Comparative study of two modeling approaches for predicting heavy metals contaminant migration from polyethylene bags

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Abstract: Plasto-Foam brand, medium size of 30 mm thickness (black and green) commonly used polyethylene bags for preparing foods were selected from those available in local markets. The polyethylene bag samples were crushed into pieces, ashed and then acid digested to determine the concentrations of heavy metals selected (Pb, Cr, Co and Cd) using Atomic Absorption spectrophotometer. All the polyethylene samples were tested positive for heavy metals. Concentrations of heavy metals in polyethylene bags ranged from 1080 ppm to 1725 ppm, 76 ppm to 112 ppm, 35 ppm to 52 ppm, 18 ppm to 31 ppm for Pb, Cd, Cr and Co, respectively. Forty-eight posho (Ugali) samples were prepared and wrapped in these polyethylene bags and migration studies were carried out at 65°C and 80 ℃. The experimental data obtained were then compared to the modeled data using the models developed by Baner et al., and Limm and Hollifield to determine which model was a better estimator. Model fitting was done based on Non-linear least square analysis using Microsoft EXCEL 2003. Diffusion and partition coefficients both between food and the contact material were also obtained by fitting experimental data to the model equation. The modeling approaching could best describe the experimental data of the measured contaminants. The study revealed that all polyethylene bags showed highest contaminant concentration (above USFDA limit) of Pb, Cd, Cr and Co, respectively confirming the potential health risk to individuals if continuously eat food thermally prepared in polyethylene bags.

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1 Introduction

In Uganda, different communities have different traditionally wrapped and prepared foods in banana leaves and the trend that polyethylene bags replacing banana leaves is growing gradually. The increase of the use of polyethylene bags is due to their high thermo-sealability and good water resistance, depending on which commercial food vendors usually serve a hot meal without spending a lot on energy. However, very little attention has been focused on the potential risk of plastic bag contaminants bioaccumulation to human health. A number of studies[2-5] have found that polyethylene materials contain a wide range of potential migrants, for example, residues from polymerization process, degradation compounds and additives including Ni, Cu, Pb, Cr and Cd. These metals are cumulative poison which can bring possibility of bioaccumulation in a man even when exposed to low concentrations continuously. Bananas wrapped in green banana leaves

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and polyethylene bags are shown in Figure 1.

Figure 1 Green bananas (*matooke*) prepared in banana leaves and polyethylene bags

Hence, it is necessary to know how much of these compounds that we expose ourselves to them when we consume food prepared, wrapped and stored in polyethylene bags. However, due to low concentrations of migrated substances found in the food stuff and the complexity of the food matrix, analysis of these migrants in the food stuff or stimulant is very expensive and time consuming. In an effort to overcome these inherent difficulties associated with migration tests, researchers have built predictive models to estimate the extent of migration. In this study, we evaluate two modeling approaches that describe the migration process of contaminants from the food contact material (polyethylene) into solid food under different time temperature combinations. This will therefore find the best modeling approach to describe the migration from food contact materials into foodstuff, and will also provide avail crucial information for regulatory authorities to set up guide-lines regarding the use of food contact materials containing high risk contaminants.

2 Materials and methods

2.1 Determination of amount of heavy metals in polyethylene bags

Plasto-Foam brand, medium size of 30 mm thickness polyethylene bags commonly used for wrapping foodstuffs (black and green) were crushed into pieces and placed in large silica crucibles. The pieces were then charred on a hot plate until the smoking stopped, and then converted into ashes in a furnace. The crucible was taken out of the furnace and cooled, after cooling, the sample was homogenized and 1 g of the sample was placed in separate silica crucible for acid digestion. Analytical grade HNO_3 (65%) and H_2O_2 (30%) were used for digestion in an open container. The digest was then filtered through a filter paper to remove the insoluble particles and brought to a final volume of 50 mL with de-ionized water. The resultant solution was then analyzed using atomic absorption spectrophometer to identify the content of heavy metals.

2.2 Experimental determination of heavy metal migrated into food

NaOH solution (0.1 mol/L) was prepared by dissolving sodium hydroxide pellets in water. This solution was used together with 95% ethanol to sterilize all the equipment and apparatus used in this study. De-mineralized water was used to prepare all solutions. Posho was then wrapped in a black polyethylene bags (Plasto-Foam brand, medium size of 30 mm thickness commonly used for wrapping foodstuffs in local markets) to prevent heat loss which always been done in the field conditions. Forty-eight samples were prepared and placed in three well-stirred thermo-stated water bath (Grant instruments, Cambridge England), each pre-set at temperatures of 65℃ and 80℃. Tests were then done at intervals of 1 h after cooling to determine the amounts of heavy metals that had migrated into posho. At each test, the amounts of heavy metals migrated were determined by the selected models. This was then compared to levels determined experimentally, obtained by drying the samples (contaminated food) in the oven for 24 h, and grounded into a uniform powder to increase surface area for easy digestion and homogenization. The samples were then weighed, digested with analytical grade HNO_3 to enhance decomposition. De-ionized water was added to make up the volume to 25 mL, and the atomic absorption spectrophotometer (Perkin-Elmer 2380) was calibrated. The samples were then aspirated to analyze the concentration of heavy metals in the samples. This was done also to determine the baseline concentration of the heavy metals in the food. The sample (posho) was analyzed up to a maximum of 5 h.

2.3 Evaluation of available models

Traditionally, migration data were obtained from migration tests performed using food simulating liquids such as water, edible oils, and ethanol-water solutions. However, these efforts are quite time consuming and expensive. In an effort to overcome these inherent difficulties associated with migration tests, researchers suggested the use of predictive migration model to estimate the extent of migration. In general, studies have shown that migration is controlled by diffusion through the polymer according to Fick's law and follows Arrhenius behavior with temperature. Hence the extent of migration could be predicted at least theoretically, quite a number of mathematical models have been established for such purposes. The simplest model was developed by Crank[6] to predict the extent of migration from polymer into the extraction solvent. The available models and their previous use application scenarios are summarized in Table 1.

Table 1 Migration models for heavy metals contaminant migration from plastics

Model No.	Expression	Description
1	$M_t = 2C_{po}\sqrt{\frac{D_p t}{\pi}}$	Developed by Till et al.[7]: Model assumes the solvent is well mixed and never saturates with the migrant.
2	$C_{F,t} = \frac{A}{M_F}\cdot\rho_p 2C_{po}\sqrt{D_p}$	Developed by Baner et al.[1]: The results indicated a tendency of over estimation of actual migration.
3	$M_t = 2C_{po}\sqrt{\frac{D_p t}{\pi}}\cdot\left[\frac{\beta}{(1+\beta)}\right]\beta = K\sqrt{\frac{D_s}{D_p}}$	Developed by Till et al.[7]: Results from the model failed to agree well with the levels actually determined.
4	$M_t = \frac{\sqrt[2]{D_s t\cdot KC_{po}}}{1+K\propto}\left[\frac{1}{\sqrt{\Pi}} - ierfc\left(\frac{L}{2\sqrt{D_p t}}\right)\right]$	Developed by Limm and Hollifield[2]: Final equation is complex, but predicted results agreed with the actual migrant levels within 22%.

The model developed by Crank[6] was not adopted because it was developed on the assumption that the solvent is well mixed and never saturates with the migrant, and according to Limm and Hollifield[2], results from model developed by Till et al.[7] failed to agree with levels actually determined.

Mathematical models used in this study were model 2 and model 3 in Table 1, and they are two widely accepted models identified through literature review and were then simulated using experimentally determined data. Model fitting was carried out using Microsoft EXCEL 2003 to evaluate which modeling approach best fits the experimentally determined data.

2.4 Diffusion coefficients and partition coefficients

Diffusion coefficients for food/polymer D_p and D_s as well as the partition coefficient K for the posho polymer system were solved by fitting the experimental data to the model using nonlinear square analysis (Microsoft Excel 2003). Because D_s and K are two independent parameters suggested in the above models, the value of K had to be estimated by other means in order to solve the value of D_s. The partition coefficient K was estimated by computing the ratio of surface concentration in both phases after equilibrium (Equation (1)):

$$K = \frac{[Plast.]_{food}}{[Plast.]_{pack}} = \frac{[M_t]_{eqm}}{C_o.L - [M_t]_{eqm}} \tag{1}$$

The partition coefficient K and the diffusion coefficient D_p and D_s system were then calculated.

3 Results and discussion

3.1 Analysis of heavy metals in polyethylene bags

The results for the heavy metal concentration in the low density polyethylene bag samples are presented in Table 2. Samples 1-4 represents black polyethylene bags from different bags of Plasto-Foam brand and Samples 5-8 represent green polyethylene bags from different bags of Plasto-Foam brand.

Table 2 Mean (SD) values of heavy metal concentration in polyethylene samples

Black samples	Pb/ppm	Cd/ppm	Cr/ppm	Co/ppm
1	1333±60.83	88±23.45	35±15.4	25±0.180
2	1245±42.14	85±16.23	36±12.50	28±14.77
3	1080±43.16	78.23±28	37±12.12	23±18.01
4	1125±47.82	76±22.43	36±28.72	18±13.24
Green samples	Pb/ppm	Cd/ppm	Cr/ppm	Co/ppm
5	1725±62.78	112±35.62	45±16.10	30±14.04
6	1545±49.23	120±25.34	48±29.12	32±14.40
7	1600±50.33	98±14.23	50±19.41	28±0.000
8	1324±41.12	100±0.000	52±14.31	31±14.42

All the low density polyethylene bag samples analyzed were found containing Pb, Cd, Cr and Co in varying concentration levels. The results ranged from 1725-1080 ppm, 120-76 ppm, 50-36 ppm, 32-18 ppm for Pb, Cd, Cr and Co, respectively. The results are comparable to most of the results presented by Omolaoye et al.[8] where plastic toys were analyzed for heavy metals with the maximum mean concentrations for Pb (1445 ppm), Cd (373.33 ppm), Cr (191.67 ppm) and Co (73.33 ppm), and the observed results of Pb (1725 ppm), Cd (120 ppm), Cr (50 ppm) and Co (32 ppm) in this study are a little higher. Though with high difference in the means between the two studies, mean values of this study showed little variation than [8] and this might due to the similarity of the samples analyzed in both studies. Furthermore, a study conducted by Ogunfowokan et al.[9] showed higher concentrations of Pb and Cd in some Nigerian confection wrappers, which consisted with results obtained in this study. Generally, the green polyethylene bag samples showed higher concentrations of all the chemical contaminants (Pb, Cd, Cr and Co), and analysis of variance ANOVA showed that these were significantly (p>0.05) from the black samples while the concentration differences between different samples (green & black) were not significantly (p<0.05). The difference between green and black samples might due to the difference of the formulations used during their manufacture. The highest concentration in both green and black polyethylene bag samples was Pb followed by Cd, Cr and Co, respectively.

3.2 Correlation analysis

A correlation analysis for heavy metals in both samples was done to find out if some metals were interrelated with each other and the results are presented in Table 3. There was a strong positive correlation at p<0.1 between Pb, Cd, Cr and Co. This consists with the results of Omolaoye et al.[8] which studied correlation among heavy metals in toys while it's in contrast with the research results of Ogunfowokan et al.[9] that obtained a negative correlation between the concentration of Pb and Cd in some Nigerian confection wrappers.

The correlation analysis results also indicated a significant influence of one metal on another. There is a possibility of metals coming from the same source such as stabilizers and plasticizers used in the production of polyethylene bags to achieve specific objectives. Therefore removal of one heavy metal may affect the performance of another. Because the correlation coefficient between Pb, Cd, Cr and Co in the polyethylene samples was statistically significant (0.985, 0.991, 0.958), it can be indicated that Pb, Cd, Cr and Co are used as stabilizers in polyethylene bags.

Table 3 Correlations among heavy metals in polyethylene bags

Sample	Pb	Cd	Cr	Co
Pb	1			
Cd	0.985	1		
Cr	0.991	0.977	1	
Co	0.958	0.954	0.971	1

Note: Correlation is significant at the 0.1 level (2-tailed).

3.3 Determination of Diffusion and Partition coefficients (D_p, D_s and K)

Experimental data were fitted to the two proposed models based on nonlinear least square analysis using Microsoft EXCEL 2003. The diffusion and partition coefficients (Dp, Ds and K) were also solved by fitting the experimental data to the two models using a mathematical optimization technique in EXCEL 2003. The partition and diffusion coefficients obtained for the mathematical optimization technique showed some general trends. The diffusion coefficients of the contaminants (Pb, Cd, Cr and Co) in the polymer (Dp) varied only slightly but were much dependent on the storage temperature. These diffusion coefficients (Dp) obtained from the mathematical optimization technique in EXCEL 2003 were all consistent, at least to the same order of magnitude with previous findings by [10]. The diffusion coefficients of the contaminants (Pb, Cd, Cr and Co) in the food (Ds) were also mainly dependent on the storage temperature. Although the average values for Dp, Ds and K reported above are only estimated values, they are good enough for making predictions in certain food/polymer systems. The average K and diffusion coefficients were determined in the present study at two storage temperatures.

3.4 Data fitting using model 2

The experimental and predicted amounts of Pb from polyethylene bags into food according to Baner et al.[1] is shown in Table 4.

Table 4a Experimental and predicted amounts of Pb from polyethylene bags into food at 65°C

Time/h	Experiment/ppm	Predicted value/ppm	Deviation/%
2	300	277	−7.7
3	400	416	+4.0
4	560	554	−1.1
5	692	680	−1.8

Note: Sample: posho (black polyethylene); D_p = 1.3×10^{-12} cm^2/s; D_s = 2.7×10^{-12} cm^2/s; L = 0.002 cm; C_o = 1333 ppm.

Table 4b Experimental and predicted amounts of Pb from polyethylene bags into food at 80°C

Time/h	Experiment/ppm	Predicted value/ppm	Deviation/%
2	456	450	−1.3
3	498	480	−3.8
4	690	694	+0.6
5	720	715	−0.7

Note: Sample: posho (black polyethylene); D_p = 4.8×10^{-12} cm^2/s; D_s = 3.7×10^{-12} cm^2/s; L = 0.002 cm; C_o = 1333 ppm.

The graphical representation of the experimental and predicted values using model 2 showed an initial rapid migration of the contaminants followed by a slow increase. The model further illustrated that contaminant migration increased with increase in contact time. This concurred with Fick's first law of diffusion upon which the model was developed, since a concentration gradient exists between the polyethylene bag and the posho, diffusion takes place and creates another concentration gradient within the posho cube leading to a diffusive flux that is time dependent.

The amounts of Pb migrated at 65 ℃ and 80 ℃ for the posho/polyethylene system were estimated using model 2 and the results are shown in Tables 5 and 6 where the experimental values were also included for comparison. It can be seen that the results for Pb migration are within 8% of the experimental values. In fact, the same estimates were made for a total of 45 samples out of which 36 had an absolute deviation of less than 10% from the respective experimental values.

Table 5 Experimental and predicted values for Pb predicted by Limm and Hollifield at 65°C

Time/h	Experiment/ppm	Predicted value/ppm	Deviation/%
2	300	290	−3.3
3	400	480	+20.0
4	560	600	+7.1
5	680	720	+5.9

Note: Sample: posho (black Polyethylene); D_p = 1.3×10^{-12} cm^2/s; D_s = 1.6×10^{-11} cm^2/s; L = 0.002 cm; C_o = 1333 ppm.

Table 6 Experimental and predicted values for Pb predicted by Limm and Hollifield at 80°C

Time/h	Experiment/ppm	Predicted value/ppm	Deviation/%
2	456	508	+11.4
3	570	600	+5.3
4	660	720	+10.2
5	720	810	+12.5

Note: Sample: posho (black Polyethylene); D_p = 1.4×10-11 cm^2/s; D_s = 1.6×10^{-11} cm^2/s; L = 0.002 cm; C_o = 1333 ppm.

3.5 Discussion of results

As expected, both models predicted increase of contaminant migration with the extension of contact time. And both models showed that there was a slow increase followed by rapid migration of the contaminants. This is because temperatures were initially below the glass transition temperature (T_g) of polymer. Below T_g, the polymer molecules are stiff (glassy state) and the chance for a migrant contaminant to find a sufficiently large hole is limited. Above T_g, however, the polymer molecules are highly flexible (rubbery state), which makes the chance of migration higher[11-13]. From the obtained results, it can be seen that the tested models of 2 and 3 in Table 1 are good estimators for experimental data. Since predicted data for both models were predicted data for both models were between 20% of the experimental data. It indicated that the experimental migrations were not significantly different from the modeled migrations. From these observations, the study has thus further demonstrated that modeling could be used as a reliable tool to predict contaminant migration from polymers. This was also supported by the degree of association between experimental and modeled contaminant migration which showed (r>0.90) for model 2 and (r>0.70) for model 3, for Pb and Cd contaminant migration[14-16].

However, graphs of experimental migration for model 3 showed that the equation tended to overestimate migration values with too many false positives. It can be concluded that model 2 is a better estimator for experimental values than model 3[17-20].

4 Conclusions

There are quite a number of plastics that are used for packaging and thermal processing of different foods in

Uganda's plastic market. The most preferred polyethylene bag in regard to thermal processing is Plasto-Foam brand, medium size of 30 mm thickness. Laboratory analysis showed that Plasto-Foam brand black polyethylene bag contains heavy metals (Pb, Cd, Co and Cr) in varying concentrations with the concentration of these heavy metals being higher than in green polyethylene bags. This was mainly attributed to the different formulations used during manufacture. There are not any enforceable standard for the total content of Pb, Cd, Cr and Co in polyethylene bags in Uganda. There are scarcely polyethylene manufacturer that produced plastic bags based on prescriptive procedures of foreign standards. This study showed that modeling as an alternative tool could be used to predict contaminant migration since predicted values were within 20% errors compared with experimental values. The study further showed that the model 2 approach was a better estimator of migration values when compared to model 3 as seen from the root mean square and the degree of association between experimental and predicted values.

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