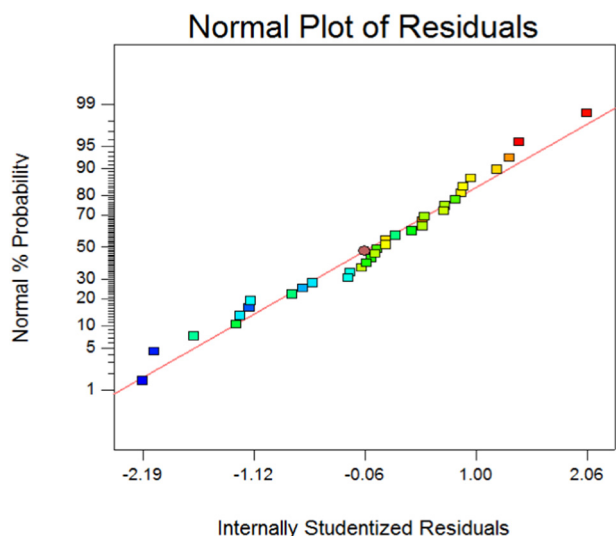


Fig. 6. Curve of normal probability percentage versus residuals.

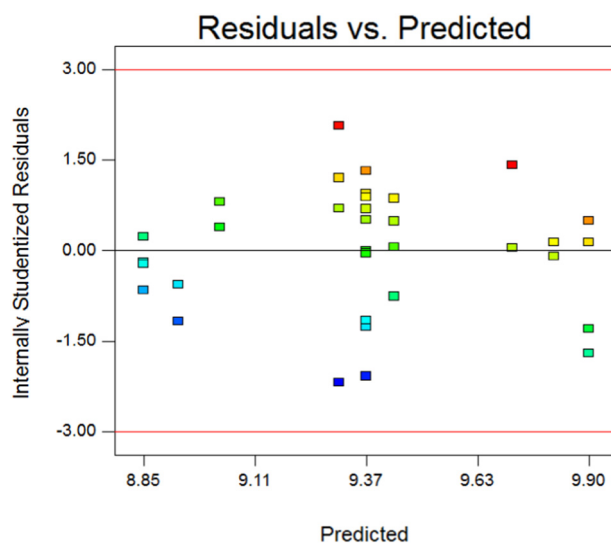


Fig. 7. Curve of additional values versus predicted values.

becomes positive and cationic in pHs less than pH_{pzc} and the adsorbent appears in an anionic form with a negative charge in pHs higher than 2.1. Therefore, the surface charge of carbon aerogel is negative at pH range of 3 to 4.92. Therefore, it can be concluded that the electrostatic interaction of the surface of carbon aerogel with negative charge and ibuprofen with positive charge leads to the interaction of between ibuprofen and carbon aerogel as the adsorbent. A repulsive force was observed at $\text{pH} > 4.92$ due to the negative charge of adsorbent and adsorbate; therefore, the removal efficiency was reduced. Given the insignificance of pH in the process of ibuprofen removal by the experimental design, this parameter has a low impact on the removal process. On the other hand, the carbon aerogel with H-donor functional group ($-\text{OH}$) is based on the performance of hydrogen bonding with deprotonated IBP as an H-acceptor molecule in alkaline pH (>4.92). The π - π stacking interaction between IBP molecules and the carbon aerogel and hydrogen bonding can be established at all pH ranges due to the aromatic rings in CA and adsorbate molecules and therefore the removal process of the ibuprofen controlled depending on these parameters.

3.3. Optimization

The proposed model (in Eq. (3)) was used to determine the optimum conditions of carbon aerogel for the removal of ibuprofen from the aqueous solution. For this happen, the desired inputs and expected

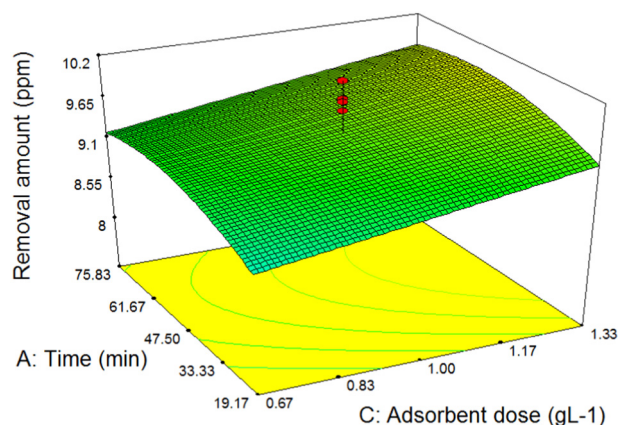


Fig. 8. 3D diagram of ibuprofen removal in terms of time and the adsorbent dosage by carbon aerogel.

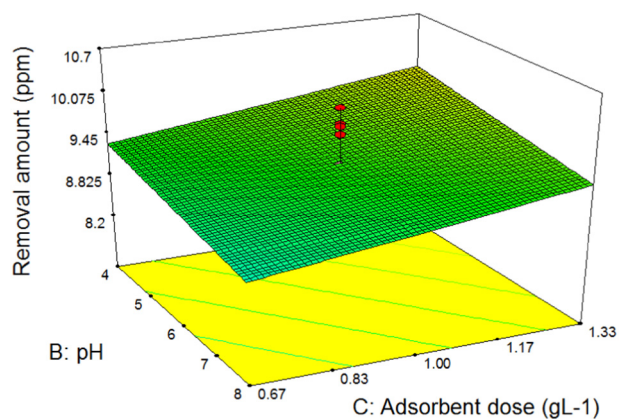


Fig. 9. 3D diagram of ibuprofen removal in terms of pH and the adsorbent dosage by carbon aerogel.

outputs should be selected based on an arbitrary approach. Here, the optimization was carried out to gain access to the maximum ibuprofen removal. Other operating parameters were considered within the default range of the Design-Expert. According to the proposed response, if the effluent with an initial ibuprofen concentration of 10 mg L^{-1} and $\text{pH} = 4$ is placed in contact with 1.33 g L^{-1} of carbon aerogel for 1164 s, the predicted removal by the model will be 9.89 mg L^{-1} , which equals to 7.43 mg g^{-1} of adsorption capacity (Table 4). The validity of the proposed model is also demonstrated with the compatibility of the experimental data with the predicted data.

3.4. Kinetic study

A key point to note here is that the evaluation of adsorption kinetics is essential to examine the rate of reaction. Two models of adsorption kinetics, which are widely used for the adsorption processes, are first-order kinetics and second-order kinetics [51]. Lagergren's kinetic equation (first-order), which is the first model for describing the adsorption of solid-liquid systems based on solid capacity, is according to the following equation [52]:

$$\text{Log}(q_e - q_t) = \text{Log}(q_e) - \frac{k_1 t}{2.303} \quad (4)$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) indicates the adsorption capacities in equilibrium and time (t) respectively; k_1 ($\text{g mg}^{-1} \text{ min}^{-1}$) is the pseudo-first-order kinetic constant. The diagram of $\text{Log}(q_e - q_t)$ in terms of t has the gradient of k_1 and the y-intercept of $\text{Log}(q_e)$.

Ho's equation (second-order), which describes chemical adsorption caused by valence forces through electron sharing and electron exchanging between the adsorbent and the adsorbate, follows the relation below [53]:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \quad (5)$$

where h ($\text{mg g}^{-1} \text{ min}^{-1}$) is the initial adsorption rate in the form of $h = k_2 q_e^2$. k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$) is the constant of Eq. (5), which is determined by drawing the curve of t/q_t versus t . The kinetic studies

Table 4
Optimal operating conditions and the amount of predicted removal.

Optimized condition				Ibuprofen removal (mg L^{-1})	
Time (s)	pH	Adsorbent dosage (g L^{-1})	Desirability	Experimental	Predicted
1164	4	1.33	0.746	9.97	9.89

Table 5

Adsorption kinetic parameters obtained from comparing experimental data with the models of Ho and Lagergren.

Ho's model (pseudo-second-order)				Lagergren's model (pseudo-first-order)			
q_e (cal)	q_e (exp)	R^2	K_2	q_e (cal)	q_e (exp)	R^2	K_1
8.984	8.847	0.999	0.263	4.648	8.847	0.819	0.378

on the adsorption of IBP were carried out at 600 rpm and 25°C using a syringe filter ($0.45 \mu\text{m}$) for separation. The residual concentration of the pollutant was determined by UV-Vis spectroscopy (Analyticjena-Spekol 1300.1) at the maximum wavelength ($\lambda = 224 \text{ nm}$). At first, a 10 mg L^{-1} solution of ibuprofen was provided to perform kinetic experiments. All experiments were conducted in the volume of 50 mL of ibuprofen solution with an adsorbent dosage of 0.05 g and $\text{pH} = 2$. The contact times considered for investigating the equilibrium adsorption capacity were 1, 3, 5, 10, 15 and 20 min, respectively. As for the results of the experimental design, the adsorption outputs were significant in acidic pHs; therefore, $\text{pH} = 2$ was considered for the above solutions. The constants extracted from the curve fitting of Lagergren's and Ho's models for ibuprofen removal are listed in Table 5. As can be seen, the results of Ho's model are more consistent with the experimental data. Thus, the chemical interactions between ibuprofen molecules and carbon aerogel particles control the adsorption rate and show the chemical adsorption nature of the process. The amount of q_e , predicted by Ho's model is more compatible with the experimental q_e .

The effect of contact time on the efficiency of ibuprofen removal by carbon aerogel is shown in Fig. 10. Increasing contact time in the range of 1 to 20 min leads to enhanced ibuprofen removal efficiency by carbon aerogel. According to the results, the efficiency of ibuprofen removal reaches about 84.25% after 10 min, which is a slight change in comparison with the observed efficiency of 88.47% after 20 min. Thus, an equilibrium time of 10 min was considered for the process.

3.5. Adsorption isotherms

Equilibrium adsorption isotherms of Langmuir and Freundlich were determined at different adsorbate dosage [9,27]. Freundlich adsorption isotherm for describing the adsorption characteristics is according to the following equation:

$$\text{Log}(q_e) = \text{Log}(K_f) + \frac{1}{n} \text{Log}(C_e) \quad (6)$$

where K_f (L mg^{-1}) is the Freundlich isotherm constant and n is the adsorption capacity. Also, q_e (mg g^{-1}) and C_e (mg L^{-1}) are the equilibrium adsorption capacity and the concentration of remaining IBP at the

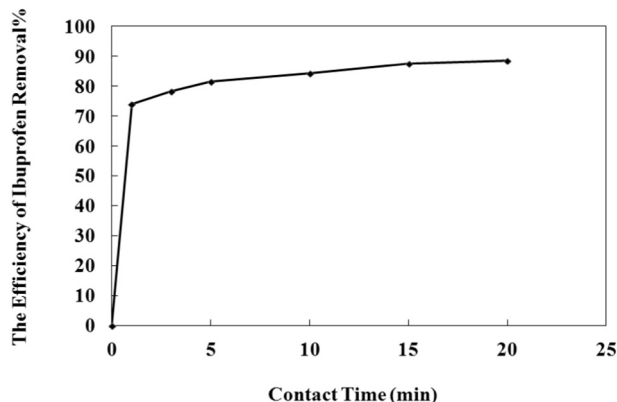


Fig. 10. Effect of contact time on the efficiency of ibuprofen removal by carbon aerogel.

Table 6
Adsorption isotherm parameters obtained from Freundlich isotherm model.

R ²	1/n	K _f (L mg ⁻¹)
0.933	3.034	6.472

equilibrium, respectively. The diagram of Log (q_e) in terms of Log (C_e) has the slope of 1/n and the y-intercept of Log (K_f).

Langmuir adsorption isotherm can be obtained using the following linear equation:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m k_L C_e} \quad (7)$$

where k_L (L mg⁻¹) is the Langmuir isotherm constant and q_m (mg g⁻¹) is the maximum monolayer coverage capacity. For this purpose, six different solutions with an initial concentration of 10–35 (mg L⁻¹) IBP were prepared. Each ibuprofen solution with the volume of 50 mL and 0.02 g dose of adsorbent was stirred with 600 rpm for 90 min at pH = 2 and 25 °C. The residual concentration of the IBP was determined by UV–Vis spectroscopy (Analyticjena-Spekol 1300.1) at the maximum wavelength (λ = 224 nm). Adsorption data was fitted better with Freundlich isotherm (R² = 0.933) compared with R² = 0.906 using Langmuir isotherm. The parameters of fitting the Freundlich adsorption isotherm are listed in Table 6. This demonstrates the multilayer adsorption with a heterogeneous system for IBP molecules on the carbon aerogel surface. The value of 1/n above one indicates cooperative adsorption.

4. Conclusion

In this study, carbon aerogel was prepared by the sol-gel process and drying in ambient pressure as a cost-effective method using the pyrolysis of the organic aerogel of RF. According to the results, the synthesized hydrophilic carbon aerogel had a high surface area with the mesoporous structure. This carbon nanostructure was used to remove the pharmaceutical contaminant of ibuprofen from the aqueous effluent. The surface response method (CCD) was employed to determine the final model and examine the effects of different parameters such as pH, time and adsorbent dosage. The coefficient of determination (0.966), the coefficient of adjusted determination (0.958) and adequate precision (32.63), obtained from the ANOVA results confirmed the accuracy of the predicted second-order statistical model. The adsorbent dosage, time, the interaction of time-adsorbent dosage and the interaction of pH-adsorbent dosage were considered as the most effective operating parameters in the process of adsorbing ibuprofen by carbon aerogel. Under optimal conditions, the effluent with an initial ibuprofen concentration of 10 mg L⁻¹, pH = 4 and contact time of 1164 s with 1.33 g L⁻¹ of carbon aerogel predicted a removal value of 7.43 mg g⁻¹, which was equivalent to a removal efficiency of 98.90%. With regard to the results of pseudo-second-order model, this adsorption was in keeping with the model and the adsorption process was performed heterogeneously for the mesoporous adsorbent of carbon aerogel and the organic compound of ibuprofen. The role of π-π stacking interaction and hydrogen bonding during the adsorption, the small size of the ibuprofen molecules compared with the pore size of carbon aerogel (average pore diameter of 7.48 nm), chemical interactions (kinetic results) and multilayer adsorption with a heterogeneous system (isotherm results) demonstrated both mesoporous structure and surface chemistry are important in the adsorption mechanism.

Acknowledgements

The project was supported by Ferdowsi University of Mashhad (research grant 3/44727) that are greatly acknowledged.

References

- [1] S. Álvarez-Torrellas, M. Muñoz, J. Gläsel, Z.M. de Pedro, C.M. Domínguez, J. García, B.J.M. Etzold, J.A. Casas, Highly efficient removal of pharmaceuticals from water by well-defined carbide-derived carbons, *Chem. Eng. J.* 347 (2018) 595–606, <https://doi.org/10.1016/j.cej.2018.04.127>.
- [2] C. Ridruejo, F. Centellas, P.L. Cabot, I. Sirés, E. Brillas, Electrochemical Fenton-based treatment of tetracaine in synthetic and urban wastewater using active and non-active anodes, *Water Res.* 128 (2018) 71–81, <https://doi.org/10.1016/j.watres.2017.10.048>.
- [3] A. Olalla, N. Negreira, M. López de Alda, D. Barceló, Y. Valcárcel, A case study to identify priority cytostatic contaminants in hospital effluents, *Chemosphere* 190 (2018) 417–430, <https://doi.org/10.1016/j.chemosphere.2017.09.129>.
- [4] J.Q. Xiong, M.B. Kurade, B.H. Jeon, Can microalgae remove pharmaceutical contaminants from water? *Trends Biotechnol.* 36 (2018) 30–44, <https://doi.org/10.1016/j.tibtech.2017.09.003>.
- [5] R.R. Zepón Tarpani, A. Azapagic, Life cycle environmental impacts of advanced wastewater treatment techniques for removal of pharmaceuticals and personal care products (PPCPs), *J. Environ. Manag.* 215 (2018) 258–272, <https://doi.org/10.1016/j.jenvman.2018.03.047>.
- [6] J. Garcia-Ivars, L. Martella, M. Massella, C. Carbonell-Alcaina, M.I. Alcaina-Miranda, M.I. Iborra-Clar, Nanofiltration as tertiary treatment method for removing trace pharmaceutically active compounds in wastewater from wastewater treatment plants, *Water Res.* 125 (2017) 360–373, <https://doi.org/10.1016/j.watres.2017.08.070>.
- [7] C. Gadipelly, A. Pérez-González, G.D. Yadav, I. Ortiz, R. Ibáñez, V.K. Rathod, K.V. Marathe, Pharmaceutical industry wastewater: review of the technologies for water treatment and reuse, *Ind. Eng. Chem. Res.* 53 (2014) 11571–11592, <https://doi.org/10.1021/ie501210j>.
- [8] A. Carmalin Sophia, E.C. Lima, N. Allaudeen, S. Rajan, Application of graphene based materials for adsorption of pharmaceutical traces from water and wastewater - a review, *Desalination. Water Treat.* 57 (2016) 27573–27586, <https://doi.org/10.1080/19443994.2016.1172989>.
- [9] A.O. Dada, A.P. Olalekan, A.M. Olatunya, O. Dada, Langmuir, Freundlich, Temkin and Dubinin – Radushkevich isotherms studies of equilibrium sorption of Zn²⁺ onto phosphoric acid modified rice husk, *IOSR J. Appl. Chem.* 3 (2012) 38–45.
- [10] J. Akhtar, N.A.S. Amin, K. Shahzad, A review on removal of pharmaceuticals from water by adsorption, *Desalination. Water Treat.* 57 (2016) 12842–12860, <https://doi.org/10.1080/19443994.2015.1051121>.
- [11] R.N. Coimbra, V. Calisto, C.I.A. Ferreira, V.I. Esteves, M. Otero, Removal of pharmaceuticals from municipal wastewater by adsorption onto pyrolyzed pulp mill sludge, *Arab. J. Chem.* (2015), <https://doi.org/10.1016/j.arabj.2015.12.001>.
- [12] M. Grassi, G. Kaykioglu, V. Belgiorno, Emerging Compounds Removal From Wastewater, 2012 15–38, <https://doi.org/10.1007/978-94-007-3916-1>.
- [13] H. Maleki, Recent advances in aerogels for environmental remediation applications: a review, *Chem. Eng. J.* 300 (2016) 98–118, <https://doi.org/10.1016/j.cej.2016.04.098>.
- [14] W. Yuan, X. Zhang, J. Zhao, Q. Li, C. Ao, T. Xia, W. Zhang, C. Lu, Ultra-lightweight and highly porous carbon aerogels from bamboo pulp fibers as an effective sorbent for water treatment, *Results Phys.* 7 (2017) 2919–2924, <https://doi.org/10.1016/j.rinp.2017.08.011>.
- [15] L. Yuan, L. Chang, Z. Fu, X. Yang, X. Jiao, Y. Tang, X. Liu, C. Wang, Optimized synthesis of carbon aerogels via ambient pressure drying process as electrode for supercapacitors, *J. Wuhan Univ. Technol. Mater. Sci. Ed.* 30 (2015) 1325–1331, <https://doi.org/10.1007/s11595-015-1316-1>.
- [16] S. Wang, Y. Xu, M. Yan, Z. Zhai, B. Ren, L. Zhang, Z. Liu, Comparative study of metal-doped carbon aerogel: physical properties and electrochemical performance, *J. Electroanal. Chem.* 809 (2018) 111–116, <https://doi.org/10.1016/j.jelechem.2017.12.045>.
- [17] S. Zhang, J. Feng, J. Feng, Y. Jiang, F. Ding, Carbon aerogels by pyrolysis of TEMPO-oxidized cellulose, *Appl. Surf. Sci.* 440 (2018) 873–879, <https://doi.org/10.1016/j.apsusc.2018.01.252>.
- [18] Y. Xu, S. Wang, M. Yan, L. Zhang, Z. Zhai, Z. Liu, Synthesis of carbon aerogels based on resorcinol-formaldehyde/hydroxyethyl cellulose/carbon fiber and its electrochemical properties, *J. Porous Mater.* 25 (2018) 1505–1511, <https://doi.org/10.1007/s10934-018-0563-x>.
- [19] E. Lei, W. Li, C. Ma, S. Liu, An ultra-lightweight recyclable carbon aerogel from bleached softwood kraft pulp for efficient oil and organic absorption, *Mater. Chem. Phys.* 214 (2018) 291–296, <https://doi.org/10.1016/j.matchemphys.2018.04.075>.
- [20] L. Jothinathan, J. Hu, Kinetic evaluation of graphene oxide based heterogeneous catalytic ozonation for the removal of ibuprofen, *Water Res.* 134 (2018) 63–73, <https://doi.org/10.1016/j.watres.2018.01.033>.
- [21] H. Tian, Y. Fan, Y. Zhao, L. Liu, Elimination of ibuprofen and its relative photo-induced toxicity by mesoporous BiOBr under simulated solar light irradiation, *RSC Adv.* 4 (2014) 13061–13070, <https://doi.org/10.1039/c3ra47304j>.
- [22] H.R. Buser, T. Poiger, M.D. Muller, Occurrence and environmental behavior of the chiral pharmaceutical drug ibuprofen in surface waters and in wastewater, *Environ. Sci. Technol.* 33 (1999) 2529–2535, <https://doi.org/10.1021/es981014w>.
- [23] H.H. Yen, W.W. Su, Y.H. Chiu, Y.Y. Chen, M.S. Soon, Acute parotitis after double-balloon endoscopy, *Gastrointest. Endosc.* 68 (2008) 1017–1019, <https://doi.org/10.1016/j.gie.2008.02.042>.
- [24] T. Rohani, A. Ahmadpour, F. Ahmadi, Synthesis of Fe₃O₄/Bi₂WO₆ nanohybrid for the photocatalytic degradation of pharmaceutical ibuprofen under solar light, *J. Ind. Eng. Chem.* 51 (2017) 244–254.
- [25] G. Gonzalez, A. Sagarzazu, T. Zoltan, Influence of Microstructure in Drug Release Behavior of Silica Nanocapsules, 2013.

- [26] A.S. Mestre, J. Pires, J.M.F. Nogueira, J.B. Parra, A.P. Carvalho, C.O. Ania, Waste-derived activated carbons for removal of ibuprofen from solution: role of surface chemistry and pore structure, *Bioreour. Technol.* 100 (2009) 1720–1726, <https://doi.org/10.1016/j.biortech.2008.09.039>.
- [27] P. Banerjee, P. Das, A. Zaman, P. Das, Application of graphene oxide nanoplatelets for adsorption of Ibuprofen from aqueous solutions: evaluation of process kinetics and thermodynamics, *Process Saf. Environ. Prot.* 101 (2016) 45–53, <https://doi.org/10.1016/j.psep.2016.01.021>.
- [28] H. Guedidi, L. Reinert, Y. Soneda, N. Bellakhal, L. Duclaux, Adsorption of ibuprofen from aqueous solution on chemically surface-modified activated carbon cloths, *Arab. J. Chem.* 10 (2017) S3584–S3594, <https://doi.org/10.1016/j.arabjc.2014.03.007>.
- [29] T. Ren, Y. Han, M. Zhang, B. Zhang, X. Gou, Formation of carbon aerogels from glucose and as adsorbents for removal of methylene blue, *J. Mater. Sci. Res.* 3 (2014) 74–81, <https://doi.org/10.5539/jmsr.v3n2p74>.
- [30] S. Han, Q. Sun, H. Zheng, J. Li, C. Jin, Green and facile fabrication of carbon aerogels from cellulose-based waste newspaper for solving organic pollution, *Carbohydr. Polym.* 136 (2016) 95–100, <https://doi.org/10.1016/j.carbpol.2015.09.024>.
- [31] S. Xing, M. Zhao, Z. Ma, Removal of heavy metal ions from aqueous solution using red loess as an adsorbent, *J. Environ. Sci.* 23 (2011) 1497–1502, [https://doi.org/10.1016/S1001-0742\(10\)60581-5](https://doi.org/10.1016/S1001-0742(10)60581-5).
- [32] J. Goel, K. Kadirvelu, C. Rajagopal, V.K. Garg, Investigation of adsorption of lead, mercury and nickel from aqueous solutions onto carbon aerogel, *J. Chem. Technol. Biotechnol.* 80 (2005) 469–476, <https://doi.org/10.1002/jctb.1212>.
- [33] H. Tian, J. Wu, W. Zhang, S. Yang, F. Li, Y. Qi, R. Zhou, X. Qi, L. Zhao, X. Wang, High performance of Fe nanoparticles/carbon aerogel sorbents for H₂S removal, *Chem. Eng. J.* 313 (2017) 1051–1060, <https://doi.org/10.1016/j.cej.2016.10.135>.
- [34] D. Long, R. Zhang, W. Qiao, L. Zhang, X. Liang, L. Ling, Biomolecular adsorption behavior on spherical carbon aerogels with various mesopore sizes, *J. Colloid Interface Sci.* 331 (2009) 40–46, <https://doi.org/10.1016/j.jcis.2008.11.026>.
- [35] J.P.C. Kleijnen, Response surface methodology, *Int. Ser. Oper. Res. Manag. Sci.* 216 (2015) 81–104, https://doi.org/10.1007/978-1-4939-1384-8_4.
- [36] I.H. Cho, K.D. Zoh, Photocatalytic degradation of azo dye (Reactive Red 120) in TiO₂/UV system: optimization and modeling using a response surface methodology (RSM) based on the central composite design, *Dyes Pigments* 75 (2007) 533–543, <https://doi.org/10.1016/j.dyepig.2006.06.041>.
- [37] A.R. Yaqubzadeh, A. Ahmadpour, T.R. Bastami, M.R. Hataminia, Low-cost preparation of silica aerogel for optimized adsorptive removal of naphthalene from aqueous solution with central composite design (CCD), *J. Non-Cryst. Solids* 447 (2016) 307–314, <https://doi.org/10.1016/j.jnoncrysol.2016.06.022>.
- [38] X. Wu, D. Wu, R. Fu, Studies on the adsorption of reactive brilliant red X-3B dye on organic and carbon aerogels, *J. Hazard. Mater.* 147 (2007) 1028–1036, <https://doi.org/10.1016/j.jhazmat.2007.01.139>.
- [39] E. Hu, X. Wu, S. Shang, X.M. Tao, S.X. Jiang, L. Gan, Catalytic ozonation of simulated textile dyeing wastewater using mesoporous carbon aerogel supported copper oxide catalyst, *J. Clean. Prod.* 112 (2016) 4710–4718, <https://doi.org/10.1016/j.jclepro.2015.06.127>.
- [40] T. Ren, L. Han, R. Liu, C. Ma, X. Chen, S. Zhao, Y. Zhang, Influence of inorganic salt on retention of ibuprofen by nanofiltration, *Sep. Purif. Technol.* 189 (2017) 382–388, <https://doi.org/10.1016/j.seppur.2017.08.035>.
- [41] J. Madhavan, F. Grieser, M. Ashokkumar, Combined advanced oxidation processes for the synergistic degradation of ibuprofen in aqueous environments, *J. Hazard. Mater.* 178 (2010) 202–208, <https://doi.org/10.1016/j.jhazmat.2010.01.064>.
- [42] S.J. Mousavi, M. Parvini, M. Ghorbani, Experimental design data for the zinc ions adsorption based on mesoporous modified chitosan using central composite design method, *Carbohydr. Polym.* 188 (2018) 197–212, <https://doi.org/10.1016/j.carbpol.2018.01.105>.
- [43] A. Hassani, A. Khataee, S. Karaca, M. Karaca, M. Kiranşan, Adsorption of two cationic textile dyes from water with modified nanoclay: a comparative study by using central composite design, *J. Environ. Chem. Eng.* 3 (2015) 2738–2749, <https://doi.org/10.1016/j.jece.2015.09.014>.
- [44] N. Gabilondo, M. Larrañaga, C. Peña, M.A. Corcuera, J.M. Echeverría, I. Mondragon, Polymerization of resole resins with several formaldehyde/phenol molar ratios: amine catalysts against sodium hydroxide catalysts, *J. Appl. Polym. Sci.* 102 (2006) 2623–2631, <https://doi.org/10.1002/app.24017>.
- [45] X.K. Pei, M. Cai, B.Y. Shi, Kidney transplantation for treating lower urinary tract abnormality: a follow-up in 4 cases, *J. Clin. Rehabil. Tissue Eng. Res.* 12 (2008) 6158–6160, <https://doi.org/10.1007/978-1-4419-7589-8>.
- [46] M. Bakierska, A. Chojnacka, M. Świętosławski, P. Natkański, M. Gajewska, M. Rutkowska, M. Molenda, Multifunctional carbon aerogels derived by sol-gel process of natural polysaccharides of different botanical origin, *Materials (Basel)* 10 (2017) <https://doi.org/10.3390/ma10111336>.
- [47] M. Kruk, M. Jaroniec, Gas adsorption characterization of ordered organic-inorganic nanocomposite materials, *Chem. Mater.* 13 (2001) 3169–3183, <https://doi.org/10.1021/cm0101069>.
- [48] V. Mahmoodi, J. Sargolzaei, Optimization of photocatalytic degradation of naphthalene using nano-TiO₂/UV system: statistical analysis by a response surface methodology, *Desalin. Water Treat.* 52 (2014) 6664–6672, <https://doi.org/10.1080/19443994.2013.861774>.
- [49] J. Zolgharnein, M. Bagtash, N. Asanjarani, Hybrid Central Composite Design Approach for Simultaneous Optimization of Removal of Alizarin Red S and Indigo Carmine Dyes Using Cetyltrimethylammonium Bromide-modified TiO₂ Nanoparticles, Elsevier, 2014 <https://doi.org/10.1016/j.jece.2014.03.017>.
- [50] A. Asghar, A.A.A. Raman, W.M.A.W. Daud, A comparison of central composite design and Taguchi method for optimizing Fenton process, *Sci. World J.* 2014 (2014) <https://doi.org/10.1155/2014/869120>.
- [51] B. Royer, N.F. Cardoso, E.C. Lima, J.C.P. Vaghetti, N.M. Simon, T. Calvete, R.C. Veses, Applications of Brazilian pine-fruit shell in natural and carbonized forms as adsorbents to removal of methylene blue from aqueous solutions-kinetic and equilibrium study, *J. Hazard. Mater.* 164 (2009) 1213–1222, <https://doi.org/10.1016/j.jhazmat.2008.09.028>.
- [52] C.G. Committee, S. Manager, Policy on Medical Equipment Purchasing, vol. 59, 2008 171–177.
- [53] Y.S. Ho, Review of second-order models for adsorption systems, *J. Hazard. Mater.* 136 (2006) 681–689, <https://doi.org/10.1016/j.jhazmat.2005.12.043>.