



Experimental design and response surface modeling for optimization of humic substances removal by activated carbon: A kinetic and isotherm study

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Original Article

Abstract

The presence of humic acid (HA) in water treatment processes is very harmful and the cause of undesirable color, taste, and smell. Drinking water containing high concentrations of humic substances can be the cause of many health problems. Therefore, the removal of these compounds from water resources is a very important topic. In this research, response surface methodology (RSM) has been used to optimize the effect of main operational variables responsible for higher HA removal by activated carbon (AC). A three-level Box–Behnken factorial design (BBD) was used to optimize initial concentration of HA, time, pH, and AC dose for humic substances removal. The characterization of AC was carried out using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD) analysis. A coefficient of determination (R^2) value of 0.98, model F-value of 82.32 and its low P ($F < 0.0001$), and low value of coefficient of variation (9.94%) indicated the fitness of the response surface quadratic model during the present study. At initial optimum concentration (5.25 mg HA/l), pH (5.85), contact time (36.01 minutes), and dose (1.38 g AC/L), the model predicted 1.90 mg HA/l. Equilibrium adsorption of HA onto AC had best fitness with the Freundlich isotherm and pseudo-second-order kinetic model.

KEYWORDS: Humic Substances, Kinetics, Drinking Water, Adsorption

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Introduction

Humic substances are a group of non-biodegradable organic material which must be removed from drinking water sources. An essential part of humic substances in water is humic acids (HAs).¹ HAs are natural polyelectrolytes which are formed due to the decomposition of plants, animals, and other

organisms in the form of biological activity in soil and natural waters.² Hydrophilic compounds are amorphous and have varied molecular weight. Their physical and chemical properties make them special.³ Functional groups of humic substances are carboxylic, phenolic, carbonyl, and hydroxyl acids, acetaldehyde, and methoxy. The presence of phenolic and carboxyl groups creates a stable negative charge in aqueous environments.^{4,5} Humic substances make up about 40 to 90% of dissolved organic matter in water. The physical

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and chemical properties of these organic materials in water depend on their source.⁵ Sources of humic substances in water include leakage through the soil, sediment, aquatic animals, plants, and effluents from sewage treatment plants.¹ The concentration of humic substances in natural waters is usually in the range of 0.1 to 10 mg/l.^{5,6} The presence of humic substances in water treatment processes is very harmful and the cause of undesirable color, taste, and smell. On the other hand, as a result of chlorination of these waters, dangerous and carcinogenic byproducts such as trihalomethanes (THMs) are produced.⁷ Humic substances in water interfere with the removal of heavy metals by forming complexes with metal. In addition, humic substances can form complexes with heavy metals, pesticides, and herbicides that lead to a migration of these compounds in aqueous solutions and an increase in their concentration. This is an important issue in water.⁷ The high concentrations of humic substances in water disrupt the performance of ion exchange resins and membranes in water treatment.⁸ In addition to the above problems, some sources have reported that drinking water containing high concentrations of HA can be a cause of black foot disease.^{5,6} Thus, the removal of these compounds from drinking water and other water resources is of significant importance.

Conventional treatment methods (coagulation, flocculation, sedimentation, and disinfection) cannot completely remove humic substances from water and are only able to remove 20 to 50% of them.^{4,9} On the other hand, other methods of removing organic materials, including ion exchange, evaporation, reverse osmosis, and chemical precipitation, often have high costs and disposal of their sludge is difficult.^{10,11} Therefore, the use of a low-cost adsorbent that is able to remove high amounts of organic matter and improve the quality of drinking water is a necessity. Several adsorbents such as clay, zeolite, chitosan, and metal oxides

are used to adsorb humic substances.^{10,12,13} Activated carbon (AC) is extensively used in the removal of organic compounds from water, because the adsorbent has a high active surface and has shown an efficient performance.¹⁰ The purpose of this study was to investigate the use of AC as a model adsorbent for the removal of HA from water. The experimental work includes the assessment of factors influencing the adsorption of HA on AC by means of Box-Behnken factorial design (BBD) in response surface methodology (RSM). The adsorption kinetics of HA on AC under various conditions were also studied.

Materials and Methods

Commercial AC used in this study was a Merck (Merck KGaA, Darmstadt, Germany) product. The stock solution of HA was made according to the standard method¹⁴ and was stored in a refrigerator at 4 ± 0.1 °C before use. All solutions used in each run were prepared by diluting the stock solution. The commercial AC was dipped in 5% hydrochloric acid for 24 hours, followed by washing with deionized water until the water pH was stable (pH = 6.52–6.70). After drying for 24 hours at 105 °C, AC was used as an adsorbent. The morphological properties of AC were observed using a scanning electron microscope (SEM-EDS, TESCAN Vega Model, Brno, Czech Republic). The crystal structure and crystallinity of the composites were examined using X-ray diffraction (XRD) analysis with a Rigaku D/MAXYA diffractometer with Ni-filtered Cu K α radiation as X-ray source (Theta-Theta model, STOE, Germany).

The BBD consisted of three levels (low, medium, and high coded as -1, 0, and +1). The complete design consisted of 29 runs which were performed in duplicate to optimize the levels of selected variables (initial concentration of HA, pH, contact time, and AC dose). The lowest and highest levels of HA initial concentration were 5 and 50 mg/l, pH 3 and 9,

time 1 and 60 minutes, and AC dose 0.5 and 1.5 g/l. The HA removal efficiency was multiplying regressed the different parameters by the least square methods as follows:

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ij} X_i^2 + \sum \beta_{ij} X_i X_j \quad [2]$$

where Y is the predicted response variable, β_0 , β_i , β_{ii} , and β_{ij} are constant regression coefficients, and X_i and X_j ($i = 1, 3; j = 1, 3, i \neq j$) represent the independent variable.¹⁵

The accuracy and fitness of the above model was evaluated by R^2 and F values. Table 1 shows the BBD matrix along with experimental and predicted values for HA removal. The predicted values for HA removal were obtained by applying the quadratic model (Design Expert software, version 7, Stat-Ease, Inc., Minneapolis, Mn, USA). The optimum values of the variables for HA removal were obtained by solving the regression equation, and analyzing the response surface contour plots and constraints for the variables using the same software. The goal determined for HA removal was maximum HA removal.

All experiments were performed at room temperature and in batch mode in 250 ml beakers by mixing 100 ml of the desired HA solution. The mixture was shaken at 200 rpm for the desired duration of time. The mixture was then filtered through 0.45 μ filter and the final concentration of HA in the supernatant solution was determined by measuring the absorbance at the maximum wavelength of 254 nm using a UV-visible spectrophotometer (DR5000). The amount of HA adsorbed (mg/g) was calculated based on the following equation:

$$q_e = \frac{(C_0 - C_e)V}{M} \quad [3]$$

where q_e is the amount (mg) of adsorbed HA on per g of AC, C_0 and C_t are HA concentration (mg) before adsorption and after adsorption in time t , respectively. V is initial volume of solution (l), and m the weight of adsorbent (g).

The pH of zero charge point (pH_{zpc}) of AC

was determined according to the pH drift procedure.^{4,5}

Among the various isotherm equations that are used for analysis of absorption data in aqueous environments, the Langmuir and Freundlich isotherms are more common. The linear form of these isotherms is shown as equation 5 (Langmuir) and 6 (Freundlich):

$$\frac{C_e}{q_e} = \frac{1}{k_1 q_0} + \frac{1}{q_0} C_e \quad [5]$$

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \quad [6]$$

where q_0 (mg/g) is the maximum adsorption capacity, q_e (mg/g) is the amount of HA adsorbed on the adsorbent, C_e (mg/l) is the equilibrium HA concentration, k_F and n are the Freundlich constants, and k_1 (l/mg) is the Langmuir constant. For the Langmuir model, the linear plot of $1/(X/m)$ versus $1/C$, and for the Freundlich model, the linear plot of $\ln q_e$ versus $\ln C_e$ is drawn. The determination coefficient (R^2) is used to determine the goodness of fit of the models.

In this study, pseudo-first order and pseudo-second-order kinetics were used to describe the data. The pseudo-first order (equation 7) and the pseudo-second order (equation 8) are as follows:

$$\ln(q_e - q_t) = -K_1 t + \ln q_e \quad [7]$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad [8]$$

where q_e and q_t are the amount of HA adsorbed on AC at time t and equilibrium time, respectively. K_1 and k_2 are constants of adsorption rate. For the pseudo-first order model, the plot of $\ln(q_e - q_t)$ versus t , and for the pseudo-second order model, the plot of t/q_t versus t is drawn. The determination coefficient (R^2) is used to determine the goodness of fit of the models.

Results and Discussion

Characterization of AC

Properties and morphology of AC were

determined using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) analysis in the operating voltage of 20 keV (Figure 1). The electron image is magnified 9000 times. These analyses show the quantitative characteristics, such as particle size, shape/morphology, and surface area, of AC. The results of the analysis of SEM-EDS (Figure 2) show the elemental analysis of AC. As can be seen in figure 1, the two main elements in the AC were carbon and oxygen that included 90.39 and 9.61% by total weight, respectively. All these features show that AC has a high potential to absorb pollutants from water.

The XRD pattern of AC is illustrated in figure 3. In the pattern of AC, there was only one broad peak at 24.14 corresponding to amorphous carbon.²

Optimization of parameters for HA removal

Table 1 shows that there was a considerable variation in HA removal by AC at different values of selected parameters. Multiple regression analysis method based on equation 2 was used for analyzing the data. The predicted response Y for HA removal was obtained as following:

$$Y = 3.73 + 1.97X_1 + 0.52X_2 - 0.49X_3 - 0.2X_4 + 0.28X_1X_2 - 0.23X_1X_3 - 0.004X_1X_4 + 0.11X_2X_3 + 0.021X_2X_4 - 0.029X_3X_4 - 0.41X_1^2 + 0.22X_2^2 + 0.39X_3^2 + 0.013X_4^2 \quad [4]$$

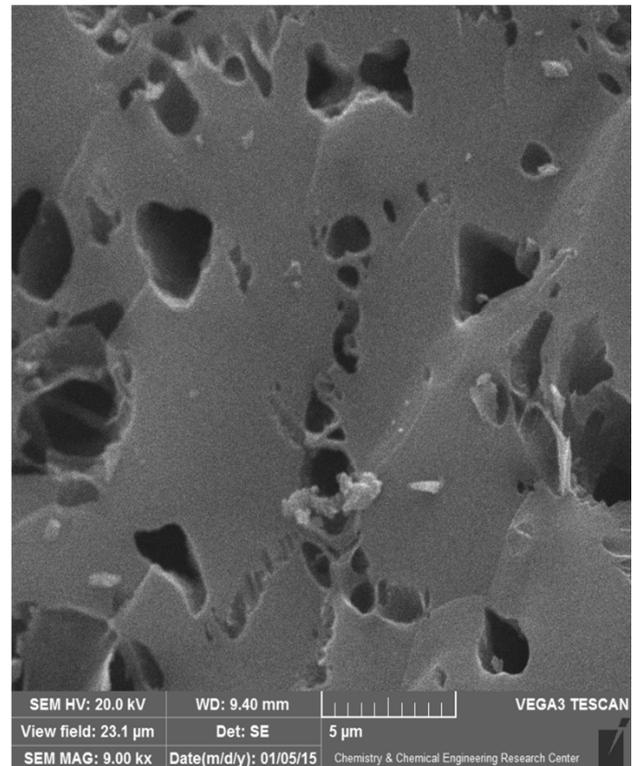


Figure 1. Scanning electron microscopy (SEM) image of activated carbon (AC)

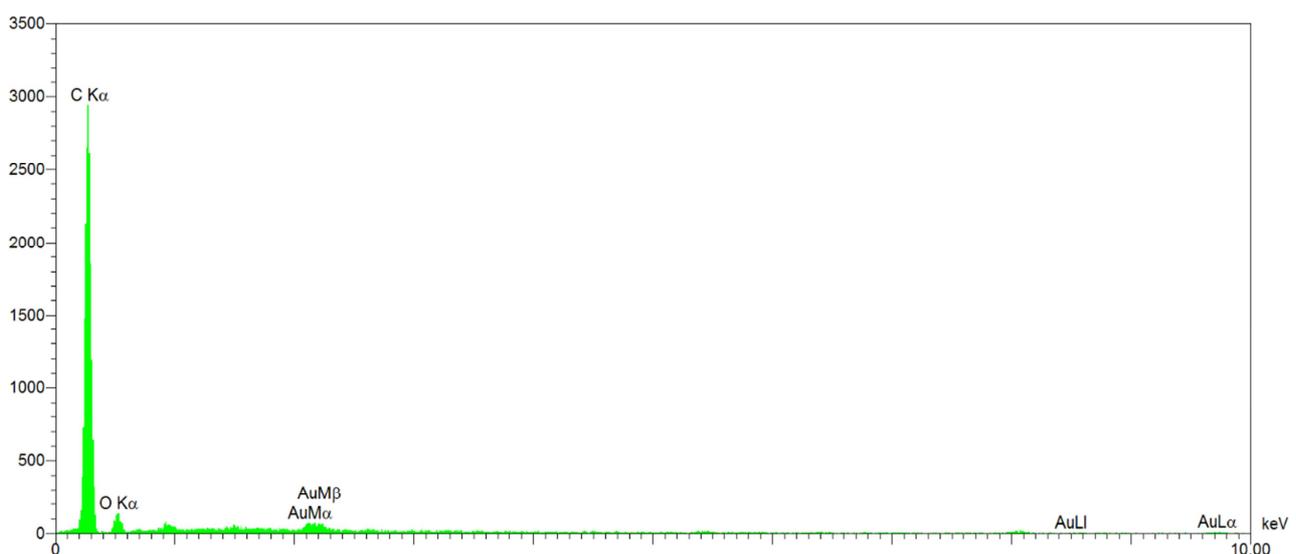


Figure 2. Energy-dispersive X-ray spectroscopy (EDS) diagrams of activated carbon (AC)

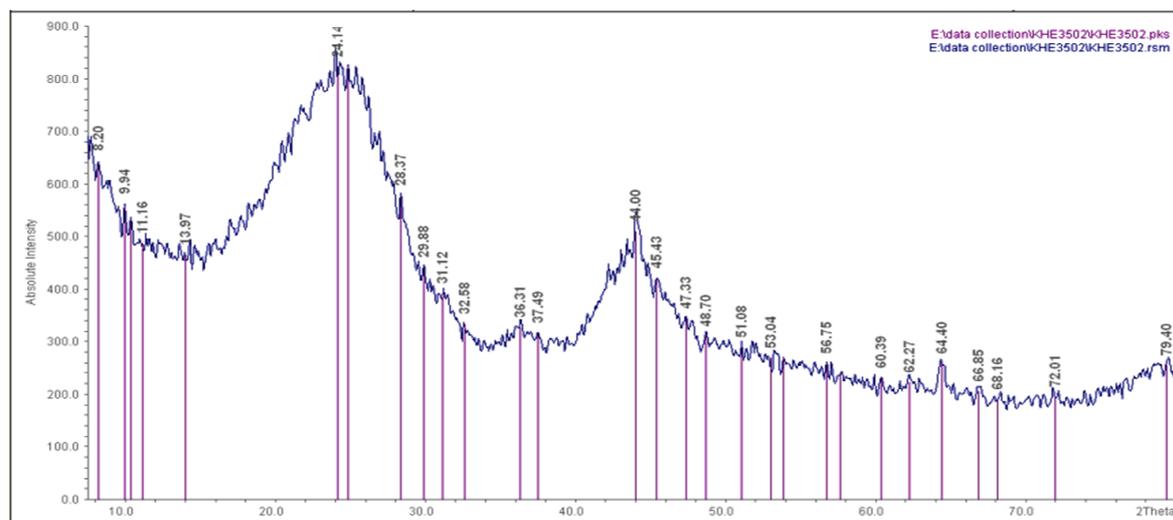


Figure 3. X-ray diffraction (XRD) patterns of activated carbon (AC)

Table 1. Box–Behnken factorial design (BBD) matrix in coded terms along with experimental and predicted values for humic acid (HA) removal

Runs	Independent variables (coded)				Humic acid removal (mg/l)	
	X ₁	X ₂	X ₃	X ₄	Experimental	Predicted
1	-1	-1	0	0	1.70	1.77
2	0	0	1	-1	13.36	13.55
3	1	0	1	0	26.19	24.67
4	1	0	0	-1	27.32	30.38
5	1	-1	0	0	23.18	22.24
6	0	-1	0	-1	12.16	12.12
7	0	0	0	0	12.37	12.36
8	-1	1	0	0	3.29	3.30
9	0	0	0	0	12.37	12.36
10	0	1	1	0	17.65	18.21
11	-1	0	1	0	2.00	2.19
12	0	1	0	-1	20.59	19.56
13	1	1	0	0	41.56	39.98
14	0	0	-1	1	18.57	17.84
15	0	0	0	0	12.37	12.36
16	0	-1	1	0	9.86	9.37
17	1	0	-1	0	42.83	41.11
18	-1	0	0	1	1.84	1.37
19	0	0	0	0	12.37	12.36
20	0	0	1	1	9.81	10.39
21	0	1	0	1	17.00	16.53
22	0	-1	0	1	8.94	9.25
23	-1	0	-1	0	3.68	4.06
24	1	0	0	1	24.33	26.50
25	0	0	0	0	12.37	12.36
26	0	-1	-1	0	17.23	17.86
27	0	1	-1	0	22.62	24.82
28	0	0	-1	-1	22.25	20.82
29	-1	0	0	-1	2.58	2.44

X₁ = Initial concentration of humic acid; X₂ = pH; X₃ = Time; X₄ = activated carbon dose

Table 2. Analysis of variance (ANOVA), regression coefficient estimate, and test of significance for humic acid (HA) removal

Factor	Sum of squares	Mean squares	Coefficient estimated \pm S.E.	d.f.	F-value	P > F
Intercept	55.16	3.94	3.730 ± 0.072	14	154.00	< 0.0001
X ₁	46.55	46.55	1.970 ± 0.046	1	1819.25	< 0.0001
X ₂	3.21	3.21	0.520 ± 0.047	1	125.46	< 0.0001
X ₃	2.89	2.89	-0.490 ± 0.047	1	112.99	< 0.0001
X ₄	0.47	0.47	0.200 ± 0.047	1	18.36	0.0008
X ₁ X ₂	0.32	0.32	0.280 ± 0.080	1	12.56	0.0032
X ₁ X ₃	0.21	0.21	-0.230 ± 0.080	1	8.15	0.0127
X ₁ X ₄	6.9×10^{-5}	6.9×10^{-5}	$(-4.13 \times 10^{-3}) \pm 0.08$	1	2.7×10^{-3}	0.9593
X ₂ X ₃	0.05	0.051	0.110 ± 0.080	1	1.99	0.1804
X ₂ X ₄	1.71×10^{-3}	1.71×10^{-3}	0.021 ± 0.080	1	0.07	0.8000
X ₃ X ₄	3.46×10^{-3}	3.46×10^{-3}	-0.029 ± 0.08	1	0.14	0.7186
X ₁ ²	1.05	1.05	-0.410 ± 0.064	1	40.91	< 0.0001
X ₂ ²	0.33	0.33	0.220 ± 0.063	1	12.80	0.0030
X ₃ ²	1.01	1.01	0.390 ± 0.063	1	39.41	< 0.0001
X ₄ ²	1.14×10^{-3}	1.14×10^{-3}	0.013 ± 0.063	1	0.04	0.8359
Residual	0.36	0.03		14		
Corrected total	55.52			28		

X₁: Initial concentration of humic acid; X₂: pH; X₃: Time; X₄: Activated carbon dose

In this equation Y is the HA removal (mg/l), and X₁, X₂, X₃, and X₄ are initial concentration of HA, pH, contact time, and AC dose, respectively. The data obtained from Eq. 4 were verified by F value and the analysis of variance (ANOVA) in response surface quadratic model. All p-values below 0.05 were considered as significant. The linear effect of coefficients of initial concentration of HA (P < 0.0001), pH (P < 0.0001), contact time (P < 0.0001), and AC dose (P = 0.0008) were significant. Similarly, the interactive effects of initial concentration and pH (P = 0.0032), and initial concentration and time (P = 0.0127) were also significant. However, the interactive effect of initial concentration and dose (P = 0.9593), pH and time (P = 0.1804), pH and dose (P = 0.8), and time and dose was insignificant. The p-values of the quadratic terms, [initial concentration (X₁²) (P < 0.0001), pH (X₂²) (P = 0.003), and time (X₃²) (P < 0.0001)] were significant. The F-value (154), R² value (0.99), probability (P < 0.0001), and coefficient of variation (C.V. = 4.32%) obtained through ANOVA for response surface quadratic model signify that the model is significant (Table 2). Statistical parameters listed in table 2 and the

high value of the regression coefficient (R² = 0.98) suggest that the removal of HC by AC can be well described through this model. On the other hand, the F value showed that the model was significant. The F value in this study is equal to 82.32. Since the F parameter is higher than 18, the significance of the model for the removal of HC is clear.

As can be seen in table 1, experimental and predicted values for HA removal lie within a narrow interval. This also shows the outstanding degree of fitness for the model equation.

The main objective of the optimization is to determine the optimum values of variables for HA removal efficiency. In optimization, the desired aim in terms of HA removal efficiency was defined as achieving maximum removal efficiency. At optimum initial concentration (5.25 mg HA/l), pH (5.85), contact time (36.01 minutes), and dose (1.38g AC/l) the model predicted 1.90 mg HA/l or 67.52% removal efficiency.

The effect of the HA initial concentration and pH

Contour plots show the type of interaction between test variables and help to achieve the optimum conditions.¹⁶ Figure 4 shows HA

removal as a result of interaction between initial concentration (5, 25, and 50 mg/l) and pH (3, 6, and 9). Colors for the contour plots represent the removal efficiency. For example, red means maximum removal, green medium, and blue minimum removal efficiency. With increased initial concentration, HA removal efficiency decreased, and maximum sorption (65.99%) was predicted at 5 mg HA/l. The results show that with increase in initial concentration, HA organic molecules are adsorbed on the surface of AC and these molecules can occupy greater number of active sites on the adsorbent.¹⁷ Thus, at lower concentration, a greater number of pores was available on the AC surface.

As the results verified, acidic conditions were more suitable for the removal of HA, and efficiency decreased when pH was greater than 5. Most of the organic contaminants were reduced effectively at lower pH values.¹⁸ At

low pH values, surface sites are closely coupled to H⁺ ions; therefore, these sites become unavailable for other cations. Thus, HA could not be easily adsorbed onto AC. In alkaline conditions, HA is negatively charged and the efficiency slightly decreased.¹⁵

The effect of contact time and AC dosage

Removal efficiency for HA was investigated at contact time of 1, 30, and 60 minutes. The results showed that the optimum time for HA removal by AC was 60 minutes. Therefore, HA adsorption was found to increase with increase in time as shown in figure 5. The HA removal in the abovementioned time duration was attributed to the surface connection between active surface groups and HA ion. Furthermore, further sorption at the described times can be illustrated with an increased availability in the active boundary sites on the sorbent surface area.^{19,20}

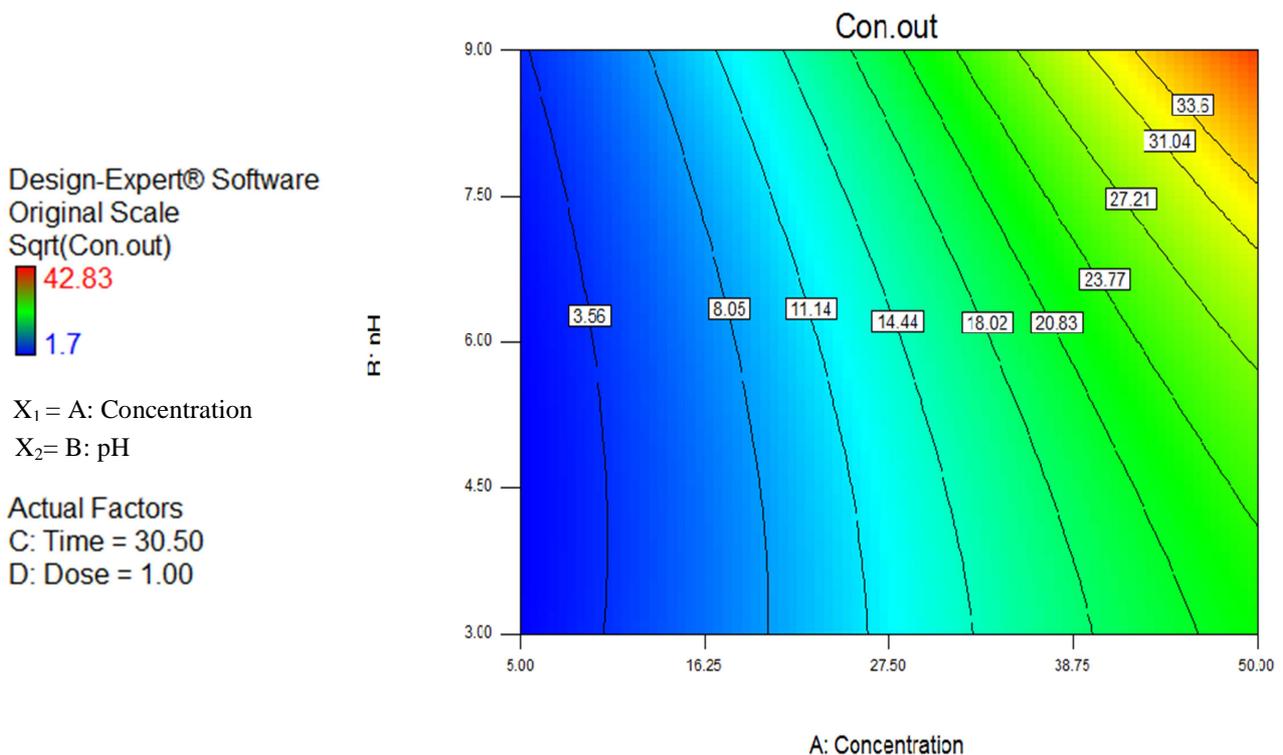


Figure 4. Response surface contour plots showing effect of initial concentration (mg HA/l) and pH on humic acid (HA) removal (mg/l)

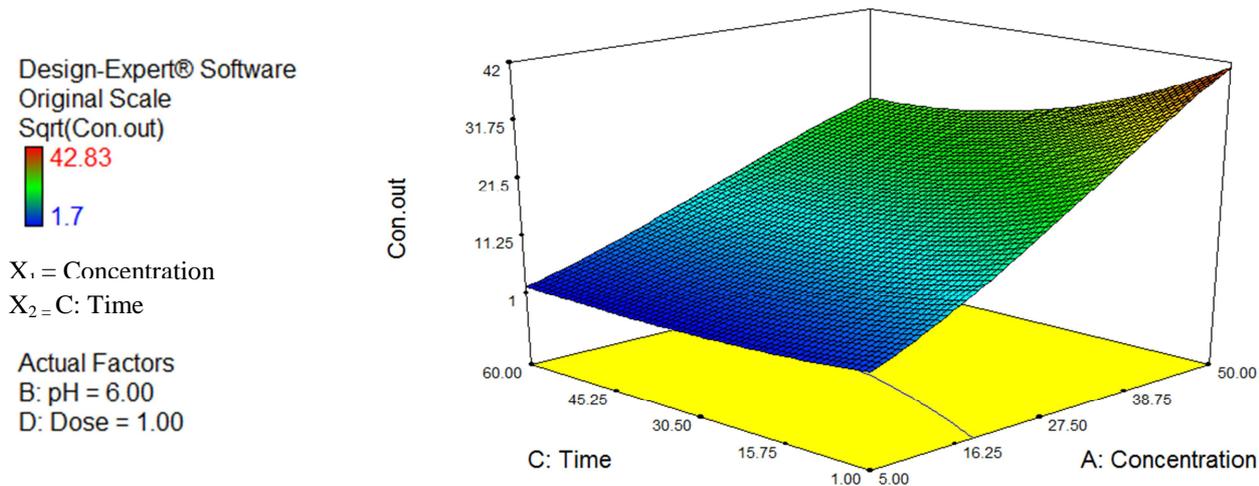


Figure 5. Response surface 3D plots showing effect of initial concentration (mg HA/l) and time on humic acid (HA) removal (mg/l)

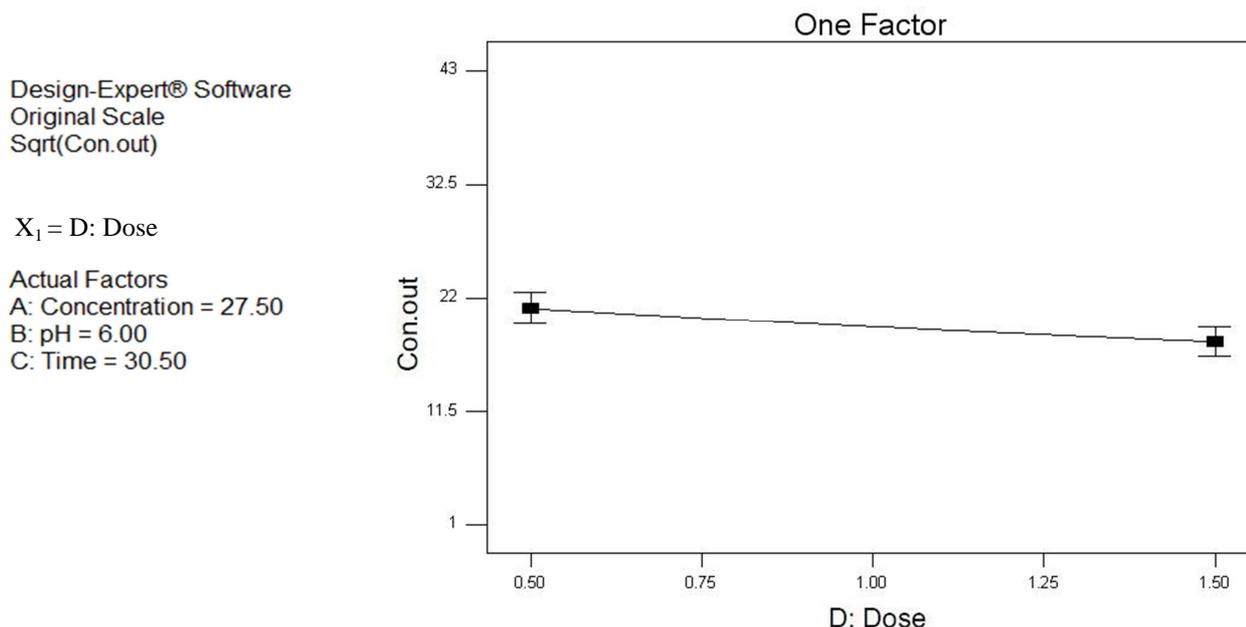


Figure 6. Response surface one factor plots showing effect of activated carbon (AC) dose (g AC/l) on humic acid (HA) removal (mg/l)

Consideration of the effect of one factor (AC dose) alone shows that its effect is in accordance with figure 6. As shown in figure 5, with increase in AC dosage, the removal efficiency also increased. The removal of organic compounds such as HA by AC implicates direct contact between the organic

matter and cavity on the AC particle surface. ANOVA analysis showed the significant effect of adsorbent dosage on HA removal ($P < 0.0001$). Nevertheless, the interaction effects of these variables with other variables in this study (initial concentration, pH, and contact time) were not significant.

Isotherm and kinetic study

Equilibrium time is the primary result of absorption kinetics. If this parameter is specified, adsorption isotherms can be achieved. In this study, to obtain absorption equilibrium time, a 250 ml HA solution with concentration of 25 mg/l was prepared, and then, 125 mg of adsorbent was added to the container. The pH value of the solution was adjusted between 5.6 and 7. Mixing speed and temperature were 200 rpm and 25 °C, respectively. The sampling was conducted at specified intervals and after passing samples from a 0.45 μ filter, absorbed HA was measured using a spectrophotometer at a wavelength of 254 nm. The results of this phase were examined by drawing a diagram of the concentration versus time and when concentration changed over time and reached zero, it was recorded as the equilibrium time. As can be seen in figure 5, the equilibrium time in this study was 960 minutes (Figure 7).

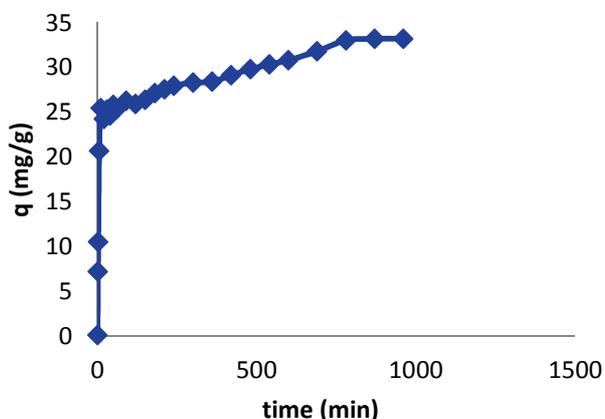


Figure 7. Equilibrium time curve of humic acid (HA) absorption on activated acid (AC)

Adsorption isotherms are equilibrium data used to describe the interaction between adsorbent and adsorbate. Isotherms also suggest the capacity of an adsorbent. The results of Langmuir and Freundlich isotherm models are shown in figures 8 and 9 and also in table 3. As is clear from the results and determination coefficient, the Freundlich

isotherm model is able to better explain test results ($R^2 = 0.9971$). The empirical equation isotherm of Freundlich is based on multi-layer, non-homogeneous, and heterogeneous materials adsorbed on the adsorbent.³

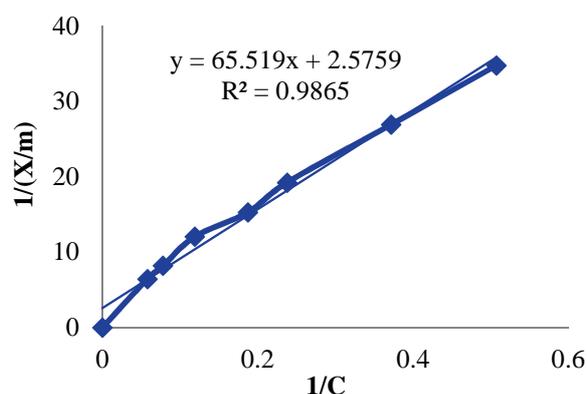


Figure 8. Langmuir model of humic acid (HA) absorption on activated acid (AC) (pH = 6-7.5, T = 25 °C, mixing time for AC = 16 hours)

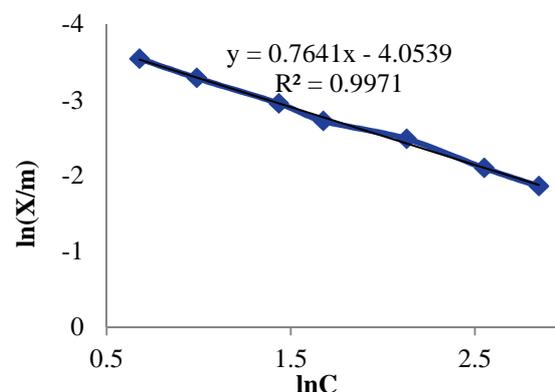


Figure 9. Freundlich model of humic acid (HA) absorption on activated carbon (AC) (pH = 6-7.5, T = 25 °C, mixing time for AC = 16 hours)

Table 3 illustrates that the obtained value of n in the Freundlich model is 1.322; representing the average absorption of HA on AC.⁹

To investigate the factor influencing the reaction rate, it is necessary to study the kinetics of the process. Adsorption kinetics were studied in order to better understand the adsorption dynamic of HA on the adsorbent and produce a predictive model to estimate the amount of ions absorbed during the process.

Table 3. Parameters of Langmuir and Freundlich models in adsorption of humic acid (HA) on activated carbon (AC)

Langmuir			Freundlich		
b	q_m	R^2	k	n	R^2
0.2385	33.2	0.9865	0.0175	1.322	0.9971

Figures 10 and 11 show pseudo-first-order and pseudo-second-order kinetics curves, respectively. R^2 obtained for the pseudo-first-order and pseudo-second-order models were 0.9855 and 0.9999, respectively. Therefore, the pseudo-second-order kinetic model is more acceptable for analysis of HA on AC.

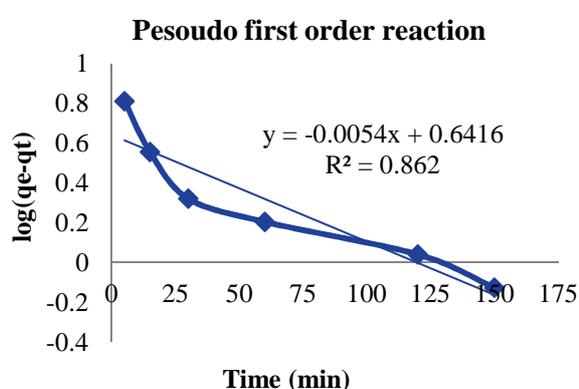


Figure 10. Pseudo-first-order kinetic model of humic acid (HA) absorption on activated carbon (AC) (initial concentration = 25 mg/l, pH = 6-7.5, T = 25 °C)

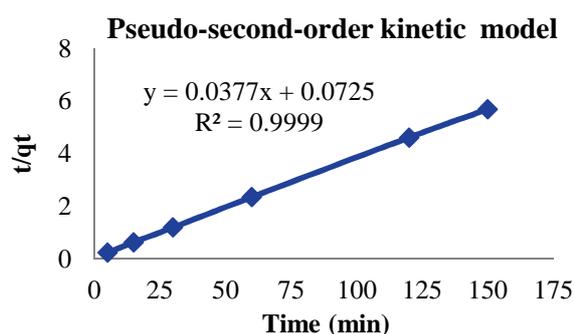


Figure 11. Pseudo-second-order kinetic model of humic acid (HA) absorption on activated carbon (AC) (initial concentration = 25 mg/l, pH = 6-7.5, T = 25 °C)

The pseudo-first-order kinetic model is based on absorbent capacity and is applied

when adsorption, using diffusion mechanism, occurs within a boundary layer. While, the pseudo-second-order kinetic model shows that chemical adsorption is dominant and shows the controlling mechanism in the process of adsorption.²¹

Conclusion

In the present study, RSM based on the four-factor-three-level BBD was employed as an experimental design tool to explain the effect of main operating parameters (including HA concentration, pH, contact time, and adsorbent dose) and their interactions on the removal of HA. RSM showed that HA removal efficiency was significantly affected by all the mentioned variables. AC is quite efficient in the removal of humic substances from solution. According to the ANOVA results, the model presents a high R^2 value (0.98) for HA removal efficiency. At optimum initial concentration (5.25 mg HA/l), pH (5.85), contact time (36.01 minutes), and dose (1.38 g AC/l) the model predicted 1.90 mg HA/l or 67.52% removal efficiency.

Conflict of Interests

Authors have no conflict of interests.

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