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OPTIMIZATION OF ANTIMONY LEACHING FROM FOOD PACKAGING COVERS MADE OF LOW DENSITY POLYETHYLENE USING RESPONSE SURFACE METHODOLOGY

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Abstract

Heavy metal contamination in the environment, especially in packaged food and drinking water, are always of great concern due to their health impact. The use of heavy metal as catalysts during plastic syntheses, particularly antimony, human exposure to metal release from plastic covers has been a serious concern in recent years. The antimony (Sb) leaching from food packaging materials made of low density polyethylene (LDPE) was investigated and optimized using response surface methodology (RSM). The individual and interactive effect of three main independent variables such as pH (X1), temperature (ºC) (X2) and retention time (min) (X3) on the efficiency of leaching of antimony from plastic cover has been assessed. A second-order empirical relationship between the response and the independent variable was derived. Analysis of variance (ANOVA) showed a high coefficient of determination value (R^2 = 0.8998 and an adjusted R^2 0.8097). The maximum leachability of Sb was found at, alkaline pH with high temperature and less retention time. This study evidently showed that response surface methodology was one of tool to optimize the variables response for leaching of antimony from low density polyethylene covers.

Key words: *Antimony; Central composite design (CCD); Leaching; LDPE; Response surface methodology (RSM).*

1. INTRODUCTION

Plastic is an organic, synthetic or processed material that is a high molecular weight polymer. The material used for plastic covers varies from country to country, but the most widespread material in use is polyethylene terephthalate (PET). PET has become the most favorable packaging material world wide for water and soft drinks bottles. The reason for this development is the excellent material properties, especially its durability and very low weight of the bottles compared to glass bottles of the same filling volume. In comparison to other packaging polymers, PET has also a high clarity as well as good barrier properties towards moisture and oxygen [1]. They are light, durable, moldable, hygienic and economic, making them suitable for a wide variety of applications including food and product packaging, car manufacturing, agriculture and housing products. Ninety percent of the worldwide manufacture of polyethylene terephthalate (PET), polyester of terephthalic acid and ethylene glycol, employs Sb_2O_3 as a catalyst [2]. The amount of PET covers for the package is still increasing worldwide. Antimony trioxide is the preferred polycondensation catalyst for the fabrication of PET due to its adequate catalytic activity, colour and cost. The Sb concentration of the commercialized PET resin is between 190 and 300 μg/g [3]. USEPA and EU have established 6 and 10 μg/L, respectively, of maximum permissible Sb concentration in drinking water [4-5]. In contrast, an earlier study of metal content of food given to institutionalized children showed about 0.209 to 0.693 mg/kg of antimony in food which is identical with a guideline for drinking-water quality with regard to antimony by the World Health Organizations WHO (1996)[6]. Werrin (1963) reported that the intake of a drink containing 30 μg/ml Sb concentrations might cause nausea, vomit, and diarrhea. In chronic exposure to lesser Sb doses, myocardial atrophy could be observed; meanwhile higher doses cause increased occurrences of lung, liver and bile cancers [7-9]. The USEPA has not classified antimony as a human carcinogen in water due to lack of studies. However, research shows that antimony and arsenic, a proven carcinogen, are similarly toxic [10].

The commercialization of mineral water in PET covers dates back several decades; however, the determination of the nature and extent of toxic substances that can dissolve from the bottle covers into the water has only been achieved with the development of modern analytical techniques. In early investigations, the possible leaching effect of water on the material of the cover was not considered. Response surface methodology (RSM) is based on the statistical analysis of regression consisting in determining an optimal model, which minimizes the residual variations [11]. Recently, RSM has been successfully applied to different processes, which includes, O_3 oxidation of acid dye effluent [12], Landfill leachate [13], Selenite and Selenate Biosorption [14] and electrochemical oxidation of textile dye wastewater [15]. The major objective of this study is to optimize the variables such as pH, temperature, and the retention time on the leachability of antimony from the food packaging material.

2. MATERIALS AND METHODS

2.1 Chemicals and materials

The food packaging, plastic covers of low-density polyethylene (No.4) having the size of 40μm, purchased from market (Kamala Plastics, Coimbatore, India). The ultra pure water was used for all the experiments. The pH was adjusted as per the design experiment by adding 0.1 N HCl and 0.1 N NaOH using the pH meter (Susima AP-1 Plus, Chennai, India). The temperature was varied by boiling the water in an Induction stove (TTK Prestige Limited, Hosur, India). The water temperature was measured using a thermometer (Brannan, UK). All glassware, polyethylene covers, and sample vessels (Borosil) used for the experiments were immersed and rinsed three times with ultrapure water before use. All chemicals used in this study were analytical grade, purchased from Loba Chemie, Mumbai, India.

2.2 Sample Preparation

Each experiment, 100 mL of ultra pure water was taken in the glass vessel and adjusted the pH, temperature according to the design of experiments. Then poured the water into the low density polyethylene cover and retained it for the duration given in the design of experiments. After attaining the retention time, it was transferred to glass vials and analyzed immediately.

2.3 Experimental Design

To optimize the conditions for variables at which maximum antimony leaches out from the food packaging material was found using response surface methodology. The experimental conditions were designed as a function of the selected main variables such as pH (X_1), temperature °C (X_2) and residential time (X_3). The central composite design (CCD) was selected because it is ideal for sequential experimentation and allows a reasonable amount of information for testing lack of fit while not involving an unusually large number of design points [16].

The factors (independent variables) range selected for this experiment were pH (X_1): 3-11, temperature ºC (X_2): 4 – 90 ºC and retention time (X_3): 1- 60 min. A three-level factorial design was established with the help of the Design Expert 8.0.4 Trial software (USA). In order to develop the regression equation, the test factors were coded according to the following equation:

$$X_i = \frac{U_i - U_{i0}}{\Delta U_{i0}} \qquad (1)$$

where X_i is the coded value of the i^{th} independent variable, U_i the natural value of the i^{th} independent variable, U_{i0} the natural value of the i^{th} independent variable at the center point, and ΔU_{i0} is the step change value [16] The actual values of the variables and its coded values are shown in Table 1.

Table 1 Actual values of the variables for the coded values

Variables	Actual values for the coded values				
	-1.682	-1	0	1	1.682
pH (X_1)	2	3.8	6.7	9.2	11
Temp., (ºC) (X_2)	4	21	47	73	90
Retention Time (min) (X_3)	1	13	30.5	48	60

The rotatable experimental plan was carried out as a central composite design with three variables and at five levels consisting of 20 experiments as shown in Table 2. The three significant independent variables

X_1, X_2, and X_3 and the mathematical relationship of the response Y (Sb leachability) on these variables can be approximated by quadratic/(second-degree) polynomial equation as shown below:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{12}X_1 X_2 + b_{13}X_1 X_3 + b_{23}X_2 X_3 \quad (2)$$

where Y is the predicted response, b_0 the constant, b_1, b_2, and b_3 the linear coefficients, b_{12}, b_{13}, and b_{23} the cross-product coefficients, and b_{11}, b_{22}, and b_{33} are the quadratic coefficients. ANOVA was applied to obtain the interaction between the process variables and the response. The coefficients of determination, R2 and R^2_{adj} expressed the quality of fit of the resultant polynomial model, and statistical significance was checked by *the F - test*.

2.4 ICP-OES analysis

Antimony was analyzed following the US Environmental Protection Agency (USEPA) method 2008 [17] using ICP- OES (Inductive coupled plasma - optical emission) spectrometer (Perkin Elmer optima 5300DV). Table 3 lists the conditions adopted for ICP-OES.

Table 3 ICP –OES instrumental conditions adopted for the Analysis

Parameters	Operation conditions
Plasma RF power	1500 W
Plasma flow	15 L/min
Nebulizer flow	0.8 L/min
Nebulizer pressure	0.8 L/min
Sample uptake rate	1.5ml/min

Detector mode	Pulse
Sweeps/replicate	3
Sample delay time	60sec
Sample read delay	5 sec
Sampler wash time	60 sec
Points/peak	2
Number of replicates	3

3. RESULTS AND DISCUSSION

3.1 Preliminary studies

In this first stage, prior to establishing the response surface methodology, three variables were selected in order to analyze whether the experimental domain was suitable for the variables that could influence the leaching of antimony from the plastic covers. The variables such as pH, temperature, and retention time were chosen for this study. The reason for selecting these variables are, many of the shops in and around the city of Coimbatore, Tamilnadu, India were storing the food and beverages in the low density polyethylene covers. Also, many of the unrecognized food shops were pouring the hot soups, or soft food or liquid or gravy or food samples etc, in the plastic cover. The pH of the liquid or gravy or food samples may vary from 2-11. The temperature of the food also varies from 4-90^{o}C. For the holding time in the plastic cover may vary from 5 to 60 minutes. Based on the above reason the three variables and at the ranges were selected.

3.2 Central composite design analysis

The most important parameters that affect the leaching of antimony from plastic cover are pH, temperature and retention time. In order to study the combined effect of these factors, experiments were performed in different combinations using statistically designed experiments. The results of the Y (response) of antimony concentration by leaching were measured according to design matrix and the measured response is listed in Table 2.

Table 2 Experimental design of RSM and its actual and predicted values

Run	Variables in uncoded levels			Sb (ppm)	
	(X_1)	(X_2)	(X_3)	Y	
	pH	Temp	Time	Actual Value	Predicted Value
	(pH^0)	(ºC)	(min)		
1	6.5	90	30.5	BDL	BDL
2	3.8	73	13	0.036	0.027
3	6.5	47	1	BDL	BDL
4	9.2	73	13	BDL	BDL
5	6.5	47	30.5	BDL	BDL
6	2	47	30.5	0.056	0.055
7	9.2	21	48	0.034	0.042
8	6.5	47	30.5	BDL	BDL
9	6.5	47	30.5	BDL	BDL
10	6.5	47	30.5	BDL	BDL
11	9.2	21	13	0.063	0.047
12	6.5	47	30.5	BDL	BDL
13	3.8	21	48	0.035	0.028
14	11	47	30.5	0.049	0.051
15	6.5	47	30.5	BDL	BDL
16	9.2	73	48	BDL	BDL
17	3.8	21	13	BDL	BDL
18	6.5	4	30.5	BDL	BDL
19	3.8	73	48	0.036	0.051
20	6.5	47	60	0.033	0.028

BDL: Below Detectable Level

3.3 The second-order model and analysis of variance (ANOVA)

After the evaluation of experimental results, the quadratic function for the leaching of antimony was obtained by utilizing Design-Expert® 8.0.4 Trial software. To estimate the coefficients of the polynomial, at least square fit procedure was applied, and then based upon the fitted surface response analysis was performed. Analysis of the fitted surface nearly corresponded to that of the actual system if the fitted surface was an adequate approximation of the true response function [18]. Quadratic equations based upon the coded values, for leaching of antimony are presented in Eq. (3), i.e.,

$$Y\text{ (Sb ppm)} = -3.380 \times 10^{-5} - 1.715 \times 10^{-3}X_1 - 4.454 \times 10^{-3}X_2 + 4.503 \times 10^{-3}X_3 - 0.017X_1X_2 - 8.000 \times 10^{-3}X_1X_3 - 7.500 \times 10^{-4}X_2X_3 + 0.019X_1^2 + 2.086 \times 10^{-4}X_2^2 + 6.029 \times 10^{-3}X_3^2 \quad ...(3)$$

The statistical importance of the generated model evaluated by the Fisher test (i.e., *F*-test) was quantified by dividing the Model Mean Square by its Residual Mean Square for analysis of variance (ANOVA). The results of ANOVA for the leaching of antimony are presented in Table 4. According to ANOVA (Table 4), the Fisher *F*-values for all regressions were higher. The large value of *F* indicates that most of the variation in the response can be explained by the regression equation. The associated *p*-value is used to estimate whether *F* is large enough to indicate statistical significance. *p*-values lower than 0.05 indicates that the model is statistically significant [19]. The ANOVA result in the leaching of antimony in plastic cover shows *the F*-value of 9.98, which implies that the terms in the model have a significant effect on the response. The model gives the coefficient of determination, R2 value of 0.8998 and an adjusted-R^2 value of 0.8097, which is high and advocates a high correlation between the observed and the predicted values. The probability *p* (~0.0001) is less than 0.05 indicates that the model terms are significant at 95% probability level.

Table 4 Analysis of variance (ANOVA) for the fitted quadratic model of Sb (ppm)

Source	Sum of squares df	Mean square		*F* value	Prob >*F*	Remarks
Model	8.75E-03	9	9.72E-04	9.98	0.0006	significant
Residual	9.74E-04	10	9.74E-05			
Lack of Fit	9.74E-04	5	1.95E-04			
Pure Error	0	5	0			
Cor Total	9.72E-03	19				
R^2	0.8998					
R^2_{adj}	0.8097					

df degrees of freedom

Data were also analyzed to check the normality of the data by constructing a normal probability plot of the residuals. The residuals are normally distributed if the points on the plot follow a straight line [13, 15, 20]. The actual leaching rate is the measured value for a particular run and the predicted value is evaluated from the model. A large value of R^2 does not imply that the regression model is a good one. However, R^2 adj is preferred to use to determine the fit of a regression model, as it does not always increase when variables are added. Good agreement has obtained between the predicted leaching value and the actual experimental value. The R^2 and R^2_{adj} of 0.8998 and 0.8097 respectively, indicate that the proposed model had an adequate approximation to the actual value.

3.4 Effect of variables on antimony leaching

3.5 Effect of pH

It is always a big concern whether pH has any effect on metal contamination leaching from the plastic covers. It has been reported that pH between 6-8 had no effect on antimony leaching from drinking water [21]. However, it is still worth investigating whether metal leaching out could happen low pH as well as very high pH because many fruit juices that are used in daily life, such as orange juices, apple juices etc., may have very low pH e and soup, gravy have very high pH. In order to study the effect of pH on antimony leaching out from plastic cover, pH varied from 2 to 11. Results obtained from these studies were incorporated into the design and plotted in Figures 1 and 2.

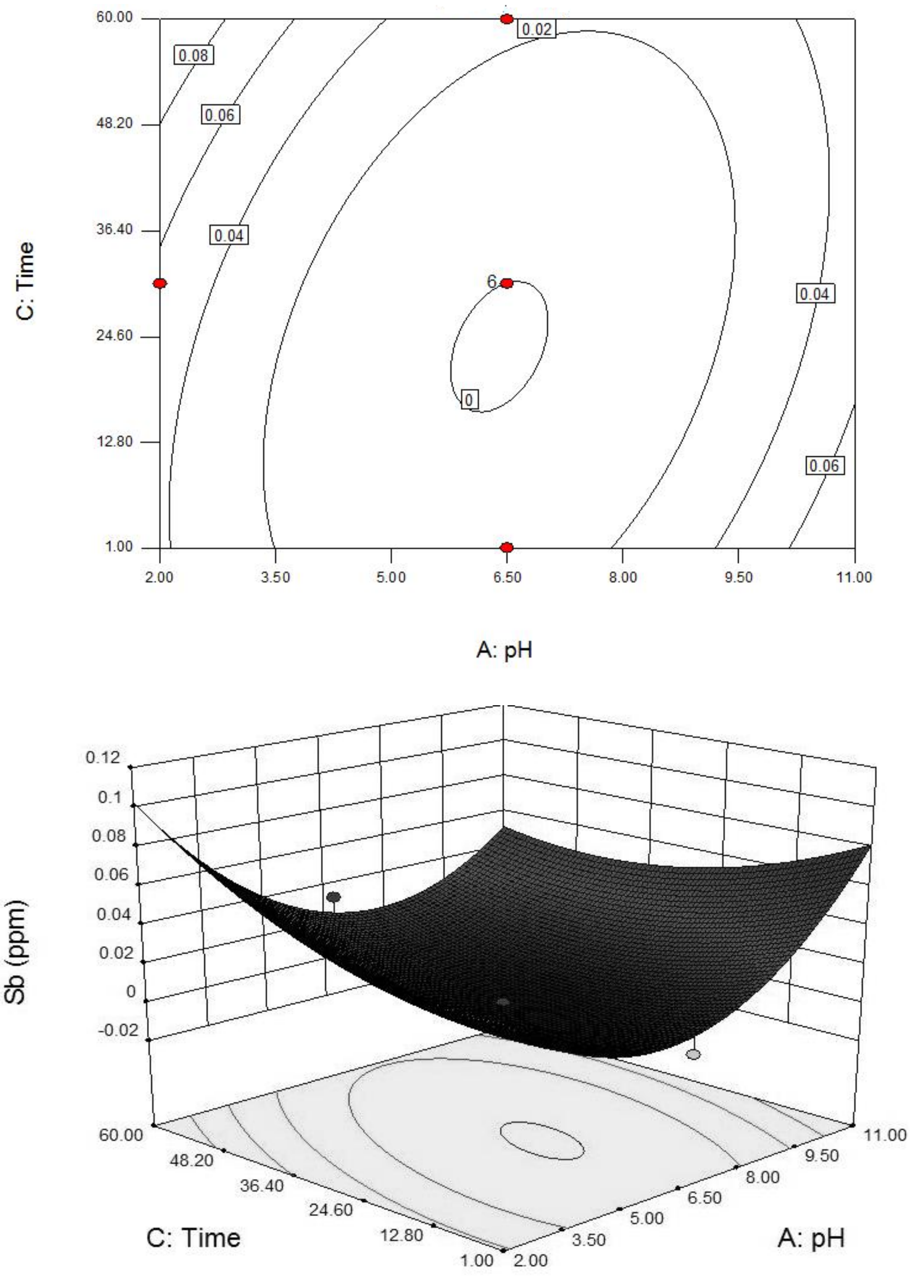


Figure. 1 Response contour and surface plot for the **e**ffect of pH with respect to retention time for antimony leaching from plastic covers

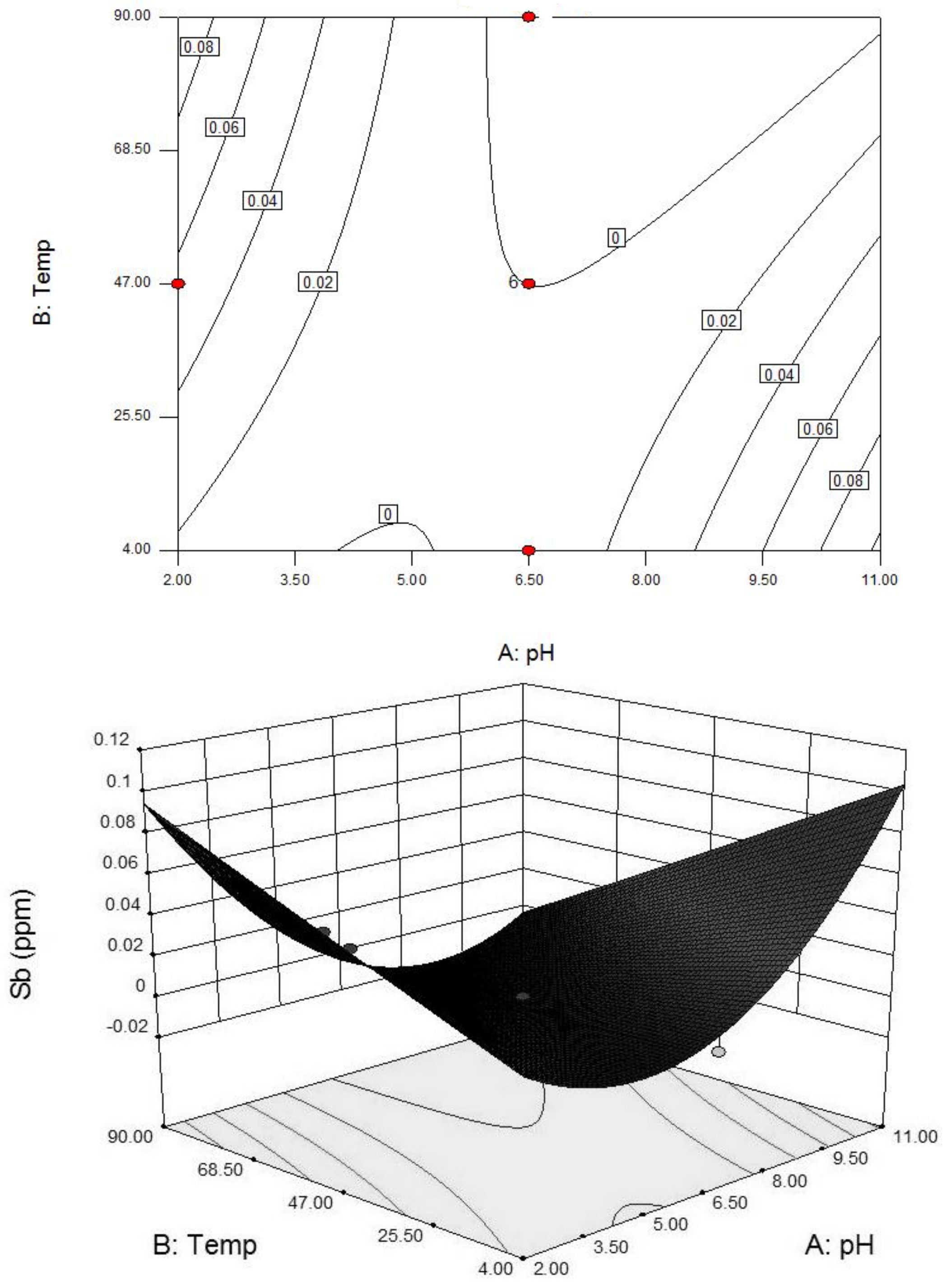
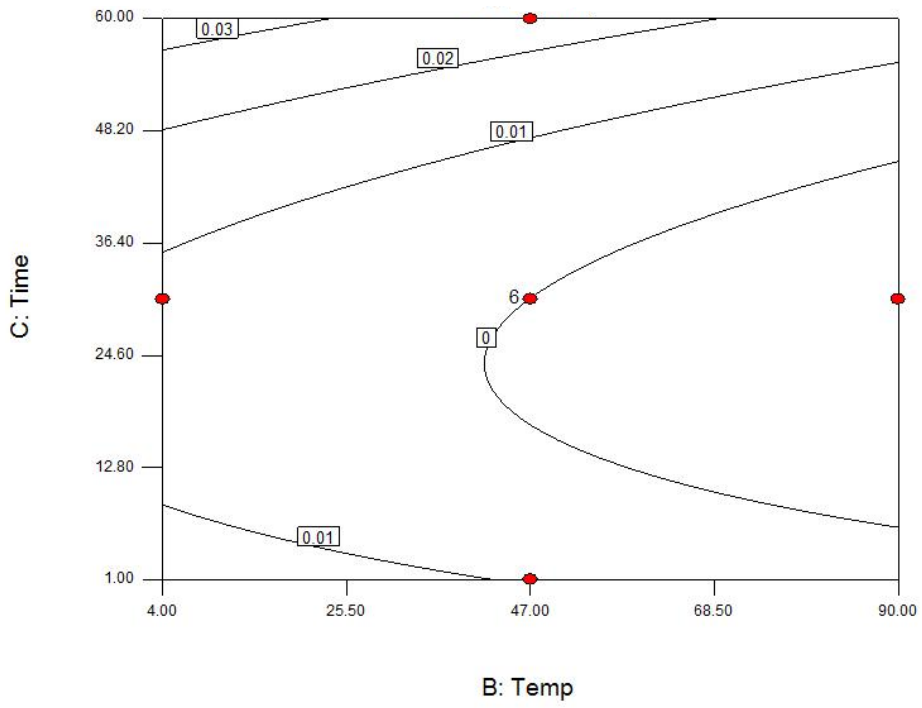


Figure. 2 Response contour and surface plot for the effect of pH with respect to temperature for leaching of antimony from plastic covers

It was found that as the pH increase from acidic to neutral the leachability of antimony concentration decreases. The concentration of antimony increases from neutral to alkaline pH. It concludes that pH is an important variable for antimony leach out from the sample. The pH around 6-7 is the safe level and the leach out almost below detectable limit. Many researchers have investigated that antimony leaching from plastic PET bottles at low pH and the concentration between 0.233 and 1.967 mg/L [2, 21 ,22, 23].

3.6 Effect of Temperature

Temperature was considered as one of the variables because food samples shown the temperature between 4-90^{o}C. Hence the temperature was varied from 4-90^{o}C to find out the leachability of antimony. The results obtained from these experiments are plotted in Figures 2 and 3.



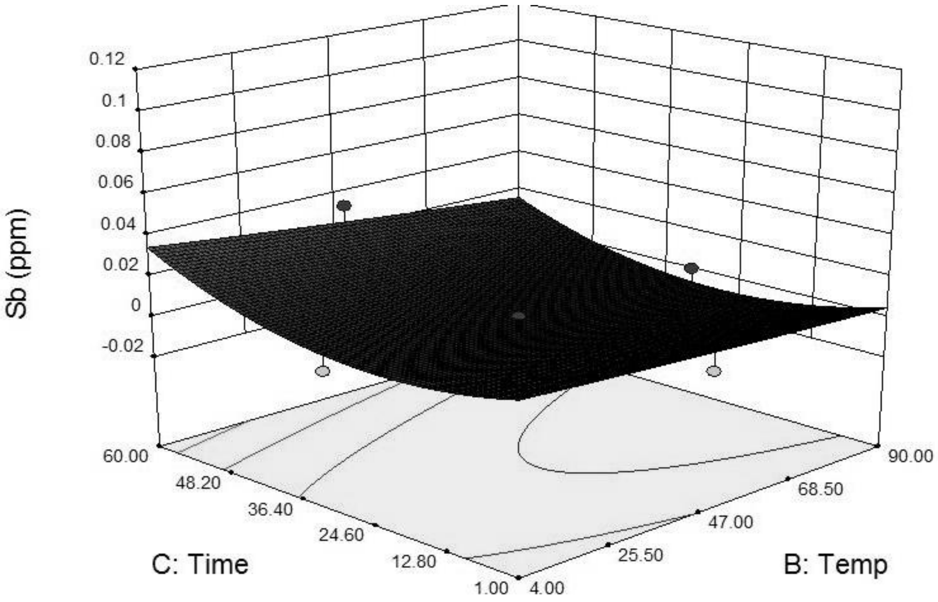


Figure. 3 Response contour and surface plot for the **e**ffect of temperature with respect to retention time for leaching of antimony from plastic covers

At a given time and given pH, varying the temperature from 4 to 90°C shows not much effect on leaching of antimony. However, temperature combined with pH plays an, active role. It was observed that at acidic pH with high temperature as well as alkaline pH with low temperature shows maximum antimony concentration, in turn shows the maximum leachability of antimony. It also observed from the Figure 3 that temperature interact with the retention time shows the effect on leachability of antimony. Low temperature with long retention time shows maximum leachability, when compared with less retention time. Also it was noted that high temperature with less retention time shows less leachability. It was reported that storage of the water in PET bottles at 60 to 85°C resulted in an increasing rate of Sb release into the water [21].

3.7 Effect on Time

The duration of food (or) liquid samples in the covers may vary from sample to sample (or) food to food. Some of the food material may be eaten fast and some cannot be. So retention time in the plastic cover may play a role for leaching of antimony. In order to find the effect of retention time on leachability of antimony, it varied from 1 to 60 minutes. The results obtained are plotted in Figure 3. It was found that at a given pH and Temperature, by varying retention times the leachability of antimony increases. It was also observed that at high pH with less duration and low pH with longer duration shows maximum leachability of antimony. Also observed that increasing retention time with increasing temperature shows maximum leachability. Earlier investigator observed that Sb leaching from PET containers was time and temperature dependent [21].

4. Conclusion

Experiments were conducted to investigate the factors that could potentially influence antimony leaching from low density polyethylene covers. Experiments were designed using a statistical tool response surface methodology. The results obtained from this study reveals that pH, temperature and retention time, interacts with each variable enhancing the leachability of antimony from plastic covers. Acidic pH with high temperature, alkaline pH with low temperature shows maximum leachability of antimony from low density polyethylene covers. It is concluded that low density polyethylene covers should be avoided for storing (or) carrying the food samples because the leaching of antimony was confirmed.

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