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Original Article

Adsorptive Removal of Bisphenol A from Aqueous Solutions by Activated Carbon Derived from Walnut Shells: Optimization by Response Surface Methodology

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ABSTRACT

Background: Presence of bisphenol A in water resources is harmful for health of human being. Therefore, it should be addressed to eliminate and prevent its contamination. The aim of this study was to evaluate the activated carbon adsorbent efficiency of walnut shells in removing bisphenol A from aqueous solutions.
Methods: In this study, adsorbent preparation using walnut shells was performed according to standard methods. The independent variables are pH, initial concentration of bisphenol A and adsorbent dose. The surface response method was used to design the experiment and determine the optimum adsorption conditions
Results: The results showed that output of removal rate of the contaminating increased at a dose of 1.5 g, pH = 3, and initial concentration of bisphenol A was 40 mg/L. Also, the analysis of variance of data revealed that the model obtained from the response surface method was statistically significant.
Conclusion: Based on the results using walnut shell as an inexpensive and available adsorbent, it is possible to remove up to 97% of the bisphenol A from the aqueous solution by creating optimal conditions.
Keywords: Bisphenol A, wastewater, active carbon, walnut shell, response surface methodology
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Introduction

Bisphenol A ($C_{15}H_{16}O_2$) is an organic compound with two phenolic groups. This material was first recognized in 1891 and produced annually from 2 to 3 million tons (1, 2). Bisphenol A is used in a variety of industries, including food packaging, medical equipment, plastics, leather, paper making, and so forth, which potentially may contaminates surface and underground waters and is considered as an Environmental pollutant (3-6). Generally, the concentration of bisphenol A in surface water varies from 0.05 to 0.1 g/l,

but in some rivers, it is about 0.4 g/l due to the entry of industrial wastewater (7). The maximum allowed level for bisphenol A in surface waters is 1-15 mg / ml (8).
The effects of exposure to bisphenol A include sperm reduction, breast cancer, prostate cancer, and reduced fertility and impaired endocrine function. The mechanism of the effect of bisphenol A is within the mitochondria cell, which is the center for the formation of free oxygen radicals (9, 10). Accordingly, the use of environmental technologies is necessary to remove bisphenol A from water sources. Different physical, chemical and biological methods such as adsorption, reverse osmosis, ultrasound, advanced oxidation, ion exchange, and etc. are used to remove bisphenol A (11). Due to disadvantages of these methods such as high costs, necessity for additional purification and formation of hazardous additional products and complex operations technologies are difficult, which has led researchers to seek effective and economical methods. One of the effective treatment processes is to remove phenolic compounds of the adsorption process due to the fact that the pollutant is removed from one phase to other phase, due to the ease of design and operation, and non-toxicity to toxic contamination and flexibility compared to some of other methods with less efficiency is a better approach (8, 12, 13). Previous studies have shown that activated carbon adsorbents from various sources such as sawdust, ash, coconut shells, and rice husk have been used to remove organic matter from liquid environments. But so far, no study has been conducted to remove bisphenol A by activated carbon derived from walnut shells. Therefore, considering the proper physical properties and availability of walnut shells, the aim of this study was to determine the efficiency of activated carbon derived from walnut shells in removing bisphenol A from aqueous solutions. Also, in this study, the effects of initial concentration of bisphenol A, pH and concentration of adsorbent were investigated.

Methods

The present study was an experimental study performed on a batch system in a bench scale. In this study, the carbon derived from walnut shells as an adsorbent was used to remove bisphenol A and all materials used, such as chloride and sodium hydroxide, bisphenol A were provided from Merck company. All experiments were based on the Standard Methods for the Examination of Water and Wastewater (14).

Preparation of solution

In this study, a stock solution of 1000 mg/L was prepared by dissolving 1 g of bisphenol A in 1 liter of distilled water. Then, sample solution of 100 ml with the specific concentrations of Bisphenol A was prepared by diluting the stocks solution in 250 ml Erlenmeyer. To adjust the pH, a 0.1 normal solution of chloride and sodium hydroxide was used.

Preparation of the adsorbent

To make activated carbon from walnut shells, the walnut shells was first crushed to the extent possible and turned into carbon for one hour at 700 °C. The resulting carbon, after crushing with laboratory mortar, was sieved using 20 mesh and 100 mesh sieves to maintain the diameter of the remaining carbon residues between the two sieves in the range of 0.15-0.85 mm.

Experimental design

Optimization of bisphenol A removal was carried out using the response surface method based on Behnken-Box model. As shown in Table 1, three independent variables including the amount of adsorbent, initial concentration of bisphenol A and pH were tested at three levels (+1, 0, -1). It should be noted that the time factor has been considered at all stages of the test for 45 minutes. According to the results of preliminary studies, the design of the experiments was carried out according to Table 1., taking into account the codes of +1 (high), 0 (center) and -1 (low), and the response surface method for modeling and data analysis with the goal of optimizing the desired response was carried out. In this study, the design of experiments and data analysis was done using the Design-expert version 7.0.0 software (Stat-Ease, trial version). Table 2 showed the experimental design, run number and levels of independent variables a based on Behnken-Box.
In this study, the concentration of bisphenol A was measured using an HPLC and the following equation was utilized to calculate the removal efficiency;

$$R = \frac{C_0 - C_e}{C_0} * 100$$

Where R is the percentage of adsorption efficiency, C_0 is the initial concentration of bisphenol A (mg/L), and Ce is the final concentration of bisphenol A (mg/L).

Results

Structural characteristics of activated carbon obtained from walnut shell

Figures 1 shows particles of carbon obtained from walnut shell using scanning electron microscope (SEM). Figure 1a demonstrates the activated carbon content of the walnut prior to the adsorption, which has an irregular surface that may have a place to adsorb the intended pollutant. Figure 1b is the adsorbent level after the adsorption of Bisphenol A. As it is obvious from the surface of the figure, it is a dense and stiff cake that indicates the high adsorption capacity for pollutant.

Verification of response surface model

The normal distribution of continues data were assessed by plotting predicted versus actual values (Figure 2a) and plotting the residuals (Figure 2b).

Table 1. Variables and Levels of Study

Independent variables	**Coded symbol**	**Level of variable**		
		-1	**0**	**1**
pH	A	3	7	11
Bisphenol A initial concentration (mg/L)	B	40	60	80
Adsorbent dose (g)	C	0.5	1	1.5

Table 2. Test Design Based on the Level of Response on the Base of the Bax-Bencent

Run number	Adsorbent dose	Bisphenol A concentration	PH
1	-1	0	+1
2	-1	0	-1
3	+1	+1	0
4	-1	-1	0
5	-1	+1	0
6	0	-1	-1
7	0	0	0
8	0	-1	+1
9	0	+1	+1
10	0	+1	-1
11	0	0	0
12	+1	-1	0
13	0	0	0
14	+1	0	+1
15	+1	0	-1
16	0	0	0
17	0	0	0

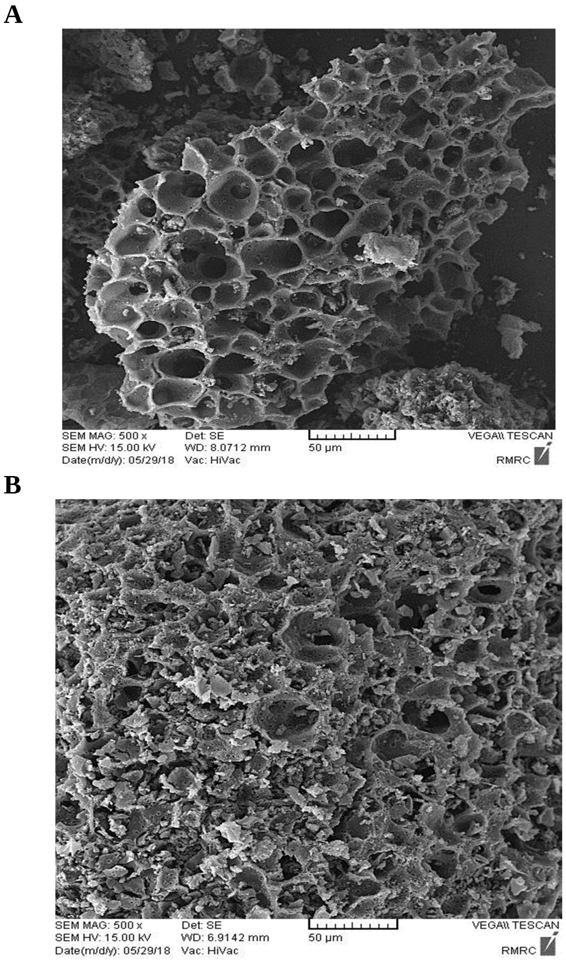

Figure 1. The carbon particles obtained from walnut shell before adsorbing (a) and after adsorbing bisphenol A (b).

In the absence of any violation from straight line, the assumption of normality is met. The adequacy of the model were checked by coefficient of determination (R^2). Based on R2 = 0.99, the second-order model was adequately described the outcome based on independent variables. According to the analysis of variance carried out on the data from the experiments (Table 3), all studied variables had significant association with the elimination of bisphenol A.

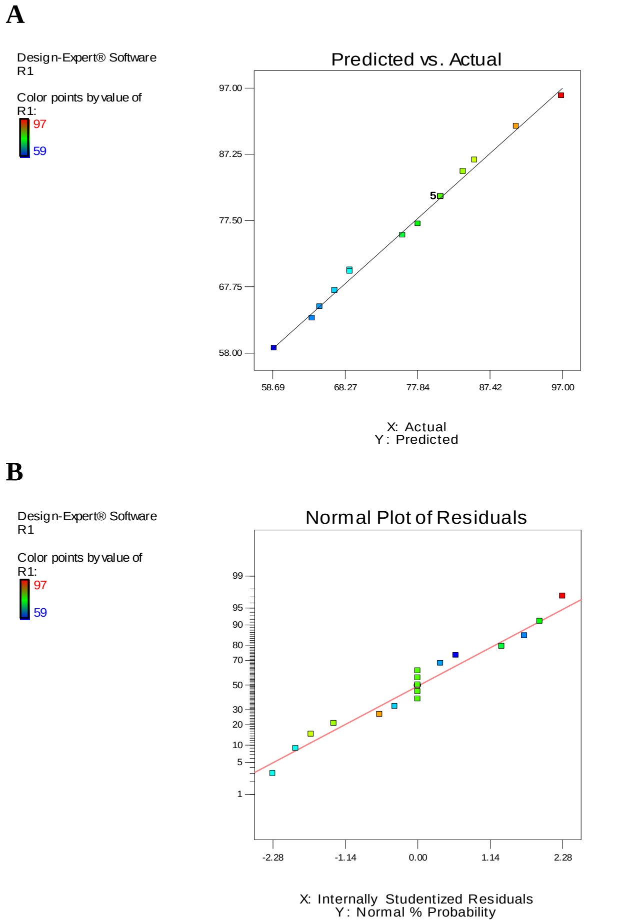

Figure 2. Q-Q plot of predicted versus actual values (A), and residuals (B)

The percentage of adsorption efficiency (R) was modeled as a function of PH (A),initial concentration of bisphenol A (B), the amount of adsorbent (C), the interaction term and squared of each term;

$$R = + 81.00 - 8.75A - 4.06B + 7.56C + 1.50AB - 4.50AC - 1.56A^2 + 2.06B^2 - 8.94C^2$$

To achieve a maximum efficiency of 100%, the model predicted the optimal values for pH, initial concentration of the bisphenol A, and adsorbent amount as 3, 40 mg/L and 1.5 g, respectively.

Table 3. Analysis of Variance for the Removal of Bisphenol A by Activated Carbon Derived from Walnut Shells

Source	Sum of Squares	df	Mean Square	F- Value	P-value
Model	1656.67	9	184.07	170.38	0.0001
A-pH	612.50	1	612.50	566.94	0.0001
B-concentrate	132.03	1	132.02	122.21	0.0001
C-dose	457.53	1	457.53	423.50	0.0001
AB	9.00	1	9.00	8.33	0.0234
AC	81.00	1	81.00	74.98	0.0001
BC	1.56	1	1.56	1.45	0.2682
A^2	10.28	1	10.28	9.52	0.0177
B^2	17.91	1	17.91	16.58	0.0047
C^2	336.33	1	336.33	311.32	0.0001

$R^2 = 0.9875$

The results of the prediction of efficiency are presented in Table 4. According to the results of the ANOVA, the variables A, B, C, AB, AC, A^2, B^2 and C^2 are statistically significant with P-value < 0.05.

Table 4. Bisphenol A Removal Efficiency at Different Levels of Variables and Predicted Efficiency by Model

Run number	Actual value (%)	Predicted Value (%)	Residual (%)
1	59	58.69	0.31
2	67	67.19	-0.19
3	78	77.00	1.00
4	69	70.00	-1.00
5	64	63.13	0.88
6	97	95.81	1.19
7	81	81.00	0.00
8	76	75.31	0.69
9	69	70.19	-1.19
10	84	84.69	-0.69
11	81	81.00	0.00
12	85.5	86.38	-0.88
13	81	81.00	0.00
14	65	64.81	0.19
15	91	91.31	-0.31
16	81	81.00	0.00
17	81	81.00	0.00

The response level for each of main factors were presented in three-dimensional graphs. Figure 3a, illustrates the interaction effect of adsorbent dose and pH on efficiency. Figure 3b shows the effect of PH and initial concentration of bisphenol A on efficiency. Figure 3c represents the effect of adsorbing dose and initial concentration of bisphenol A on efficiency. As shown in figure 3a, the efficiency decreases with increasing pH and adsorption dose. In other words, the highest removal efficiency (91%) was observed at pH = 3 and the adsorbent dose of 1.5 g. Also, in figure 53b, the highest removal efficiency (97%) was at pH = 3 and the initial concentration of bisphenol of 40 mg. The results of figure 3c manifests that the highest removal efficiency of 85.5% is achieved by adsorbent dose of 1.5 and the initial concentration of bisphenol of 40 mg/L.

Discussion

The results of the analysis of the characteristics of walnut shell revealed that this material caused significant phenol removal due to its specific superficial aspects and strong functional groups (15-17). Considering the results of taking the scanning electron microscope photos obtained from activated carbon derived from walnut shell, the limitations of the surface and volume of the cavities of adsorbent particles indicate that the physical adsorption and trapping of the pollutants in the cavities is not the dominant mechanism and probably the high density of the functional groups in the removal of the pollutant is effective.

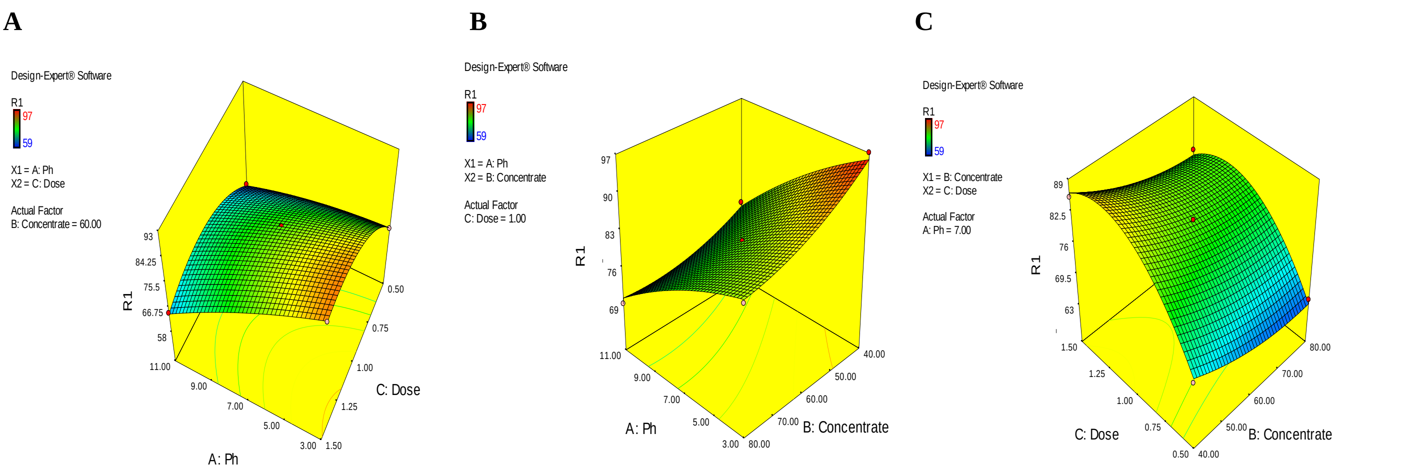

Figure 3. Interaction effect of adsorbent dose, pH (A), bisphenol A concentration, pH (B), and adsorbent dose, bisphenol A concentration (C) on removal efficiency. R1:removal efficiency

The mechanism of phenol removal by walnut activated carbon is a combination of mechanisms that includes the л-b reaction between the aromatic ring of phenol and electrons in the adsorbent structure, the formation of hydrogen bonds between hydrogen phenol and hydrogen in functional groups of adsorbent surfaces, are the mechanism of formation of an electron-adsorber on the surface of the adsorbent (18, 19). Among factors affecting the removal of phenol, pH is one of the most effective factor. From the results, it was determined that the phenol removal efficiency improved with decreasing pH. Considering that with increasing of pH the number of negative electrical loads increased and according to the nature of anionic phenol in these conditions, the electrostatic gravity between adsorbent and pollutant decreases and adsorption efficiency decreases (19).

These results are consistent with studies by other researchers, as Muthanna has reported that the phenol adsorption rate on the date core decreases with increasing pH (20). Also, the results of the study showed that phenol removal is escalated by increasing the adsorbent dose. Increasing the phenol adsorption by increasing the amount of adsorbent as a result of increasing the active surface area and effective in adsorption. Also, although the residual phenol content is reduced by increasing the adsorbent dose, the amount of phenol adsorbed in the adsorbent mass gravity unit shrinks with elevating adsorption dose (19, 21). Bazrafshan et al. showed that the increase in the adsorbent dose raised the removal efficiency of the phenol, but due to the unsaturation of some of the active site at the adsorbent level, the amount of adsorption in the adsorbent mass unit decreased, which are in agreement with the findings of the present study (22).

The results showed that the removal efficiency at high initial concentrations as well as increasing initial phenol concentration declined the removal efficiency because the number of active adsorption sites in the adsorbent level for phenol ion decreases, due to the filling of adsorption capacity and its inefficiency higher levels. The amount of phenol removal is a function of its initial concentration.

Conclusion

The results of this study revealed that:

A. The amount of bisphenol A removal was strongly dependent on pH and initial concentration of contaminant, so that the highest percentage of adsorption was observed at low pH and low initial concentration.

B) By examining the contact time and adsorbent dose, it was observed that at one time with a greater amount of adsorbent, the amount of pollutant removed would increase.

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Ethical consideration

The study protocol has been approved by institutional Review Board of Guilan University of Medical Sciences, Rasht, Iran.

Conflicts of interests

Authors declared no conflict of interest.

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