World Academy of Science, Engineering and Technology
International Journal of Chemical and Molecular Engineering
Vol:10, No:2, 2016

Modeling of Bisphenol A (BPA) Removal from Aqueous Solutions by Adsorption Using Response Surface Methodology (RSM)

Mohammad Ali Zazouli, Farzaneh Veisi, Amir Veisi

Open Science Index, Chemical and Molecular Engineering Vol:10, No:2, 2016 publications.waset.org/10003809.pdf

***Abstract*—**Bisphenol A (BPA) is an organic synthetic compound that has many applications in various industries and is known as persistent pollutant. The aim of this research was to evaluate the efficiency of bone ash and banana peel as adsorbents for BPA adsorption from aqueous solution by using Response Surface Methodology. The effects of some variables such as sorbent dose, detention time, solution pH, and BPA concentration on the sorption efficiency was examined. All analyses were carried out according to Standard Methods. The sample size was performed using Box-Benken design and also optimization of BPA removal was done using response surface methodology (RSM).

The results showed that the BPA adsorption increases with increasing of contact time and BPA concentration. However, it decreases with higher pH. More adsorption efficiency of a banana peel is very smaller than a bone ash so that BPA removal for bone ash and banana peel is 62 and 28 percent, respectively. It is concluded that a bone ash has a good ability for the BPA adsorption.

***Keywords*—**Adsorbent, banana peel, bisphenol A (BPA), bone ash, wastewater treatment.

I. Introduction

INDUSTRIAL wastewater contains the various pollutants that are dangerous. It must be treated before it is discharged to the environment [1]-[3]. Phenol and phenolic compounds such as bisphenol A (BPA) are one of organic pollutants in industrial wastewater [4]-[6]. BPA or 2.2 bis (4- hydroxyl phenol), as a typical Endocrine-disrupting chemicals (EDCs) has been widely applied in the production of polycarbonate plastics, epoxy resins and flame retardants as an important monomer.er. BPA solubility in water is 120 to 300 mg/l [7]. BPA leaches from some of above products under normal conditions of use. BPA has been detected in many places in the world. The maximum concentrations of BPA were reported in waste landfill leachates that were 17.2mg/L. It has caused great concern because of its potential risk to human health [5], [8], [9]. The previous studies have shown that BPA has the ability to change gender in several animal species, especially fish [7]. Many experiments have shown that BPA increased infertility, genital abnormalities and breast cancer [9]. Other studies have shown that BPA in the range of 1-10 milligrams per liter is strongly toxic for fish, algae and invertebrates [10]. Accordingly, there is an urgent need for developing the effective technology to remove BPA from aquatic environments. the variety of treatment techniques have been used for treating of wastewater has BPA and other phenolic compounds [11]. Physical and chemical treatment technologies such as adsorption, ozonation chemical precipitation, membrane filtration and advanced oxidation processes have been adopted for BPA removal [4], [5], [10]. the other side, the performance of the biological methods is not satisfactory due to the high toxicity of BPA for aerobic and anaerobic bacteria BPA [12]. Chemical precipitation was less pay attention due to excessive sludge production as well as the relatively low efficiency of conventional methods. From the technical and economic points of view, sorption technologies for EDC removal are very promising [13], [14]. Recently, researchers have considered some natural biosorbents to be effective as low cost sorbent alternatives for pollutants removal especially BPA [4]. Many sorbents based on low cost agricultural by-products had been used for dye sorption from wastewater, which included banana pith [15], orange peel [16], [16], wheat straw [17], sawdust [18], powdered waste sludge [19], wheat shells [20], wheat bran [21]. However, reports are low about BPA removal by banana peel and bone ash. Banana is one of the more consumed fruits in the world. Preliminary research showed that several tones of banana peels are made daily in household garbage and market places, creating an environmental nuisance and disposal problem. Banana peels is an abundant and inexpensive agricultural waste residue and is easily available in large quantities [10], [22]. The purpose of this study removal BPA by banana peel and bone ash bioadsobent and modeling them.

The objectives of this study are (1) to investigate the efficiency of banana peel and bone ash as adsorbents for BPA removal from aqueous solutions; (2) to examine the effects of sorbent dose, detention time, solution pH, and BPA concentration on the sorption efficiencies; and (3) to present the proper model of BPA removal by using response surface.

Mohammad Ali Zazouli is with the Department of Environmental Health Engineering, Health Sciences Research Center, Faculty of Health, Mazandaran University of Medical Sciences, Sari, Iran (Corresponding author; e-mail: zazoli49@yahoo.com).

Farzaneh Veisi is with the Health Sciences Research Center, Student Research Committee, Mazandaran University of Medical Sciences, Sari, Iran.

Amir Veisi, MSc student of Insurance Statistics, Shahid Beheshti University, Tehran, Iran.

II. Experimental

A. Materials

All the chemicals used were analytical grade, obtained from Merck and used without any further purification. A stock solution of BPA (10 mg/l) was prepared and desired concentration of testing solution was prepared by dilution of stock solution. The BPA concentration in experiment solution was 0.5, 2.25 and 4 mg/l. The desired pH was obtained using NaOH (0.1 N) or HCl (0.1 N) solution. Double distilled–deionized water was used throughout the experiments. The pH of the solution was obtained by adjusting to the addition of either NaOH (0.1 N) or HCl (0.1 N) solution.

B. Batch Adsorption Experiments

The experiments in batch system were carried out in a 250 ml Erlenmeyer flask Meyer. The effect of the initial concentration of BPA, pH (3, 7, 11) and contact time (30, 75, 120 min) on the removal efficiency were investigated. In each adsorption experiment, the specific concentrations of BPA solution were added into the flask. The desired condition was adjusted and then the specific dose of adsorbent (0.5 mg) was added. The samples were mixed by a magnetic stirrer with 120 rpm for 60 min. After the requirement time, the samples were centrifuged at 1400 rpm for 10 min [22]. Finally, the residual concentrations of BPA were measured using spectrophotometer (DR4000) in λmax=278nm [13], [18]. The evaluation of adsorbent performance was done by calculating the BPA removal percentage according to (1):

$$\text{Removal\%} = \frac{(C_o - C_e)100}{C_o} \tag{1}$$

C. Adsorbents Preparation

Bone ash and banana peels were used as adsorbents. Bones were put in oven to temperature 400°C for 4 h. Bone ash was cooled in desiccator. However, banana peels were firstly washed with water and then dried in the sunlight for 5 days. After that, two adsorbents were powdered and sieved to select 300-400μm particle sizes for using as adsorbents. The adsorbents were treated with 0.5MHCl for 30min followed by washing with distilled water for several times and put them in oven on 105°C for 1 h until dry [22].

D. Design of Experiments

Optimization of BPA removal was done using response surface methodology (RSM) with Box-Behnken model [23]. Three independent variables, including time, BPA concentration and pH were evaluated in levels (1, 0, -1). The variables and the corresponding surfaces are shown in Table I. The variable ranges were determined by preliminary and literature review [4], [15], [17], [24]-[27]. The sample size was performed using Box-Behnken design [28]. Its formula is according to (2):

$$N = 2K(K-1)C_o \tag{2}$$

where, N is the number of samples; K is the number of factors (variables) and C_0 is the number of the central points.

E. Statistical Analysis

The data were analyzed using Minitab 16 software. A full quadratic model was used for evaluation of data. Experiments were randomly done for preventing of systemic bias [18].The coefficient of full quadratic model is interpretation the removal rates of BPA as the independent factors. Data were analyzed by multiple regressions. Coefficient were analyzed by analysis of variance (ANOVA) that analyzed value ($p<0.05$) was determined as significant. The capabilities of final model were assessed using the Numerical analysis and Raphica, which was tested by Minitab 16 software.

TABLE I
VALUES AND SYMBOLS OF THREE VARIABLES FOR THE BOX-BEHNKEN DESIGN IN THIS STUDY

	Level	**Variable**		
		pH	BPA concentration	Contact time
Unit	-	-	mg l^{-1}	min
Symbol	-	X_1	X_2	X_3
1	High	11	4	120
0	Middle	7	2.25	75
-1	Low	3	0.5	30

III. RESULTS AND DISCUSSION

A. Full Quadratic Model

Table II shows the BPA removal by banana peel and bone ash. It is indicated that BPA removal by bone ash was more than a banana peel. Based on data analysis, correlation between the BPA removal efficiency and parameters represents by following quadratic equation. Equations (3) and (4) show the BPA of efficiency removal using bone ash and banana peel with significant variables, respectively:

$$Y = 37 + 8.375(X_1) + 10.375(X_2) + 9.5(X_3) \tag{3}$$

$$Y = 30.3333 + 9.4375(X_2) + 7.9(X_3) - 6.8167(X_1)^2 - 11.1917(X_3)^2 \tag{4}$$

where, Y is the percentage removal of BPA (%), x_1, x_2 and x_3 are the terms of the coded values of pH, BPA initial concentration and contact time, respectively.

B. Checking the Model

To check the model, the results were summarized in a common ANOVA table. The ANOVA table for the removal percentage of BPA is shown in Table III. These suggest that the model statistically follows a linear pattern for both adsorbents. To confirm the goodness of fit between the model and the experimental results, regression coefficient (Adjected R-squared) analysis was applied. The Adjected R-squared values close to 1.0 (minimizing the square of errors) indicate that the regression line fits the experimental data well [20]; this equation can be used to predict the results at specific points with accuracies of 87.4 and 99.4% for the bone ash and banana peel, respectively.

C. Confirm the Response Surface Model

Distributed describe test data against the estimated value by model in Fig. 1 than is showed acceptable model Occasion of residuals diagram for the suitability of model:

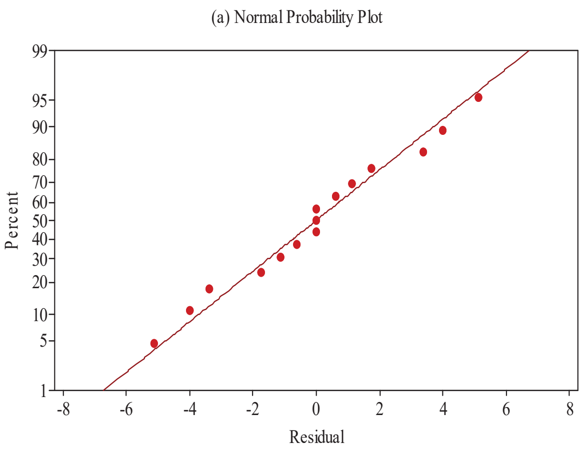
1. Residuals have a normal distribution with zero mean and constant variance.
2. Residuals are independent.

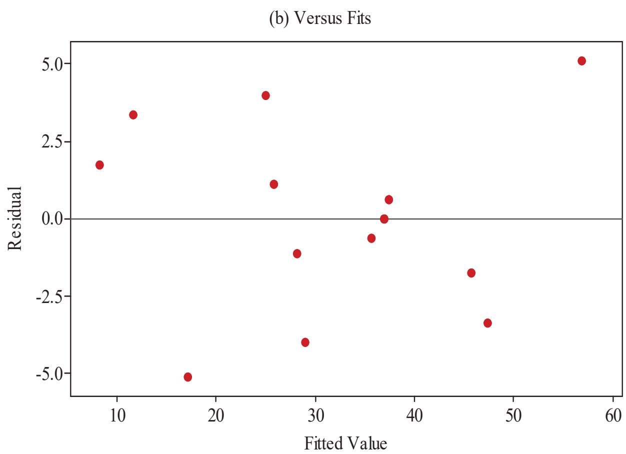
TABLE II
RESULTS OF THE EXPERIMENTS AND PREDICTIVE VALUES CONDUCTED ACCORDING TO BOX-BEHNKEN DESIGN FOR BPA ADSORPTION BY BONE ASH AND BANANA PEEL

Experiment	Factor			Removal (%)			
				By Banana peel		By Bone ash	
	x_1	x_2	x_3	Experimental	Predicted	Experimental	Predicted
1	0	0	0	10	13	29	25
2	+1	-1	0	6	8	10	8.2
3	-1	+1	0	28	25	44	46
4	+1	+1	0	14	12	25	29
5	-1	0	-1	10	12	27	26
6	+1	0	-1	3	5	15	12
7	-1	0	+1	22	20	44	47
8	+1	0	+1	10	9	27	28
9	0	-1	-1	7	3	12	17
10	0	+1	-1	13	14	38	37
11	0	-1	+1	12	12	35	36
12	0	+1	+1	13	17	62	56
13	0	0	0	25	25	37	37
14	0	0	0	25	25	37	37
15	0	0	0	25	25	37	37

TABLE III
ANALYSIS OF VARIANCE FOR PROPOSED MODEL FOR BPA REMOVAL USING BONE ASH AND BANANA PEEL

	Source	DF	Sum of square	Adj SS	Adj MS	F_{value}	P_{Value}
Bone ash	Regression	9	2472.18	2472.18	247.687	11.76	0.007
	Linear	3	2144.25	2144.25	714.750	30.61	0.001
	Square	3	321.43	321.43	107.144	4.59	0.067
	Interaction	3	6.50	6.50	2.167	0.09	0.961
	Residual error	5	116.75	116.75	23.350		
	Lack-of-Fit	5	116.75	116.75	38.917		
	Pure Error	2	0.00	0.00	0.00	R-squared	95.5%
	Total	14	258.93	258.93		Adj R-squared	87.4%%
Banana peel	Regression	9	1132.68	1132.68	125.854	279.67	0.00
	Linear	3	716.75	716.75	238.917	530.93	0.00
	Square	3	342.43	342.43	114.144	253.65	0.00
	Interaction	3	73.5	73.5	24.500	54.44	0.00
	Residual error	5	2.25	2.25	0.450		
	Lack-of-Fit	3	2.25	2.25	0.750		
	Pure Error	2	0.00	0.00	0.00	R-squared	99.8%
	Total	14	1132.68			Adj R-squared	99.4%





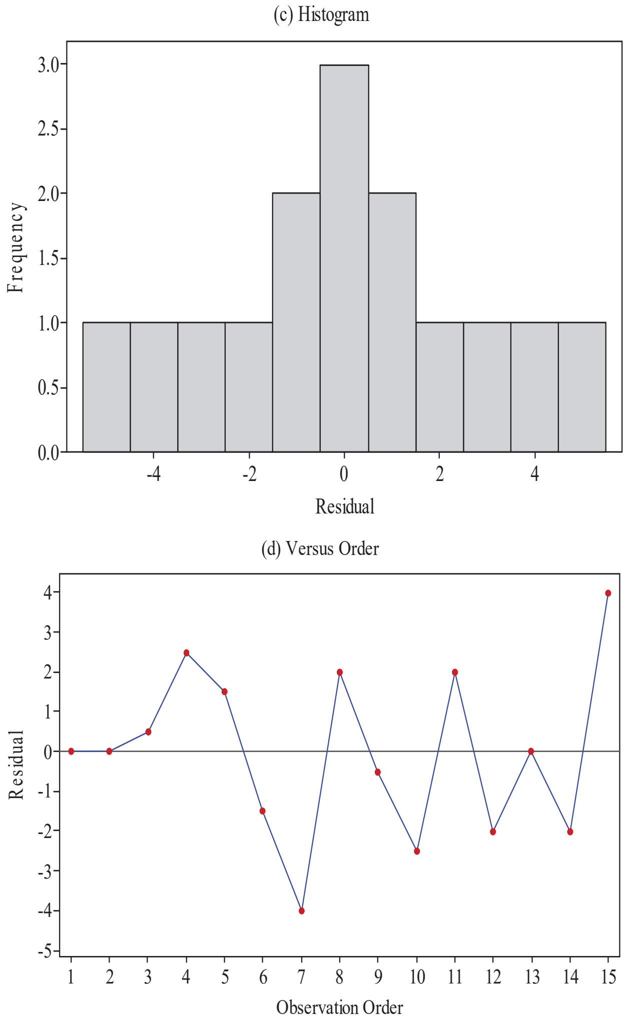
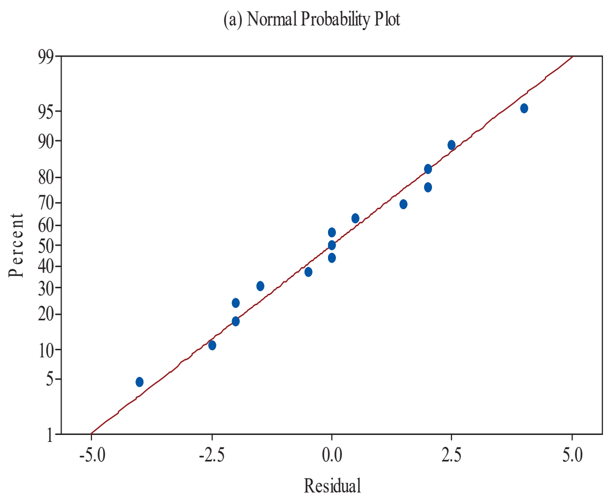


Fig.1 Residual plots of BPA adsorption via Bone ash



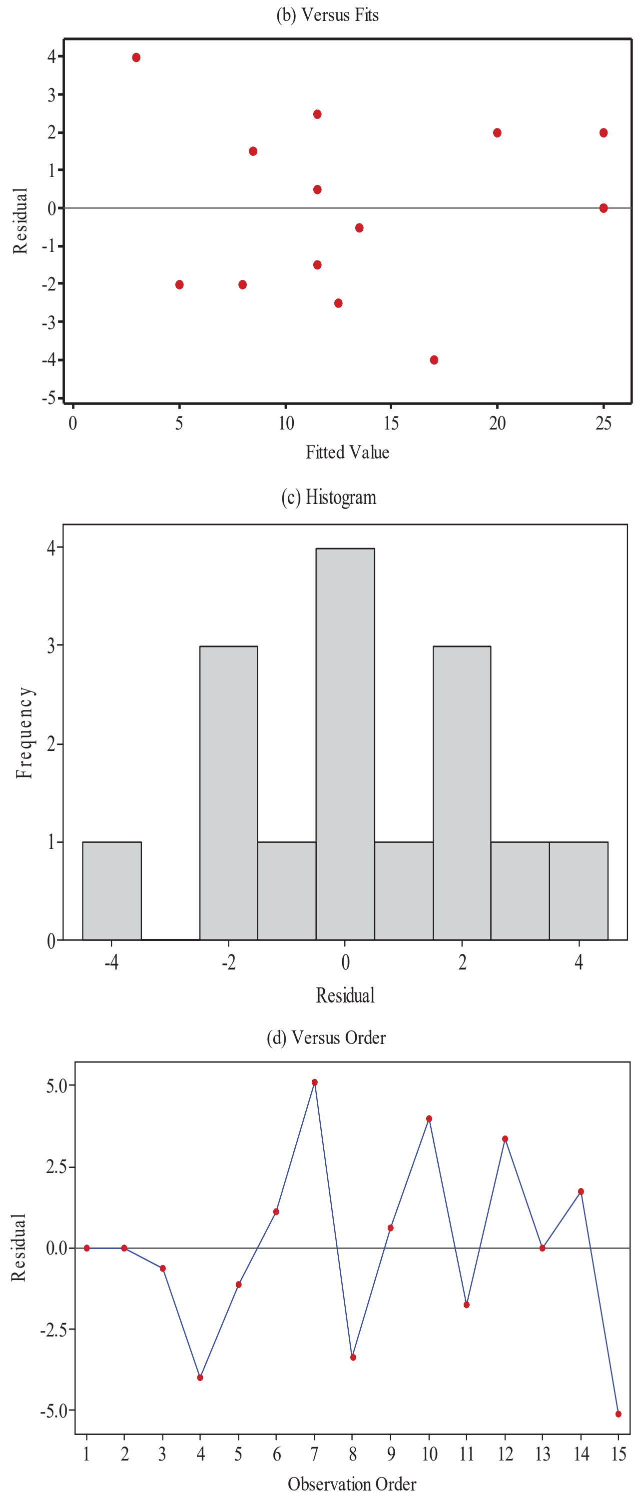


Fig. 2 Residual plots of BPA adsorption via Banana peel

If the three assumptions are correct that selected model is valid, otherwise it must be another model. Survey these assumptions is done by the following diagrams.

1. Figs. 1 (a) and 2 (a) show normal probability plots of the residuals from the least-squares fitting. The points on the plots lie reasonably close to a straight line, which

confirms that the errors have a normal distribution with a zero mean. In addition, the input variables affect the responses.

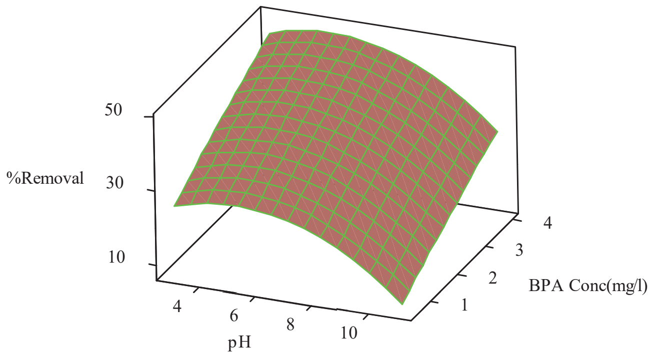
2. Figs. 1 (b) and 2 (b) show random scatter plots of the residuals versus the fitted values. The figures do not reveal an obvious pattern. The predicted results were revealed to be randomly scattered around the zero line (above and below the x-axis), which supports the adequacy of the proposed model.
3. Figs. 1 (c) and 2 (c) show the frequencies of the residuals, and indicate that there are no outliers in the data.
4. Figs. 1 (d) and 2 (d) show that the ordered residuals oscillate in a random pattern around the zero line. Accordingly, the residuals appear to be randomly scattered along the zero line, which indicates that the error terms do not correlate with each other.

Thus, the analysis of charts and assumptions of the accepted selected model is suitable for data analysis.

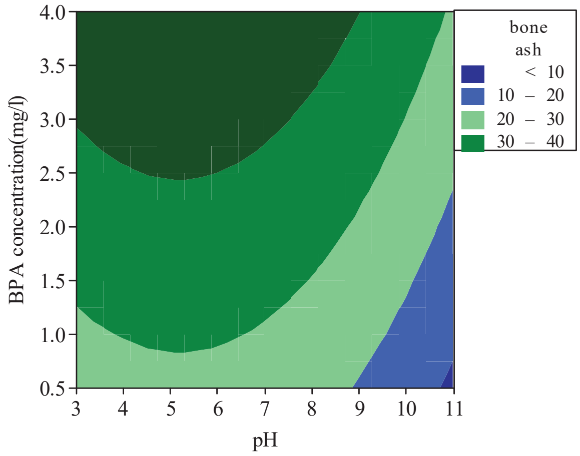
D. Response Surface and Counter Plots

These results are exited for removing BPA by adsorbing. For bone ash, according to (1) and Figs. 3 (a) and (b), with the removal process with increasing BPA concentration and time contact and decreasing pH. For the banana peel according (2) and Figs. 4 (a) and (b) like bone ash in pH acidic in order to increase the process of alkaline, and with increasing time and BPA concentration, of process on positive removal and with pH and time is decreed removal if the pH and contact time are doubled, removal is decreased. The interference of pH and concentration BPA has positive effect, but relation time and concentration BPA has effective effect of removal.

BPA removal is very lower than bone ash. BPA transfer from solution to adsorbent occurring in two stages. It means an external surface adsorption stage or rapid adsorption and an internal adsorption stage or slow absorption. More transition occurs in the first stage in order to adsorb surface in one stage all big and small particles, but in second stage only small particles adsorb [25], [29]. The more removal of BPA by bone ash in contact time 120 min and pH =3 and concentration 4mg/g is 62%. Absorption mechanism in these has not been evaluated by the banana peel. Removal BPA by a banana peel in contact time 75min and pH=3 and concentration 4mg/g is 28%. If pH is decreased, removal efficiency is increased in two adsorbs. That it constant Zhoe in 2012 on that it is done on the BPA removal by biosorbtion. Initial pH can be as an interfering factor between adsorbent [25], [29]. Initial pH can change the charge of adsorbent and molecules adsorbent. When the pH is 2 to 7, removal of BPA changes more so that linked groups accomplish easily between adsorbent and BPA in pH acidic. And H^+ can combine with BPA easily for finding suitable situation in adsorbing [5], [15], [16], [19].The most part of bone ash is made of calcium apatite with chemical formula $Ca_5(PO_4)_3OH$. The molecular formula of bone ash shows that these adsorbent is parted in mineral adsorbents and it can be used in pollutant environmental removal. On the other hand, the adsorption efficiency increases with the formation of hydroxyl in absorbent surface. That pH adsorbing can have important in adsorbing value of pollutant by adsorbent and hydroxyl group have an important effect as a surface agent group. Finally, the study showed that the bone ash has high ability in adsorbing BPA.

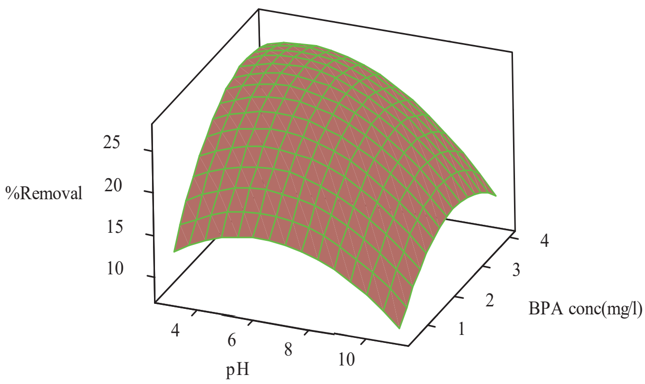


(a) Surface

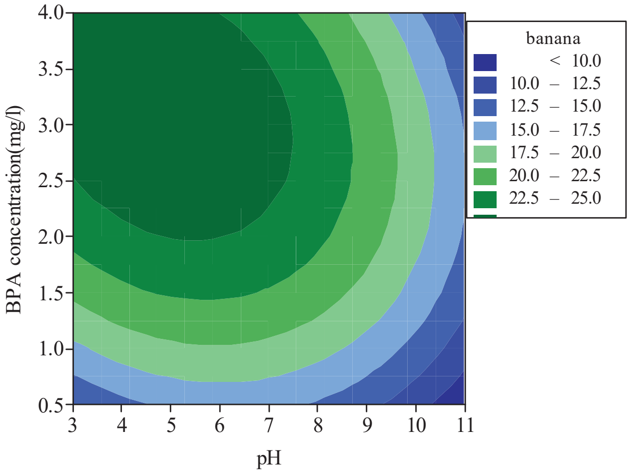


(b) Contour plot

Fig. 3 Response (a) surface plot and (b) contour plot of the BPA removal efficiency (%) as a function of BPA concentration (mg/L) and pH for bone ash



(a) Surface



(b) Contour plot

Fig. 4 Response (a) surface plot and (b) contour plot of the BPA removal efficiency (%) as a function of BPA concentration (mg/L) and pH for banana peel

IV. Conclusions

The study showed that the absorption efficiency of BPA in both adsorbents increased with time, BPA concentrations and lower pH. More removal for a bone ash and a banana peel are 62 and 28 percent, respectively. Absorption efficiency at 120 min for a bone ash is in the maximum amount. However, the maximum efficiency is at 75 min for a banana peel. BPA absorbed by the banana peel adsorbent is very smaller than a bone ash. It is in concluded that the surface response model with linear terms for banana ash and with linear, cubic and interaction terms for a banana peel has a significant relationship. Bone ash is a good adsorbent for the BPA.

Acknowledgment

The authors would like to express their thanks to the laboratory staff of the Department of Environmental Health Engineering, Faculty of Health and Health Sciences Research Center for their collaboration, and to the Research Deputy of Mazandaran University of Medical Sciences for the financial support of this study (Project No: 92-157).

References

[1] Asgari, G. and A.R. Rahmani, Preparation of an Adsorbent from Pumice Stone and Its Adsorption Potential for Removal of Toxic Recalcitrant Contaminants. 2013. Vol. 13. 2013.

[2] Asgari, G., et al., Catalytic Ozonation of Phenol Using Copper Coated Pumice and Zeolite as Catalysts. 2012. Vol. 12. 2012.

[3] Rahmani, A., M. Samadi, and A. Enayati Moafagh, Investigation of Photocatalytic Degradation of Phenol by UV/TiO2 Process in Aquatic Solutions. Vol. 8. 2008.

[4] Zhou, Y., P. Lu, and J. Lu, Application of natural biosorbent and modified peat for bisphenol a removal from aqueous solutions. Carbohydrate Polymers, 2012. 88(2): p. 502-508.

[5] Zazouli., M.A. and MTaghavi, Phenol Removal from Aqueous Solutions by Electrocoagulation Technology Using Iron Electrodes: Effect of Some Variables. Journal of Water Resource and Protectio, 2012. 4: p. 980-983.

[6] Zazouli, M.A., M. Taghavi, and E. Bazrafshan, Influences of Solution Chemistry on Phenol Removal from Aqueous Environments by Electrocoagulation Process Using Aluminum Electrodes. J Health Scope, 2012. 1(2): p. 66-70.

[7] Zhou, D., et al., Photooxidation of bisphenol A (BPA) in water in the presence of ferric and carboxylate salts. Water Research, 2004. 38(19): p. 4107-4116.

[8] Liu, G., et al., Adsorption of bisphenol A from aqueous solution onto activated carbons with different modification treatments. Journal of Hazardous Materials, 2009. 164(2-3): p. 1275-1280.

[9] Chen, J., X. Huang, and D. Lee, Bisphenol A removal by a membrane bioreactor. Process Biochemistry, 2008. 43(4): p. 451-456.

[10] Deborde, M., et al., Oxidation of bisphenol A by ozone in aqueous solution. Water Research, 2008. 42(16): p. 4299-4308.

[11] Yamanaka, H., et al., Efficient Microbial Degradation of Bisphenol A in the Presence of Activated Carbon. Journal of Bioscience and Bioengineering, 2008. 105(2): p. 157-160.

[12] Li, Q., et al., Electrochemical detection of bisphenol A mediated by (Ru(bpy)3)2+ on an ITO electrode. Journal of Hazardous Materials, 2010. 180(1-3): p. 703-709.

[13] Basile, T., et al., Review of Endocrine-Disrupting-Compound Removal Technologies in Water and Wastewater Treatment Plants: An EU Perspective. Industrial & Engineering Chemistry Research, 2011. 50(14): p. 8389-8401.

[14] Nakanishi, A., et al., Adsorption characteristics of bisphenol A onto carbonaceous materials produced from wood chips as organic waste. J Colloid Interface Sci, 2002. 252(2): p. 393-6.

[15] Li, Y.-H., et al., Adsorption thermodynamic, kinetic and desorption studies of Pb2+ on carbon nanotubes. Water Research, 2005. 39(4): p. 605-609.

[16] Bilici Baskan, M. and A. Pala, Removal of arsenic from drinking water using modified natural zeolite. Desalination. 281(0): p. 396-403.

[17] Li, Z., et al., Partitioning behaviour of trace elements in a stoker-fired combustion unit: An example using bituminous coals from the Greymouth coalfield (Cretaceous), New Zealand. International Journal of Coal Geology, 2005. 63(1-2): p. 98-116.

[18] Kabengi, N.J., S.H. Daroub, and R.D. Rhue, Energetics of arsenate sorption on amorphous aluminum hydroxides studied using flow adsorption calorimetry. Journal of Colloid and Interface Science, 2006. 297(1): p. 86-94.

[19] Pan, J., et al., Synthesis of chitosan/Î^{3}-Fe2O3/fly-ash-cenospheres composites for the fast removal of bisphenol A and 2,4,6-trichlorophenol from aqueous solutions. Journal of Hazardous Materials. 190(1-3): p. 276-284.

[20] Brugnera, M.F., et al., Bisphenol A removal from wastewater using self-organized TIO2 nanotubular array electrodes. Chemosphere. 78(5): p. 569-575.

[21] Elkady, M.F., A.M. Ibrahim, and M.M.A. El-Latif, Assessment of the adsorption kinetics, equilibrium and thermodynamic for the potential removal of reactive red dye using eggshell biocomposite beads. Desalination. 278(1-3): p. 412-423.

[22] Achak, M., et al., Low cost biosorbent banana peel for the removal of phenolic compounds from olive mill wastewater: Kinetic and equilibrium studies. Journal of Hazardous Materials, 2009. 166(1): p. 117-125.

[23] Zazouli, M.A., F. Veisi, and A. Veisi, Modeling Bisphenol A Removal from Aqueous Solution by Activated Carbon and Eggshell. Journal of Mazandaran University of Medical Sciences, 2013. 22(2): p. 129-138.

[24] Soner AltundoÄŸan, H., et al., Arsenic removal from aqueous solutions by adsorption on red mud. Waste Management, 2000. 20(8): p. 761-767.

[25] Liu, C., et al., Optimal conditions for preparation of banana peels, sugarcane bagasse and watermelon rind in removing copper from water. Bioresource Technology, 2012. 119(0): p. 349-354.

[26] Cornejo, L., et al., In field arsenic removal from natural water by zero-valent iron assisted by solar radiation. Environmental Pollution, 2008. 156(3): p. 827-831.

[27] Bilici Baskan, M. and A. Pala, Removal of arsenic from drinking water using modified natural zeolite. Desalination, 2011. 281(0): p. 396-403.

[28] Zazouli, M.A., P. Ebrahimi, and M. Bagheri Ardebilian, Study of Cd (II) and Cr (VI) biosorption by mesocarps of orange and sour orange from aqueous solutions. Environmental Engineering and Management Journal 2014. 13(2): p. 231-492.

[29] Pan, J., et al., Synthesis of chitosan/Î^{3}-Fe2O3/fly-ash-cenospheres composites for the fast removal of bisphenol A and 2,4,6-trichlorophenol from aqueous solutions. Journal of Hazardous Materials, 2011. 190(1-3): p. 276-284.