



Response Surface Methodology Approach for the Adsorption of Bisphenol A (BPA) with Activated Carbon from Bovine Horns

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ABSTRACT

In this work, activated carbon was prepared from Bovine horns and was characterized using FTIR and SEM. The prepared activated carbon was used to adsorb Bisphenol A from simulated solutions. The design of the Experiment was carried out using Box Behnken Design (BBD) and the adsorption experiment was carried out as arranged in a design matrix obtained from Design-Expert software. The factors considered were pH, adsorbent dose, contact time and initial concentration. The percentage removal of BPA was taken as the response of the design. The factor levels which was responsible for the highest removal of BPA from the experimental solutions were the initial concentration of 20mg/L, adsorbent dosage of 0.07g, contact time of 20 minutes and pH 5. A model was predicted by the design expert software and optimization solutions were pulled out from the design expert software with conditions that could give maximum adsorption. A plot of predicted against actual values was gotten too and from the R^2 value of 0.8824, less variation between the predicted percentage removal and actual percentage removal was confirmed. Revealing that the predicted values agree reasonably with the experimental values. Activated carbon from bovine horn has demonstrated to be effective in BPA adsorption from solution.

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INTRODUCTION

Water is an indispensable natural resource essential for the existence of man and the ecological system. Though water is abundantly available in the universe, only 3% of it is freshwater. Approximately, 5% of the freshwater, equivalent to 0.15% of the entire global waters is readily accessible for beneficial purposes (Usharani *et al.*, 2010). In addition, water serves as an important resource for the proper running of industries, with a majority ending up as industrial wastewater (Bhandari 2014).

Water pollution is the modification or change in the chemical, physical or biological properties of water that can cause any harmful consequences on living things and the environment. This is often caused by human activities such as; effluent discharge, indiscriminate dumping of refuse, activities of the mechanic workshop, agricultural practices, combustion of fuel, atmospheric metallic burden,

and spillage, thereby affecting all living species and the complete functioning of the entire ecosystem (Maitera *et al.*, 2011; Imasuen & Omorogieva 2013).

The release of a variety of organic pollutants by the ever-increasing number of industrial, commercial and domestic activities causes environmental problems which in turn lead to pathological effects in living systems. Most of these pollutants are recognized as **Endocrine Disruptors Chemicals (Edcs)** for their ability in interfering with the endocrine system.

Many EDCs are organic chemicals with one or more phenolic group(s), including natural estrogens such as estrone (E1), estradiol (E2), and estriol (E3); artificially synthesized estrogens such as ethynylestradiol (EE2); as well as other industrial compounds such as **BISPHENOL A (BPA)**, nonylphenol, and several other phenolic compounds (Fernandez *et al.*, 2007)

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Endocrine-disrupting chemicals (EDCs) can cause abnormalities in the functions of the endocrine systems of wildlife and humans. Such chemicals have been detected in wastewater, surface waters, sediments, groundwater, and even drinking water. As a result, EDCs have drawn great scientific and public concern in recent years.

Over time, researchers have shown concern about the fate, transport, reactivity and bioavailability of organic micro-pollutants (OMPs) as a result of the increasing number of industrial, commercial and domestic activities (Tang *et al.*, 2013)

In Nigeria, fashion shop effluents are released directly into the environment without any form of treatment. This could be harmful to the environment as the effluent contains chemicals that could alter soil and water physical and chemical properties (Bowers *et al.*, 2002). Animal and human research have associated BPA with many health problems including infertility, weight gain, behavioural changes, early-onset puberty, prostate and mammary gland cancers, cardiovascular effects, obesity, and diabetes (Birbaum *et al.*, 2012; Schug *et al.*, 2012). With the high global demand for BPA, the need to investigate its presence and removal in the environment becomes very important

Response surface methodologies (RSM) are multivariate techniques where the response functions are used to fit the domain of the experiment studied in the theoretical design. The major aim of this method is to change all significant variables at a time and then fit the experimental data to a predicted mathematical model (Krowiak *et al.*, 2014)

MATERIALS AND METHODS

Materials

The following chemicals/reagents were used during this research work; they were used as supplied without further purification; (2,2-Bis(4-hydroxyphenyl) propane) 98% purity, NaOH (Sigma Aldrich), Deionized water, Distilled water, Chloroform, Dichloromethane, 5.5M HCl, 10% HNO₃, KCl. Bovine horns used were gotten from an abattoir in Zango, Kaduna, Nigeria.

Preparation of Activated Carbon

The bovine horns were washed thoroughly and sun-dried for 21 consecutive days. They were cut to sizes of about 5 mm to 10 mm and charred. They were then grounded to powder form with mortar and pestle, sieved using 300 and 350 µm mesh size. The ground horn powder was then soaked in chloroform for 24 hours to remove the fat, after which it was sun-dried and washed with de-ionized water to remove the colour. This was stored in an airtight container for subsequent work (Tijani *et al.*, 2014).

Carbonization process and Chemical activation of the prepared carbon

About 100g of the prepared bovine horns was weighed into large ceramic crucibles and introduced into the tubular furnace in an inert atmosphere of nitrogen and was carbonized at a temperature of 400 °C for 2 hours. This was allowed to cool at room temperature. This process was repeated until a substantial amount of carbonized sample was obtained. The resulting sample was stored in sealed containers for activation (Yahya *et al.*, 2015).

The carbonized sample was chemically activated using Sodium hydroxide (NaOH, Sigma Aldrich). The charred and carbonized bovine horns were impregnated with NaOH at the ratio (1:2) with the aid of stirring. The impregnated material was introduced into a tubular furnace that was heated at a temperature of 400 °C for 2 hours and was then cooled down to room temperature. The nitrogen was streamed through the furnace at a rate of 150 cm³/min from the start of heating to the time the tubular furnace cooled down. The resulting activated carbon was then washed with 1M HCl followed by plenty of deionized water to remove any residual organic and mineral matter and to maintain a pH of 7.0 The bovine horn activated carbon was then dried at 110°C overnight, before being cooled and stored for further studies (Yahya *et al.*, 2015)

Design of Experiment using RSM

Design-Expert software version 11.0.3 (Stat-Ease, Inc., Minneapolis, MN 55413, USA) was used to carry out the design of the experiment. In the design process, four factors were considered viz; initial concentration,

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adsorbent dosage, contact time and pH. A prepared stock solution was diluted to get the various working solution. These solutions were mixed as shown in the design of the experiment matrix. After shaking for the respective time intervals, the mixture was then filtered with a 6 µm filter paper and the residual concentrations of the compound BPA in the mixture were analyzed using a UV spectrophotometer (Agilent Technologies Cary 300 Series). And the response

was the percentage removal of BPA from the various simulated solutions.

The percentage removal of Bisphenol A from each of these samples was calculated using equation
 %Removal or adsorption efficiency =

$$\left(\frac{C_0 - C_t}{C_0}\right) \times 100 \quad \text{Equation 1}$$

Where: C₀= Initial concentration
 C_t= Concentration after shaking for time, t

Table 1: Design Table (Coded Matrix of Experimental Runs)

RUNS	Bik	A	B	C	D
1	1	0	0	0	0
2	1	-1	0	0	-1
3	1	-1	0	0	1
4	1	1	0	0	-1
5	1	-1	-1	0	0
6	1	-1	1	0	0
7	1	0	1	1	0
8	1	-1	0	-1	0
9	1	0	1	-1	0
10	1	0	0	0	0
11	1	1	-1	0	0
12	1	0	-1	0	-1
13	1	0	0	-1	1
14	1	1	1	0	0
15	1	1	0	1	0
16	1	0	0	0	0
17	1	0	0	-1	-1
18	1	-1	0	1	0
19	1	0	1	0	1
20	1	1	0	-1	0
21	1	0	0	1	-1
22	1	0	0	1	1
23	1	0	-1	-1	0
24	1	1	0	0	1
25	1	0	-1	1	0
26	1	0	1	0	-1
27	1	0	-1	0	1

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Table 2: Factors and their corresponding levels

Run Order	PtType	Blocks	Concentration	Dosage	Time	pH
1	0	1	12.5	0.07	50	5
2	2	1	5	0.07	50	2
3	2	1	5	0.07	50	8
4	2	1	20	0.07	50	2
5	2	1	5	0.04	50	5
6	2	1	5	0.1	50	5
7	2	1	12.5	0.1	80	5
8	2	1	5	0.07	20	5
9	2	1	12.5	0.1	20	5
10	0	1	12.5	0.07	50	5
11	2	1	20	0.04	50	5
12	2	1	12.5	0.04	50	2
13	2	1	12.5	0.07	20	8
14	2	1	20	0.1	50	5
15	2	1	20	0.07	80	5
16	0	1	12.5	0.07	50	5
17	2	1	12.5	0.07	20	2
18	2	1	5	0.07	80	5
19	2	1	12.5	0.1	50	8
20	2	1	20	0.07	20	5
21	2	1	12.5	0.07	80	2
22	2	1	12.5	0.07	80	8
23	2	1	12.5	0.04	20	5
24	2	1	20	0.07	50	8
25	2	1	12.5	0.04	80	5
26	2	1	12.5	0.1	50	2
27	2	1	12.5	0.04	50	8

RESULTS AND DISCUSSION

Table 3 below showed the design matrix consisting of each factor combination and their respective response which is the percentage removal of BPA from the simulated solutions. The data presented in the table showed various adsorption efficiencies for the respective experimental runs, with percentage removal ranging from 64% down to 90%. A quadratic model suggested for the adsorption as shown in Table 4 had a coefficient of determination (R^2) = 0.8946 and a p-value of 0.001, from table 5. The p-value less than 0.05 indicates that it is significant. This was further confirmed by the high R^2 of the model showing its high significance. The lack of fit had an F-value and p-value of (1.09 and 0.568,) respectively as shown in table 5, pointing to its insignificance. With all these conditions met,

the model is said to be a good one (Garba *et al.*, 2016). The plot of predicted against actual values as shown in Figure 4.2 indicated that there is less variation between them, this was confirmed by $R^2=0.8824$

A model regression equation (equation 2) was developed for the adsorption of the BPA as it was influenced by the parameters considered during the experiments;

The plot of predicted against actual values as shown in Figure 1 indicated that there is less variation between them, this was confirmed by $R^2=0.8824$.

The sum of 5 solutions of variables, culled from the design software for optimum adsorption of BPA in solution is given in table 6. These conditions are predicted by the model to have the best removal and this could be validated.

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Table 3: Experimental runs and responses

Std' Order	Run Order	Pt Type	Initial conc. (ppm)	Dosage (g)	Time (mins)	pH	Final Conc. (ppm)	% Removal
27	1	0	12.5	0.07	50	5	4.0	68.00
9	2	2	5.0	0.07	50	2	1.2	76.00
11	3	2	12.5	0.07	50	2	2.4	80.80
10	4	2	20.0	0.07	50	2	3.1	84.50
1	5	2	5.0	0.04	50	5	0.7	86.00
3	6	2	5.0	0.1	50	5	1.5	70.00
16	7	2	12.5	0.1	80	5	3.9	68.80
17	8	2	5.0	0.07	20	5	0.9	82.00
14	9	2	12.5	0.1	20	5	1.6	87.20
25	10	0	12.5	0.07	50	5	4.4	64.80
2	11	2	20.0	0.04	50	5	5.9	70.50
21	12	2	12.5	0.04	50	2	2.4	80.80
7	13	2	12.5	0.07	20	8	2.0	84.00
4	14	2	20.0	0.1	50	5	5.6	72.00
20	15	2	20.0	0.07	80	5	7.1	64.50
26	16	0	12.5	0.07	50	5	3.5	72.00
5	17	2	12.5	0.07	20	2	2.0	84.00
19	18	2	5.0	0.07	80	5	0.9	82.00
24	19	2	12.5	0.1	50	8	2.5	80.00
18	20	2	20.0	0.07	20	5	1.9	90.50
6	21	2	12.5	0.07	80	2	1.9	84.80
8	22	2	12.5	0.07	80	8	2.0	84.00
13	23	2	12.5	0.04	20	5	1.8	85.60
12	24	2	20.0	0.07	50	8	6.0	70.00
15	25	2	12.5	0.04	80	5	1.5	88.00
22	26	2	12.5	0.1	50	2	2.2	82.40
23	27	2	12.5	0.04	50	8	2.0	84.00

Table 4: Model fit summary for adsorption

Std. dev	R ²	R ² _{adj.}	R ² _{pred.}
3.74577	89.46%	77.17%	55.02%

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Table 5: ANOVA for Full Quadratic model

Source	DF	Adj SS	Adj MS	F-Value	p-Value
Model	14	1429.54	102.110	7.28	0.001
Linear	4	317.33	79.332	5.65	0.009
Concentration	1	75.00	75.000	5.35	0.039
Dosage	1	99.19	99.187	7.07	0.021
Time	1	141.45	141.453	10.08	0.008
Ph	1	1.69	1.687	0.12	0.735
Square	4	600.42	150.106	10.70	0.001
Concentration*Concentration	1	28.21	28.213	2.01	0.182
Dosage*Dosage	1	131.34	131.341	9.36	0.010
Time*Time	1	406.00	406.003	28.94	0.000
pH*Ph	1	351.00	351.001	25.02	0.000
2-Way Interaction	6	511.79	85.298	6.08	0.004
Concentration*Dosage	1	76.56	76.563	5.46	0.038
Concentration*Time	1	169.00	169.000	12.04	0.005
Concentration*pH	1	150.06	150.062	10.70	0.007
Dosage*Time	1	108.16	108.160	7.71	0.017
Dosage*Ph	1	7.84	7.840	0.56	0.469
Time*Ph	1	0.16	0.160	0.01	0.917
Error	12	168.37	14.031		
Lack-of-Fit	10	142.34	14.234	1.09	0.568
Pure Error	2	26.03	13.013		
Total	26	1597.91			

Equation 2: Model equation

Regression Equation

$$\begin{aligned}
 \text{Removal (\%)} = & 121.4 + 0.09A - 7.44B - 0.307C - 4.54D + 0.0409A^2 + 5514B^2 \\
 & + 0.00969C^2 + 0.901D^2 + 19.44AB - 0.02889AC - 0.2722AD - 5.78BC \\
 & - 15.6 BD - 0.0022 CD
 \end{aligned}$$

Where

A = Concentration

B = Dosage

C = Time

D = Ph

Table 6: Optimization solutions

These conditions are predicted by the model to have the best removal.

Solution	Concentration	Dosage	Time	pH	Predicted Removal (%)
1	5	0.04	80	8	91.20
2	20	0.10	20	8	98.80
3	5	0.10	20	8	94.32
4	5	0.04	20	8	93.79
5	5	0.04	80	2	89.05

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Predicted Percentage Removal against Experimental Percentage Removal

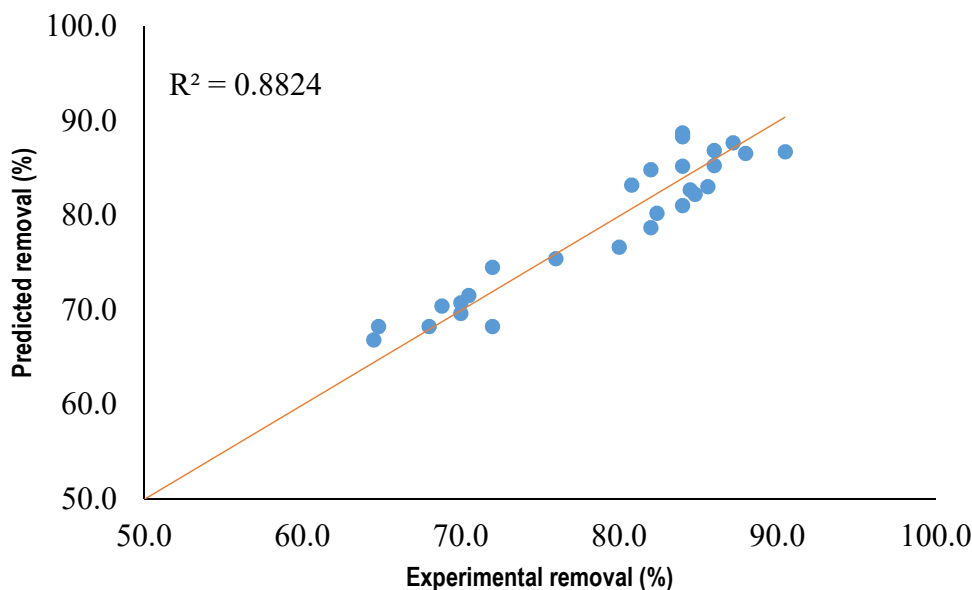


Figure 1: Predicted percentage removal against experimental percentage removal

Some Interactive Effects of Variables on Adsorption

Contour plots of interactive effects of the factors are presented in figures 2, 3, and 4 below. The Contour plot of the interactive effect of pH and contact time on the adsorption of BPA is presented in Figure 2. From the plot, it was observed that the final concentration of BPA is inversely proportional to the pH and contact time. It was however observed that the relationship between pH and the final concentration was stronger than that with the contact time. This finding implies that more BPA is removed at higher pH and longer contact time. This finding is similar to that reported in the literature. The longer the contact time, the more of a compound is adsorbed and also, bisphenol A has been reported to be adsorbed more in a basic medium (Dong *et al.*, 2010) where BPA removal was greatly influenced by high alkaline pH condition enabling the deprotonation of BPA to form organic anions.

Figure 3 presents the effect of pH and initial concentration on the final concentration of

BPA in the samples. From the plot, it can be deduced that the final concentration is inversely proportional to pH and the initial concentration. Thus, as the pH of the system increases, the final concentration of BPA decreases. Likewise, it was observed that with an increase in the initial concentration of BPA, the final concentration decreases. This finding shows a resemblance to that reported earlier; when the pH increases, the percentage adsorption also increases.

From the contour plot of the effect of pH and adsorbent dosage on the final concentration of BPA presented in figure 4, it was observed that the adsorbent dosage did not have much of a significant impact on the final concentration of BPA. This finding implies that the amount of bovine horn activated carbon used did not significantly affect the adsorption of bisphenol A. Again, it was observed that at high pH, the percentage adsorption increased. This aligned with findings in Figure 2

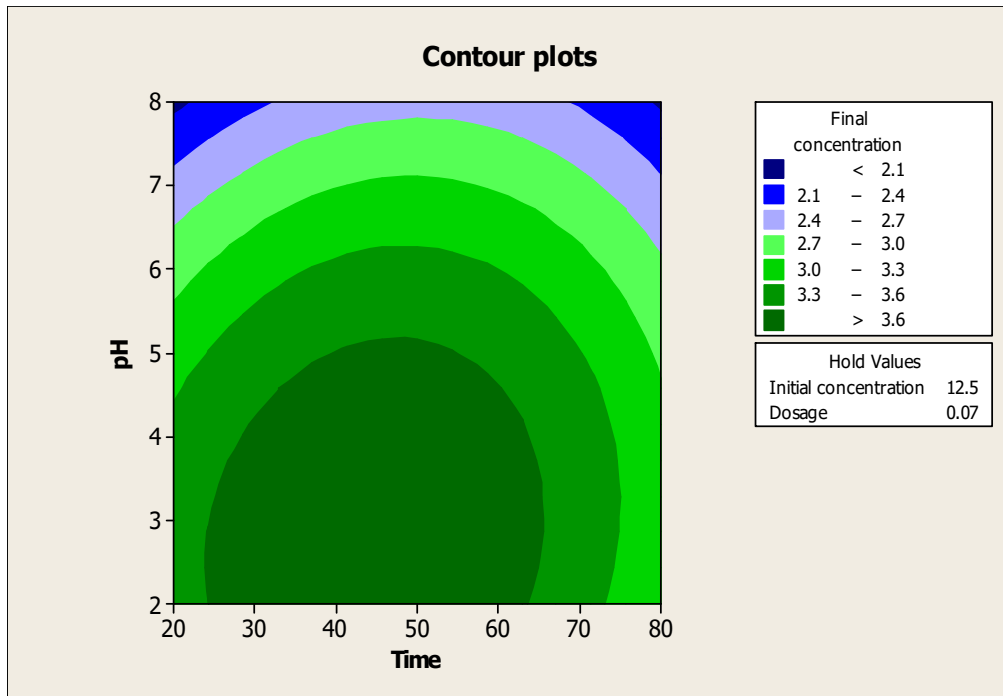


Figure 2: Interactive effects of pH and contact time on the final concentration of BPA

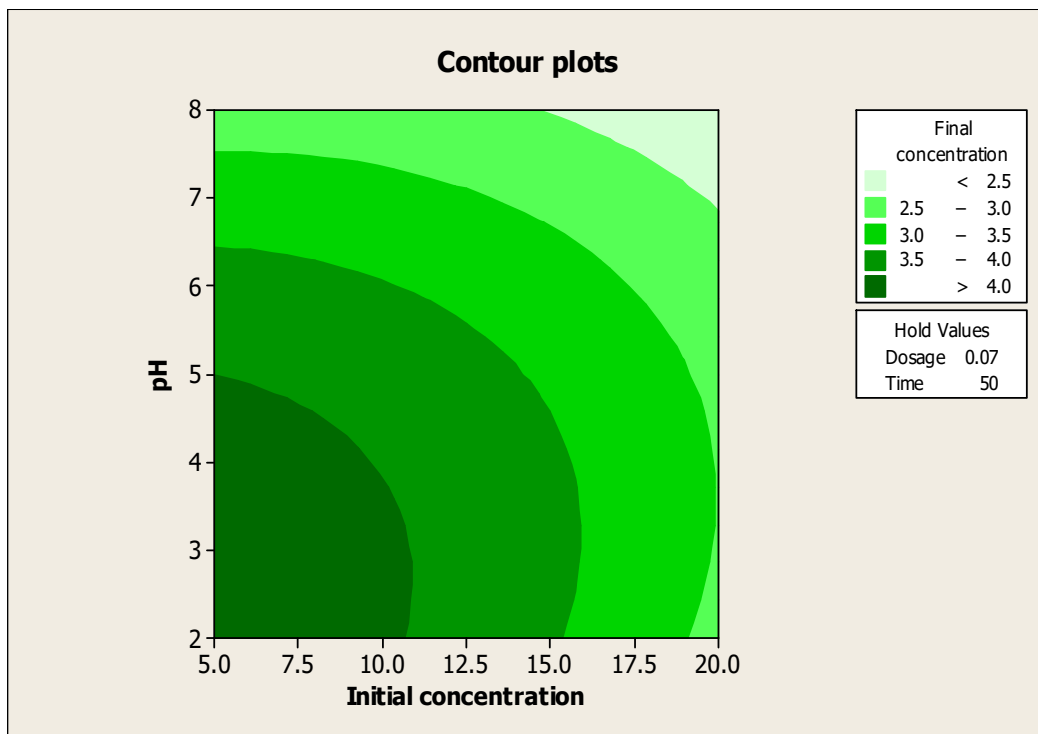


Figure 3: Effect of pH and initial concentration on the final concentration of Bisphenol A

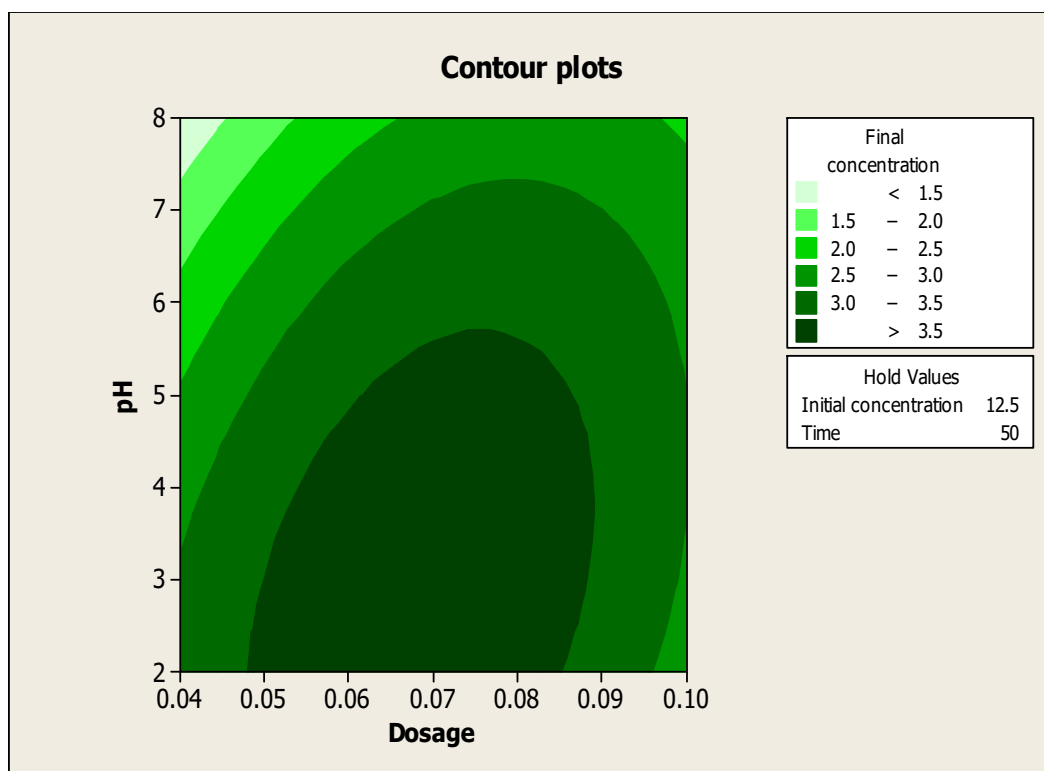


Figure 4: Effect of pH and dosage on the final concentration of Bisphenol A in Sample

CONCLUSION

The activated carbon prepared from bovine horns has demonstrated high effectiveness in the adsorption of BPA, so it can be employed in water treatment processes. Optimization of application of the activated carbon was also successfully executed thereby predicting better options or conditions for attaining maximum adsorption of BPA.

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