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Experimental design and response surface modeling for optimization of fluoroquinolone removal from aqueous solution by NaOH-modified rice husk

Seyed Davoud Ashrafi[a], Hossein Kamani[b], Jalil Jaafari[a], Amir Hossein Mahvi[c,d,e,f,*]

[a]*Department of Environmental Health Engineering, School of Health, Guilan University of Medical Sciences, Rasht, Iran, Tel. +98 2144729729; email: d_ashrafi@yahoo.com (S.D. Ashrafi), Tel. +98 2188954914; email: jalil.jaafari@yahoo.com (J. Jaafari)*
[b]*Health Promotion Research Center, Zahedan University of Medical Sciences, Zahedan, Iran, Tel. +98 5412428797; Fax: +98 2166662267; email: hossein_kamani@yahoo.com*
[c]*Center for Water Quality Research (CWQR), Institute for Environmental Research (IER), Tehran University of Medical Sciences, Tehran, Iran, Tel. +98 2188951400; Fax: +98 2188950188; email: ahmahvi@yahoo.com*
[d]*School of Public Health, Tehran University of Medical Sciences, Tehran, Iran*
[e]*Center for Solid Waste Research (CSWR), Institute for Environmental Research (IER), Tehran University of Medical Sciences, Tehran, Iran*
[f]*National Institute of Health Research, Tehran University of Medical Sciences, Tehran, Iran*

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ABSTRACT

The aim of this study is to obtain optimal adsorption conditions for enrofloxacin (ENR) as a fluoroquinolone antibiotic onto NaOH-modified rice husk using response surface methodology (RSM). On the basis of a four variable Box–Behnken design (BBD), RSM was used to determine the effect of adsorbent dose (0.25, 0.5, and 0.75 g L^{-1}), pH (5, 7, and 9), ENR initial concentration (25, 75, and 125 mg L^{-1}), and temperature (15, 30, and 45˚C) on adsorption efficiency. By applying the quadratic regression analysis, among the main parameters, the removal efficiency was significantly affected by all the four variables. The results showed that the predicted values for ENR adsorption were close to the experimental values and were in good agreement. In addition, the R^2 value (R^2 = 0.9705) indicates that the regression is able to give a good predict of response for the adsorption process in the studied range. From the BBD predictions, the optimal conditions for 92.25% ENR removal were found to be 0.69 g L^{-1} of adsorbent dose, pH 5.11, and initial concentration of ENR 25.02 mg L^{-1}, at temperature 36.43˚C.

Keywords: Fluoroquinolone; Enrofloxacin; Adsorption; Agricultural waste; Rice husk; Box–Behnken

1. Introduction

Among all the pharmaceutical products that cause pollution problems in the environment, antibiotics occupy an important situation due to high consumption rates in both human and veterinary medicine. Quinolones are a group of synthetic antibacterial agents, which were introduced about 45 years ago. Fluoroquinolones (FQs) are among the most important classes of quinolones used widely in human (since the 1980s) medicine and veterinary (since the 1990s) for therapeutic purposes and as a growth promoter [1].

*Corresponding author.

Enrofloxacin (ENR) is the most commonly used fluoroquinolone to control or to treat poultry diseases. Due to low bioavailability of fluoroquinolone [2] largely excreted as unchanged compounds in feces and urine, and consequently being discharged into environment [3,4] may result in high concentrations of ENR residues in the environment [5,6]. When antibacterial agents like ENR present in the environment, can increase the risk of resistant bacteria development and affect organisms that may increase the risk of cancer development [7,8].

Various treatment processes, such as adsorption [9,10], advanced oxidation processes [1,5], metal oxide nanoparticles [1], electrochemical oxidation, ozonation and Fenton [11], catalytic wet air oxidation and ozonation [12], membrane process [13,14], chlorine dioxide [15], sonochemical [16], and enzymatic treatment [17–20], have been researched to remove FQs and organic pollutants from aqueous solution. However, some of these methods have been limited due to several disadvantages such as low efficiency, high cost, and generation of toxic byproducts. Among these methods, adsorption was used for removal of some pollutants such as chromium [21,22], cadmium [23,24], dye [25–27], and fluoride [28,29] which is comparatively a cost-effective method [30–32]. One of these natural adsorbents which can be modified is rice husk.

Rice husk is an agricultural waste that consists of floristic fiber, lignin, proteins, silica, cellulose, and hemicelluloses with some functional groups such as carboxyl, hydroxyl, and amidogen. Adsorption capacity of natural rice husk can be increased by chemical and/or thermal modification. NaOH solution, can affect the molecular and morphological characteristics of cellulose, and modify chemical and physical properties of rice husk. Therefore, it can clean natural dirt from the surfaces and consequently revealing functional groups like –OH [33–35]. This is useful for increasing the capacity of adsorption. Rice husk has been successfully used to eliminate cadmium [34], dye [35–37], humic acids [38], dibenzothiophenes [39], and fluoride [28,29] from aqueous solution. In addition, in some literature, the adsorption of methylene blue [33], congo red [40], lead and mercury [41], cadmium, nickel, and zinc [42] by rice husk ash has been reported. But, there are few reports about the removal of antibiotics from water using adsorption process, especially by rice husk.

Therefore, adsorption studies of ENR as a model molecule of fluoroquinolone on modified rice husk as a low-cost adsorbent were carried out, and the effects of adsorbent dose, pH, initial concentration of ENR, and temperature on adsorption rate have been investigated. To optimize the ENR sorption process and introducing a mathematical model for it, response surface methodology (RSM) has been used.

2. Materials and methods

2.1. Materials

ENR, $C_{19}H_{22}FN_3O_3$, (chemical structure in Fig. 1) was purchased from Sigma–Aldrich (St. Louis, MO, USA). Sodium hydroxide (NaOH) was purchased from Merck (Darmstadt, Germany). All other chemicals and reagents were of the highest purity available.

2.2. Preparation of NaOH-modified rice husk

The rice husk was modified using the method described by Ashrafi et al. [36]. Briefly, the rice husk was passed through 2-mm sieve size, followed by washing repeatedly by distilled water to eliminate dust and other impurities. After that, it was dried in 25˚C for 48 h, then it was immersed in 5% solution of NaOH and autoclaved at 121˚C for 15 min at 10 psi. After keeping in 25˚C for 48 h, it was filtered and washed many times with distilled water until clear water with neutral pH obtained in the effluent. Then, the rice husk was dried at 25˚C for 48 h. The modified rice husk was then applied to all the adsorption experiments.

2.3. Analytical method

The stock aqueous ENR solutions were prepared using deionized water. The required concentrations were prepared by dilution with distilled water. The levels of pH were adjusted by NaOH or HCl. The concentration of ENR was measured using a high-performance liquid chromatography (HPLC), which consisted of a Knauer LPG pump, an EZ-chrom HPLC system manager program with a UV–vis diode array detector (k-2500) set at the maximum absorption wavelength of 285 nm. A column of MZ-analysentechnik

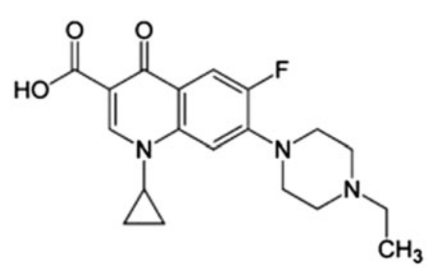

Fig. 1. Chemical structure of ENR.

ODS-3 C18 (0.46 × 25 cm) packed with 5-μm spherical particles was used for separation. The samples were injected manually and a methanol and water (pH 3, adjusted by acetic acid glacial), (18:82 vol/vol) mixture was used as mobile phase at 30℃ with a constant flow rate of 1 mL min^{-1}. The retention times in HPLC analysis were 9.2 min and the concentrations of ENR were calculated based on the peak area of known standards.

XRD analysis was carried out to identify the characteristic of both natural and modified rice husk. According to the results (Fig. 2), the peak position is nearly the same and the structure of adsorbent is not significantly changed after modification. However, there is a slight increase in the intensity of rice husk after modifying compared to that natural rice husk. It may be illustrated by this fact that NaOH treatment eliminates the impurities from the surface of rice husk.

2.4. ENR adsorption tests

In order to examine and evaluate the importance of variables (Table 1 summarizes these variables and their respective levels) on the adsorption rate of ENR, the adsorptions were performed using a batch procedure by shaking 100 ml of ENR solution in a 250-ml Erlenmeyer flask according to the pH, temperature, concentrations of ENR, and adsorbent dose in Tables 1 and 2. After keeping the solution mixture under agitation rate of 100 rpm on rotary shaker for 4 h, sufficient time to reach equilibrium, the adsorbent was separated by keeping the solution under settling condition for 30 min and the samples were stored at 4℃ followed by analyzing for ENR concentration by HPLC. The adsorption efficiency was defined as the percentage of initial ENR that was removed from the solution during the adsorption process and was calculated using the following Eq. (1):

$$\text{Adsorption efficiency } (\%) = 100 \times \frac{C_0 - C_e}{C_0} \tag{1}$$

where C_e is the concentration (mg L^{-1}) of ENR at the end of process time and C_0 is the initial concentration (mg L^{-1}) of ENR.

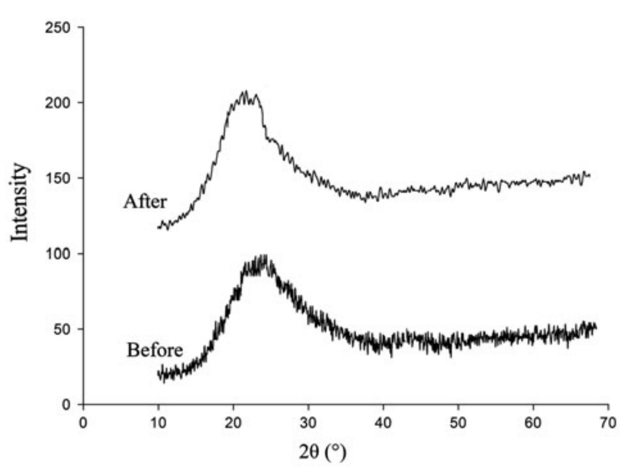

Fig. 2. XRD diffraction of natural and modified rice husk.

2.5. RSM–BBD

Box–Behnken design is a class of three-level factorial designs. Box–Behnken design (BBD) has some advantages against the classical methods. It is a time- and money-saving method, due to lesser experiments. In addition, this method is able to show the main and interaction effects of variables. As shown in Table 2, this rotatable experimental plan consisted of 27 runs for 4 variables and 3 levels (–1, 0, +1), which selected for the determination of optimal conditions as *A*, *B*, *C*, and *D*, corresponding to adsorbent dose, pH, initial concentration of ENR, and temperature, respectively. In this study, Design-expert version 7.0.0 (Stat-Ease, trial version) and MINITAB 14 (PA, USA) were used to find the optimal conditions of ENR adsorption by the NaOH-modified rice husk (NaOH-RH). The data obtained from experiments were analyzed by the analysis of variance (ANOVA) and response surface regression procedure to fit the following coded mathematical model (Eq. (2)):

$$\begin{aligned} R = {} & X_0 + X_1A + X_2B + X_3C + X_4D + X_5AB + X_6AC \\ & + X_7AD + X_8BC + X_9BD + X_{10}CD + X_{11}AA \\ & + X_{12}BB + X_{13}CC + X_{14}DD \end{aligned} \tag{2}$$

where R is the predicted percentage removal of ENR, X_0 is the intercept of quadratic model, $X_{1\text{–}14}$ are the estimated coefficients, and A, B, C, and D are the coded factors (Table 1).

3. Results and discussion

3.1. RSM–BBD adsorption experiments

The design variable matrix of coded values for factors in three levels (−1, 0, +1), response data, predicted, and residual is shown in Table 2. As shown in Table 2, this rotatable experimental plan consisted of 27 runs. The maximum removal rate of ENR was 92% and the minimum was 38% (Table 2).

Table 1
Experimental ranges and levels using Box–Behnken design of variables

Independent variables	Coded symbol	Code levels		
		−1	0	1
Adsorbent dose (g L^{-1})	*A*	0.25	0.5	0.75
pH	*B*	5	7	9
ENR initial concentration (mg L^{-1})	*C*	25	75	125
Temperature (℃)	*D*	15	30	45

Table 2
Experimental, predicted results and variable matrix from Box–Behnken

Run	Values of variables				Adsorption efficiency (%)		
	A	*B*	*C*	*D*	Experimental	Fits	Residuals
1	−1	0	0	1	54	50.95	3.04
2	0	−1	−1	0	82	85.79	−3.79
3	0	−1	0	1	77	78.37	−1.37
4	−1	1	0	0	38	40.00	−2.00
5	1	0	0	1	87	87.79	−0.79
6	−1	0	0	−1	48	47.29	0.70
7	0	0	−1	1	79	77.00	2.00
8	0	0	1	1	73	73.00	0.00
9	0	1	0	1	65	67.87	−2.87
10	0	−1	0	−1	77	75.70	1.29
11	0	0	0	0	75	75.00	0.00
12	0	1	−1	0	68	67.29	0.70
13	−1	−1	0	0	60	59.00	1.00
14	1	0	0	−1	80	83.12	−3.12
15	0	0	0	0	75	75.00	0.00
16	0	−1	1	0	72	72.79	−0.79
17	1	0	1	0	85	85.70	−0.71
18	0	1	0	−1	62	62.20	−0.21
19	0	0	−1	−1	77	75.33	1.66
20	1	−1	0	0	92	88.33	3.66
21	1	0	−1	0	90	89.70	0.29
22	1	1	0	0	84	83.33	0.66
23	0	0	1	−1	66	66.33	−0.33
24	0	0	0	0	75	75.00	0.00
25	−1	0	0	1	54	50.95	3.04
26	0	−1	−1	0	82	85.79	−3.79
27	0	−1	0	1	77	78.37	−1.37

The normal probability plot of the residuals with a 95% confidence has been provided in Fig. 3. According to this graph, it is evident that the data from the experiments come from a normally distributed population due to the points fall approximately close to the straight line.

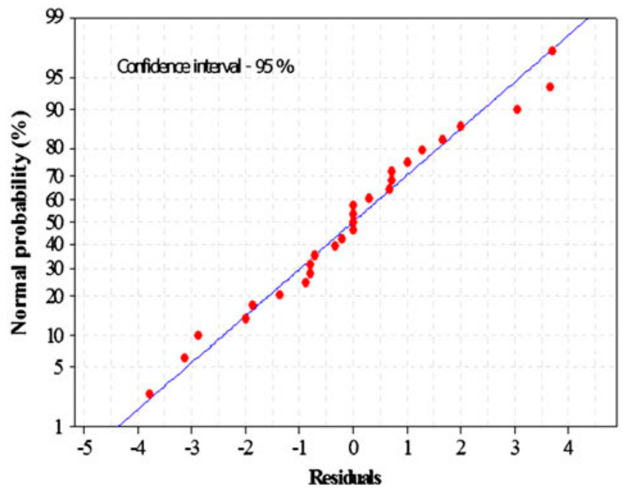

Fig. 3. Normal plot of residuals.

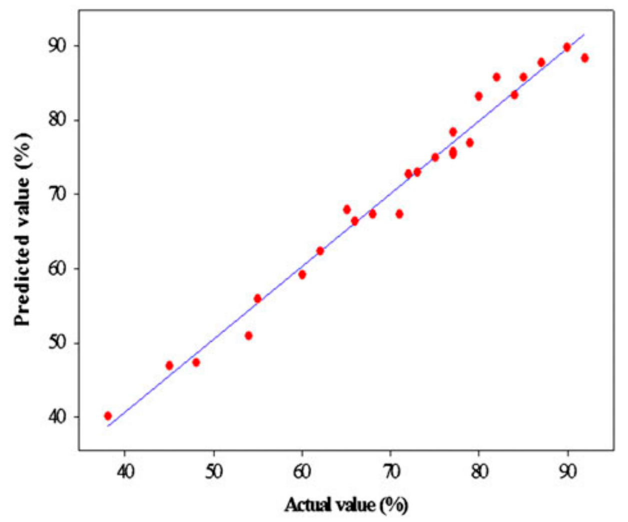

Fig. 4. Parity plot comparing the adsorption of ENR data with the model predictions.

In Fig. 4, the calculated adsorption efficiency from the model is plotted against. the experimental adsorption. The predicted efficiency values for ENR adsorption were close to the experimental efficiency values, and the correlation coefficient for the plot is 0.9815, which indicates a good performance for the model and the regression is able to give a good prediction of response for the adsorption process.

3.2. Analysis of variance

In order to determine the significant main and interaction effects of factors influencing the removal efficiency of ENR, an ANOVA was performed. The sum of squares and mean square of each factor, p-value, and the F-value are shown in Table 3. p-value is the probability value that is used to find out the statistically significant effects in the regression, and with a 95% confidence level, the p-value should be less than 0.05 for the effect to be considered significant. According to the ANOVA test (Table 3), it seems that all the main effects of A, B, C, and D, and the interaction effects of AB, BC, and A^2, are statistically high significant. The interaction effects of AC, AD, BD, CD, B^2, C^2, and D^2, which were statistically insignificant compared to the other effects, were eliminated, and by substituting the coefficients X_i in Eq. (2) by their values leads to the following simplified second-order polynomial equation, Eq. (3), in terms of coded factors:

$$R = 72.93 + 18.17A - 6B - 3.25C + 2.08D + 3.5AB + 3.25BC - 4.76A^2 \quad (3)$$

where R is the percent adsorption efficiency of ENR; A, B, C, and D are the coded values of the operational variables adsorbent dose, pH, initial ENR concentration, and temperature, respectively.

Based on Eq. (3), after eliminating insignificant factors, the model was reanalyzed and the results for the reduced model are shown in Table 4. As shown in Table 4, the second-order polynomial model, Eq. (3), was statistically high significant and sufficient to represent the actual relationship between the efficiency of adsorption and the significant variables, with p-value < 0.0001, and satisfactory coefficient of determination R^2 = 0.9705.

3.3. Main and interaction effects of variables

It can be seen from Table 4, the main effect of all four variables is statistically high significant, and the adsorbent dose was found to have the greatest effect on the response, with the highest F-value of 514.73, followed by pH of solution with the F-value of 56.14, while the initial concentration of ENR and temperature showed lower effect than pH and adsorbent dose. It can be realized that the adsorbent dose influence

Table 3
Analysis of variance for experimental responses

Source	Degrees of freedom	Sum of squares	Mean square	Coefficient estimate	F-value	p-value Prob. > F	Status
A	1	3,960.33	3,960.33	18.17	517.03	<0.0001	Significant
B	1	432	432	−6	56.39	<0.0001	Significant
C	1	126.75	126.75	−3.25	16.54	0.0016	Significant
D	1	52.08	52.08	2.08	6.79	0.0229	Significant
AB	1	49	49	3.5	6.39	0.0265	Significant
AC	1	6.25	6.25	1.25	0.81	0.3841	
AD	1	0.25	0.25	0.25	0.03	0.8596	
BC	1	42.25	42.25	3.25	5.51	0.0368	Significant
BD	1	2.25	2.25	0.75	0.29	0.5978	
CD	1	6.25	6.25	1.25	0.81	0.3841	
A^2	1	163.78	163.78	−5.54	21.38	0.0006	Significant
B^2	1	17.12	17.12	−1.79	2.23	0.1607	
C^2	1	0.037	0.03	0.08	0.01	0.9457	
D^2	1	25.03	25.03	18.16	3.26	0.0957	
Model	14	4,868.15	347.72	75	45.39	<0.0001	Significant
Residual error	12	91.917	7.65				
Lack of fit	10	91.91	9.19				
Pure error	2	0	0				
Total	26	4,960.07					

Table 4
Analysis of variance-reduced model

Source	Degrees of freedom	Sum of squares	Mean square	Coefficient estimate	*F*-value	*p*-value Prob. > *F*	Status
A	1	3,960.33	3,960.33	18.17	514.73	<0.0001	Significant
B	1	432	432	−6	56.14	<0.0001	Significant
C	1	126.75	126.75	−3.25	16.47	0.0007	Significant
D	1	52.08	52.08	2.08	6.76	0.0175	Significant
AB	1	49	49	3.5	6.36	0.0207	Significant
BC	1	42.25	42.25	3.25	5.49	0.0301	Significant
A^2	1	151.47	151.47	−4.76	19.68	0.0003	Significant
Model	7	4,813.89	687.70	72.93	89.38	<0.0001	Significant
Residual error	19	146.18	7.69				
Lack of fit	17	146.18	8.6				
Pure error	2	0	0				
Total	26	4,960.07					

the adsorption process about 10 times higher than the pH of solution. The fact of increase in percent ENR removal with increase in adsorbent dose was due to the availability of more adsorbent surfaces for the solutes to adsorb.

The pH of the aqueous solution influences both the surface charge of the NaOH-RH and the degree of ionization of the ENR. Thus, the pH of the solution can influence significantly the ENR adsorption process. According to Table 2, the maximum percent ENR removal (92%) was observed at low pH. The improved removal of ENR at low pH is probably due to amphoteric structure of ENR (Fig. 1). ENR is positively charged in acidic solutions, while at high pH values it is found in its anionic form. On the other hand, the NaOH-RH possesses a net negative charge, resulting from its –OH functional group and it results in high affinity of NaOH-RH for ENR at acidic pH. Similar effects of the acidic pH on the adsorption of ENR onto zeolite were reported in the literature [9].

It has been found from the initial concentration of ENR coefficient (Table 4), by increasing the initial concentration of ENR, the adsorption percentage was decreased, while the amount of removed ENR at equilibrium was more when the initial concentration was lower. This is the consequence of the driving force of high concentration of ENR to overcome all the mass transfer resistances of ENR between the aqueous and solid phase. This is in agreement with the other studies of pollutant adsorption by modified rice husk [43].

From Table 4, it is found that temperature significantly (*p*-value 0.0175) influenced the ENR uptake onto NaOH-RH, and adsorption efficiency of ENR increased with an increase in temperature. The increment in adsorption efficiency with the increase in temperature may be attributed to the increase in the number of active surface sites available for adsorption, increase in the rate of diffusion of the adsorbate molecules across the external boundary layer and the internal pores of the adsorbent particle due to decrease in the viscosity of the solution and increase in the mobility of the ENR molecules with an increase in their kinetic energy. Enhancement of ENR adsorption by increasing temperature indicates the chemical reaction between the ENR and NaOH-RH involvement in the adsorption process. This is in agreement with Chowdhury et al. [43] on the adsorption of malachite green on modified rice husk.

Contour plots for the interactions of *AB*, *AC*, *AD*, *BC*, *BD*, and *CD* are shown in Fig. 5. The interaction plots for *AB* (Fig. 5(a)) and *BC* (Fig. 5(d)) showed that interaction of adsorbent dose and pH and interaction of pH and initial concentration of ENR played a major role. According to Table 3, the interaction effects between adsorbent dose and pH (*p*-value 0.0265), pH and initial concentration of ENR (*p*-value 0.0368) is significant due to the higher *p*-values than 0.05. However, the interaction effects between AC (*p*-value 0.3841), Fig. 5(b), AD (*p*-value 0.8596), Fig. 5(c), BD (*p*-value 0.5978), Fig. 5(e), and CD (*p*-value 0.3841), Fig. 5(f) are statistically insignificant. In addition, according to Table 3, the quadric effect of adsorbent dose (*p*-value 0.0006) is statistically significant.

3.4. Optimization

The optimization of ENR adsorption onto NaOH-RH was carried out by a multiple response method

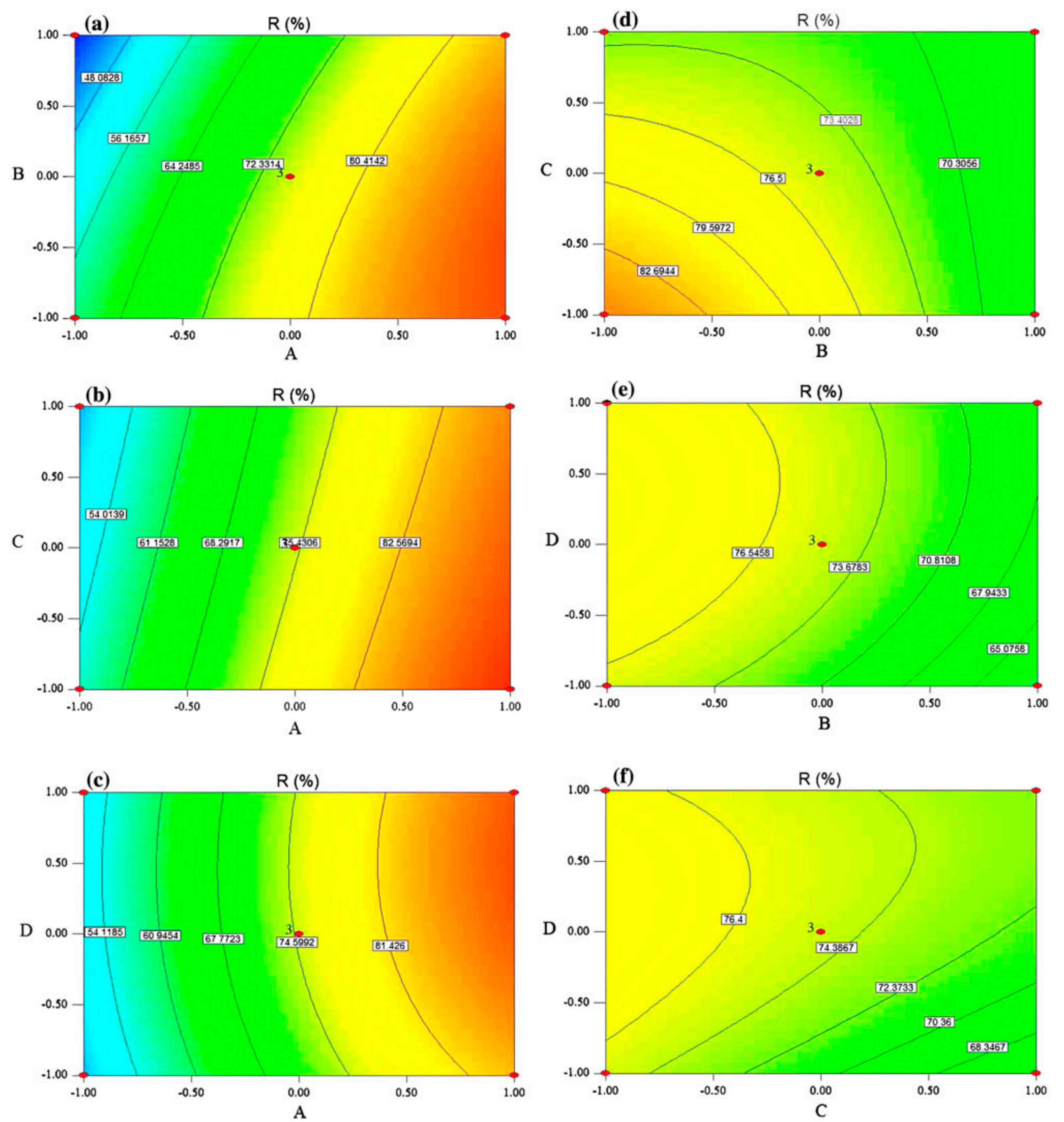

Fig. 5. Contour plots for interaction effects of (a) pH and adsorbent dose, (b) ENR initial concentration and adsorbent dose, (c) temperature and adsorbent dose, (d) ENR initial concentration and pH, (e) temperature and pH, and (f) temperature and ENR initial concentration.

called desirability (D) function to optimize different combinations of all the four process factors studied in this work. For this object, numerical technique with the software Design-expert version 7.0.0 (Stat-Ease, trial version) was used. The main objective of optimization was to maximize adsorption efficiency of ENR. Among 30 starting points, the best local maximum for ENR removal (92.25%) was found at adsorbent dose of 0.69 g L^{-1}, pH 5.11, initial concentration of ENR 25.02 mg L^{-1}, and temperature 36.43°C, and

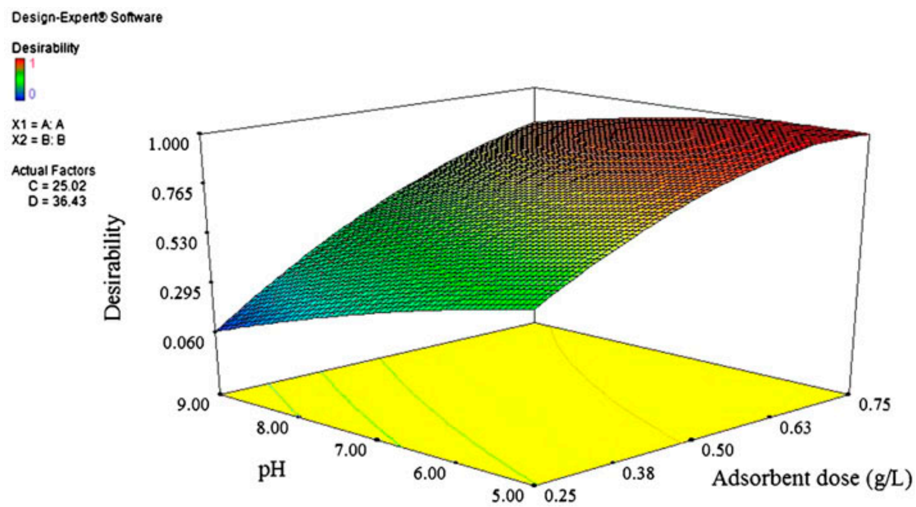

Fig. 6. Desirability fitted 3D surface for ENR removal by NaOH-RH.

Table 5
Comparison of adsorption capacity of some adsorbates onto various adsorbents

Adsorbate	Adsorbent	Adsorption capacity (mg g^{-1})	Refs.
Enrofloxacin	Natural rice husk	63.5	This study
Enrofloxacin	NaOH-treated rice husk	241	This study
Enrofloxacin	Natural zeolite	22.6	[9]
Enrofloxacin	bentonite	71.88	[44]
Malachite green	NaOH-treated rice husk	17.98	[43]
α-picoline	rice husk ash	16.807	[45]
As	rice husk activated carbon	1.22	[46]
Pb	rice husk ash	10.86	[47]
Hg	rice husk ash	3.23	[47]
Congo red	Rice hull ash (White ash)	171	[48]
Cu	Tartaric acid-modified rice husk	14.68	[49]
Pb	Tartaric acid-modified rice husk	48.92	[49]
Zn(II)	Sulfuric acid-treated rice husk (wet sorbent)	19.38	[50]
Hg(II)	Sulfuric acid-treated rice husk (wet sorbent)	384.62	[50]
Cd(II)	Sulfuric acid-treated rice husk (wet sorbent)	41.15	[51]
Cd(II)	Natural rice husk	73.96	[52]
Cd(II)	NaOH-treated rice husk	125.94	[52]
Direct red 81	NaOH-treated rice husk	14.77	[36]
Methylene blue	NaOH-treated rice husk	342.43	[36]
Cd(II)	Natural rice husk	8.58	[34]
Cd(II)	NaOH-treated rice husk	20.24	[34]

the value of desirability obtained was 1. Fig. 6 shows the graphical desirability for ENR generated from 30 optimum points via numerical optimization.

Table 5 shows a comparison of the ENR adsorption capacity onto both natural and modified rice husk with some other study with respect to adsorption capacity. According to the value of NaOH-modified rice husk, adsorption capacity (241 mg g^{-1}) against the natural rice husk, adsorption capacity (63.5 mg g^{-1}), it can be concluded that the modification of rice husk by NaOH is useful for enhancing the capacity of adsorption.

4. Conclusions

The RSM analysis was proved to be a powerful method to determine the main factors which affect ENR removal from aqueous solution. The use of BBD allowed the identification of the most important parameters for adsorption of ENR and it can be employed to develop mathematical models for ENR adsorption on NaOH-RH. According the data analysis in this work, all the four factors, adsorbent dose, pH, ENR initial concentration, and temperature, have significant influence on the adsorption of ENR onto NaOH-RH. The most significant effect for ENR adsorption was ascribed to adsorbent dose followed by pH. The adsorption efficiency decreased with the increase in pH and ENR initial concentration. But, the adsorption efficiency increased with the increase in adsorbent dose and temperature. The optimal conditions for the maximum adsorption of ENR (92.25%) were 0.69 g L^{-1} of adsorbent dosage, pH 5.11, and 25.02 mg L^{-1} of ENR initial concentration at 36.43˚C.

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