# Modeling of Silver Migration from Polyethylene Nanocomposite Packaging into a Food Model System Using Response Surface Methodology

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***Abstract*—The objective of this study is to predict the variation in silver migration as a function of silver concentration, temperature and migration duration using polynomial model. Silver nanoparticles were produced via chemical reduction by using short-chain polyethylene glycol. Silver nanocomposites were prepared via two methods, namely, melt-blending and layer-by-layer self-assembling deposition. Surface response methodology was employed to investigate the effects of processing conditions, including processing method (melt blending and layer-by-layer coating) and silver nanoparticles concentration as well as migration conditions, including temperature, duration of contact, and contact media (water, 3% acetic acid, 10% ethanol, and apple juice), on the silver-ion migration of silver nanocomposites. Second-order polynomial regression models expressing silver-ion migrations as functions of the main numerical variables were significantly fitted (p<0.05) with a high coefficient of determination (R2>0.90). Migration time was considered as the most significant variable that affects silver-ion migration from silver nanocomposites.**

***Index Terms*—silver migration, modeling, response surface, polyethylene nanocomposite**

## I. Introduction

Polymer nanocomposites are advanced functional materials composed of nanoparticles incorporated into a polymer matrix or coated onto a polymer surface. Polymer nanocomposites represent a developing area of interest because they provide improved mechanical and barrier properties, relatively high transparency and recyclability, enhanced surface characteristics, and low density compared with conventional polymer composites [1]. Among the different nanoparticles that have been incorporated into polymers, silver nanoparticles have attracted considerable attention because of their unusual physicochemical characteristics, such as catalytic activity, optical, magnetic, and electronic properties, high thermal stability, and antimicrobial activity [2]. Silver nanoparticles release monovalent silver ions in the presence of oxygen and water [3] and react with cell membrane proteins by replacing the hydrogen cation of thiol groups, which results in protein inactivation. As such, the membrane permeability is changed, thereby causing cell death [2], [4], [5]. Thus, silver nanocomposites (polymer composites containing silver nanoparticles) have attracted significant interest in the medical industry, applied microbiology, and active food packaging. Silver nanocomposites employed as antimicrobial materials have been fabricated via different methods on different polymer matrixes, such as plasma depositing on polyethylene oxide [6], ion implantation on polyethylene terephthalate [7], and polyvinyl chloride and polyethylene [8], melt processing on polyamide [3], and polyethylene [9], layer-by-layer (LBL) deposition on nylon fiber [10] and polyethylene [11], solution casting on poly lactic acid [12], and organic-inorganic hybrid coating on low-density polyethylene (LDPE) [13].

Despite the advantages of silver nanocomposites, the increase in the use of antimicrobial silver nanostructures has been the subject of concern with regard to environmental and health issues. Silver nanoparticles have been shown to be toxic to cells, and they can change the normal function of mitochondria, increase membrane permeability, and generate reactive oxygen species [14]. Migration, which is defined as the mass transfer of a component from a packaging material to foodstuff, has been known as an important safety concern of food packaging polymers [15]. To design effective silver nanocomposite as packaging materials with reduced side effects and to achieve precise risk assessment, evaluating the migration profile is essential [16]. Requirements for migration test are given by the European Union (EU) and Food and Drug Administration (FDA) regulations for food contact materials (FCMs) (EU Directives 82/711/EEC and 85/572 EEC). Migration tests consist of the contact between the plastic sample and several established liquid simulants that mimic food behavior. Legislations voted that migration tests should be performed at controlled conditions, in which migration

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level results are equal or higher than those obtained at real storage conditions. Such tests are known as “worst case” migration tests [17]. Several studies have investigated silver migration from silver polyethylene and polyamide nanocomposite [3], [14]; however, reports about the effects of processing and migration conditions on silver migration from silver nanocomposite packaging polymers are insufficient. Moreover, LDPE is a common food packaging because of its acceptable flexibility, transparency, easy processability, thermal stability, recyclability, and inexpensive properties [18]; hence, investigating the migration aspects of silver LDPE nanocomposite is important.

Different factors, such as the processing conditions of silver nanocomposites and migration conditions, affect the silver migration of silver nanocomposites. Response surface methodology (RSM) is a tool used to analyze the effect of a selected response of independent variables. RSM is a useful approach for analyzing industrial processes and has been widely used in industries and engineering research [19], [20]. The objectives of the current study were as follows: (i) to investigate the effects of processing conditions of silver nanocomposite, including procedure method (melt blending and LBL deposition) and silver concentration in the nanocomposites (low, medium, and high levels) as well as migration conditions, including temperature (4 and 40 ℃), contact duration (1, 3, 5, 7, 10, 15, 20, 25, and 30 days), and contact media (water, 3% acetic acid, 10% ethanol, and apple juice), on the silver-ion migration of silver LDPE nanocomposite; and (ii) to predict the variation in silver migration as a function of independent variables with the use of a polynomial model.

## II. Materials and Methods

### A. Silver Nanocomposite Packaging Preparation

Silver nanoparticles were prepared via the method described by Popa *et al.* [21]. It was described in our previous paper in detail [22]. Briefly, silver colloid was produced by chemical reduction using short chain poly ethylene glycol (PEG200) by stirring for 1 hour at room temperature (25 ℃). Silver nanoparticles were used for both melt blending and LBL deposition techniques. For the melt blending method, the colloid washed with acetone followed by ultra-centrifugation at 1400 rpm and then vacuum dried at 2 bar. For the LBL deposition method, the silver colloid was used directly without further modification.

LDPE nanocomposites were produced via the two methods of melt blending and LBL deposition, following the procedures described in our previous papers [9], [11], [22]. In melt blending, the silver nanoparticles were incorporated into the LDPE pellets by using a melt blender at three concentration levels (0.1%, 0.5%, and 5%). PEG was used as compatibilizer. In the LBL deposition method, LDPE films were coated by either anionic silver colloid dispersion containing PEG-capped silver nanoparticles or cationic chitosan (1Mm) periodically. The numbers of layers were of 2, 12, and 20. Finally the real silver content of nanocomposites was determined by atomic absorption spectrometry following sample preparation by mineralization in a furnace (600 ℃) (Table I).

TABLE I. Silver Nanocomposite Samples Used for Migration Test

| Silver nanocomposites | Level of silver nanoparticles addition (g/100 g) | Numbers of chitosan/silver nanoparticles layers | Real silver concentration mg kg$^{-1}$ [a] |
|---|---|---|---|
| Melt blended I | 0.1 | - | 1.19 |
| Melt blended II | o.5 | - | 6.69 |
| Melt blended III | 5 | - | 22.64 |
| LBL deposited I | - | 2 | 0.44 |
| LBL deposited II | - | 12 | 4.71 |
| LBL deposited III | - | 20 | 16.28 |

[a] Values are obtained by at least three replications

### B. Migration Test

The silver nanocomposites (melt-blended and LBL-deposited) were immersed in liquid media that were the official EU food simulants (water, 3% acetic acid, and 10% ethanol) and apple juice (Sunkist Growers, Inc., Malaysia) as the real food product. To investigate the silver-ion release from the silver LDPE nanocomposites, eight specimens (1.5cm×1.5cm) with 18 cm$^2$ total surface area were immersed in 15mL of liquid contact media and stored at 4 ℃ and 40 ℃. At the defined times, the immersion liquid was exchanged completely (day 1, 3, 5, 7, 10, 15, 20, 25, and 30). The concentration of silver ions in the immersion liquids was measured using an atomic absorption spectrometer (Perkin Elmer, 3300, USA). The silver-ion release from the silver nanocomposites into the food simulants and apple juice was determined within 30 days at two temperatures (4 ℃ and 40 ℃).

### C. Experimental Design

Considering the non-numeric feature of production method and contact media factors, the effects of three variables, namely, time ($x_1$), temperature ($x_2$), and silver concentration ($x_3$), on the silver-ion release of melt-blended and LBL-deposited nanocomposites in each contact medium (distilled water, 3% acetic acid, 10% ethanol, and apple juice) were determined via RSM. The main and combined effects of these variables were investigated and the variations in silver-ion migration as a function of numeric independent variables were determined. The generalized polynomial model proposed for predicting the response variables is given below:

$$Y_i=\beta_0+\beta_1 x_1+\beta_2 x_2+\beta_3 x_3+\beta_{11} x_1^2+\beta_{22} x_2^2+\beta_{33} x_3^2+\beta_{12} x_1 x_2 +\beta_{13} x_1 x_3+\beta_{23} x_2 x_3 \quad (1)$$

where $Y_i$ is the predicted response, $\beta_0$ is an offset term, $\beta_1$, $\beta_2$, and $\beta_3$ are the regression coefficients for the main variable effects, $\beta_{11}$, $\beta_{22}$, and $\beta_{33}$ are quadratic effects, and $\beta_{12}$, $\beta_{13}$, and $\beta_{23}$ are interaction effects of the independent variables. The significance of the estimated regression coefficient for each response variable was assessed by using the F ratio at p=0.05. The adequacy of the RSM models was determined via coefficient-of-determination ($R^2$) analysis. Variables with larger F ratios and smaller p values were considered more significant. The experimental design matrix and data analysis were performed using Minitab 14.0 (Minitab Inc., PA, USA).

## III. Results and Discussion

### A. Silver-Ion Migration into Food Simulants

Silver-ion migration from the silver nanocomposites (melt-blended and LBL-deposited) into distilled water, 3% acetic acid (w/v), 10% ethanol (w/v), and apple juice stored at 4 ℃ and 40 ℃ within 30 days were analyzed via atomic absorption spectroscopy. The results showed that silver-ion migration from nanocomposites into official EU food simulants and apple juice was less than the allowable concentration (10mg kg-1) over 30 days in all of the cases with regard to the cytotoxicity level of silver ion for human cells [3]. RSM enables the evaluation of the effects of variables on silver-ion migration and provides a polynomial model to predict the silver-ion release as a function of numeric variables. The RSM model was fitted for silver-ion migration (Yi) of melt-blended and LBL-deposited nanocomposites into each of the contact medium (distilled water, 3% acetic acid, 10% ethanol, and apple juice) as a function of linear, quadratic, and interaction effects of time (x1), temperature (x2), and silver concentration (x3) variables. The regression coefficients of the three independent variables, along with the corresponding R2 and adjusted R2, are presented in Table II. The significance of each term in terms of the p value and F ratio is shown in Table III. As shown in Table II, a high coefficient of determination (R2>0.93) was obtained for all of the polynomial regression models; R2 should be ≥0.80 for a good fitness of a model [23]. Thus, a variation of ≥93% in silver ion released from melt-blended and LBL-deposited nanocomposites into food simulants and apple juice could be represented by a second-order polynomial regression equation. Therefore, the polynomial model was adjusted for silver-ion release as a function of time, temperature, and silver concentration in the polymer.

The main and quadratic effects of time, temperature, and silver concentration in the polymer had significant effects ($p<0.05$) on silver-ion release from nanocomposites into food simulants and apple juice, except for the quadratic effect of time. The main effects of the independent variables were found to be more effective than the square and interaction effects with regard to regression coefficients (Table II) and F-values (Table III).

The positive sign of the main coefficient (β1) and the negative sign of quadratic coefficients (β11) of time indicated that at low levels of time, the increase in time results in an increase in migration. By contrast, after an extended period of time (days), the silver migration decreases. This result is consistent with that by Zapata *et al.* [24], in which silver-ion release from silver polyethylene nanocomposites decreased after 30 days and became constant after day 70. They attributed this phenomenon to the difficulty of water absorption to non-polar polyethylene film [24].

The temperature had a significant effect ($p<0.05$) on silver-ion release from either melt-blended or LBL-deposited nanocomposites into food simulants and apple juice; a higher storage temperature resulted in a higher silver-ion migration. Migration is accelerated by heat, similar to other chemical and physical processes. Silva *et al.* [17] found a significant increase in migration of diphenylbutadiene from LDPE films when the temperature was increased from 5 ℃ to 25 ℃. The increase in temperature enhanced the silver-ion release from LBL-deposited nanocomposites compared with that from melt blended composites on the basis of the regression coefficients (Table II) and F ratio (Table III). The regression coefficients of temperature variables (β2) are more in 3% acetic acid compared to other food simulants and apple juice either from melt-blended or LBL-deposited nanocomposites (Table II). Song *et al.* (2011) showed that silver-ion migration from polyethylene nanocomposites increased with increasing temperature in 3% acetic acid, but the silver migration level is unaffected by the increase in temperature in 95% ethanol food simulant [14]. Thus, the effect of temperature on the silver-ion release was more significant in LBL-deposited nanocomposites and in 3% acetic acid food simulant.

The main coefficients of silver concentration were positive, and the linear effect was significant ($p<0.05$) in all of the cases. As such, increasing the silver concentration in the nanocomposite resulted in more silver-ion release; however, the quadratic effects of silver concentration in the polymers were insignificant ($p>0.05$) for all of the fabricated polymers in food simulants and apple juice except for LBL-deposited nanocomposites in distilled water. This finding revealed that a significantly high concentration of silver in the polymer has an insignificant effect on silver migration, which could be attributed to silver dynamic equilibrium between the liquid and the polymer at a high silver concentration in the polymer. Based on the regression coefficients (Table II), the linear effect of temperature is less than the effects of time and silver concentration. Silver-ion release from both melt-blended and LBL deposited nanocomposites is influenced by silver concentration and time of contact more than temperature. In addition, the effects of time, silver concentration, and temperature on silver-ion release were found to be the same in 3% acetic acid, 10% alcohol, and apple juice. However, such effects varied in distilled water in all of the nanocomposite films. The silver concentration in the polymer can be considered as the most effective variable in distilled water, whereas time is the most effective variable that influence silver-ion migration in 3% acetic acid, 10% alcohol, and apple juice.

Moreover, in melt-blended nanocomposites, the linear, quadratic, and interaction effects of the independent variables were the most significant in 3% acetic acid. By contrast, in LBL-deposited nanocomposites, the effects of time, temperature, and silver concentration variations (linear, quadratic and interaction) were most significant in 10% ethanol. Therefore, silver-ion migration from melt-blended nanocomposite into acid food simulants is more sensitive to time, temperature, and silver concentration variations, whereas for LBL-deposited nanocomposites, alkaline food simulants are more susceptible to the independent variables.

TABLE II. REGRESSION COEFFICIENTS, $R^2$ AND ADJUSTED $R^2$ FOR RESPONSE SURFACE MODEL

| Regression coefficients | Melt blended | | | | LBL deposited | | | |
|---|---|---|---|---|---|---|---|---|
| | Distilled water | Acetic acid 3% | Alcohol 10% | Apple juice | Distilled water | Acetic acid 3% | Alcohol 10% | Apple juice |
| $\beta_0$ | 0.49555 | 0.56868 | 0.53425 | 0.56413 | 0.74594 | 0.98051 | 0.78002 | 0.73439 |
| $\beta_1$ | 0.13460 | 0.18201 | 0.15379 | 0.18059 | 0.19396 | 0.29013 | 0.22433 | 0.23710 |
| $\beta_2$ | 0.06227 | 0.08515 | 0.07726 | 0.06932 | 0.02781 | 0.13173 | 0.09570 | 0.10348 |
| $\beta_3$ | 0.13484 | 0.13777 | 0.13675 | 0.12602 | 0.20843 | 0.17694 | 0.19826 | 0.07809 |
| $\beta_{11}$ | -0.11929 | -0.14247 | -0.13304 | -0.14111 | -0.20110 | -0.24427 | -0.18044 | -0.16599 |
| $\beta_{22}$ | - | - | - | - | - | - | - | - |
| $\beta_{33}$ | 0.01804 | 0.02438 | 0.01528 | 0.00428 | 0.04114 | -0.01975 | 0.01058 | -0.03086 |
| $\beta_{12}$ | 0.03039 | 0.04435 | 0.03620 | 0.03295 | 0.02519 | 0.08098 | 0.03399 | 0.05389 |
| $\beta_{13}$ | 0.09682 | 0.09893 | 0.09896 | 0.10600 | 0.09974 | 0.06275 | 0.09227 | 0.07163 |
| $\beta_{23}$ | 0.03388 | 0.03329 | 0.02715 | 0.00204 | -0.04892 | -0.03619 | 0.03386 | 0.02075 |
| $R^2$ | 0.949 | 0.961 | 0.957 | 0.961 | 0.944 | 0.941 | 0.968 | 0.955 |
| $R^2$ (adj.) | 0.940 | 0.954 | 0.950 | 0.954 | 0.935 | 0.931 | 0.962 | 0.947 |

$\beta_0$: represent the constant value for regression model
$\beta_i$: represent the estimated regression coefficient for main linear effects
$\beta_{ii}$: represent the estimated regression coefficient for quadratic effects
$\beta_{ij}$: represent the estimated regression coefficient for interaction effects
1: time, 2: temperature and 3: silver concentration in the composite

TABLE III. THE SIGNIFICANCE PROBABILITY (P-VALUE, F-RATIO) OF THE REGRESSION COEFFICIENTS IN POLYNOMIAL MODEL

| Variables | | Melt blended | | | | LBL deposited | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Distilled water | Acetic acid 3% | Alcohol 10% | Apple juice | Distilled water | Acetic acid 3% | Alcohol 10% | Apple juice |
| Regression | p-value | 0.000* | 0.000* | 0.000* | 0.000* | 0.000* | 0.000* | 0.000* | 0.000* |
| | F-ratio | 104.54 | 139.28 | 125.71 | 139.32 | 95.71 | 90.10 | 171.000 | 118.61 |
| Linear Effect | p-value | 0.000* | 0.000* | 0.000* | 0.000* | 0.000* | 0.000* | 0.000* | 0.000* |
| | F-ratio | 236.75 | 319.16 | 288.62 | 318.16 | 211.78 | 205.62 | 405.35 | 270.53 |
| Quadratic effect | p-value | 0.000* | 0.000* | 0.000* | 0.000* | 0.000* | 0.000* | 0.000* | 0.000* |
| | F-ratio | 28.45 | 38.34 | 35.18 | 41.04 | 38.61 | 31.14 | 44.73 | 38.17 |
| Interaction effect | p-value | 0.000* | 0.000* | 0.000* | 0.000* | 0.000* | 0.000* | 0.000* | 0.000* |
| | F-ratio | 40.84 | 43.41 | 41.51 | 42.21 | 23.05 | 14.00 | 27.92 | 21.73 |
| $x_1$ | p-value | 0.000* | 0.000* | 0.000* | 0.000* | 0.000* | 0.000* | 0.000* | 0.000* |
| | F-ratio | 15.726 | 20.521 | 18.068 | 21.843 | 15.410 | 17.729 | 22.102 | 22.830 |
| $x_2$ | p-value | 0.000* | 0.000* | 0.000* | 0.000* | 0.002* | 0.000* | 0.000* | 0.000* |
| | F-ratio | 10.592 | 13.978 | 13.215 | 12.208 | 3.217 | 11.720 | 13.727 | 14.507 |
| $x_3$ | p-value | 0.000* | 0.000* | 0.000* | 0.000* | 0.000* | 0.000* | 0.000* | 0.000* |
| | F-ratio | 18.729 | 18.465 | 19.099 | 18.120 | 19.686 | 12.853 | 23.220 | 8.939 |
| $x_{11}$ | p-value | 0.000* | 0.000* | 0.000* | 0.000* | 0.000* | 0.000* | 0.000* | 0.000* |
| | F-ratio | 7.392 | 8.536 | 8.290 | 9.052 | 8.474 | 7.917 | 9.429 | 8.478 |
| $x_{33}$ | p-value | 0.141 | 0.057 | 0.209 | 0.714 | 0.025* | 0.395 | 0.462 | 0.040* |
| | F-ratio | 1.498 | 1.955 | 1.276 | 0.369 | 2.324 | 0.858 | 0.741 | 2.113 |
| $x_{12}$ | p-value | 0.000* | 0.000* | 0.000* | 0.000* | 0.051 | 0.000* | 0.002* | 0.000* |
| | F-ratio | 3.566 | 5.0521 | 4.271 | 4.003 | 2.009 | 4.969 | 3.363 | 5.211 |
| $x_{13}$ | p-value | 0.000* | 0.000* | 0.000* | 0.000* | 0.000* | 0.003* | 0.000* | 0.000* |
| | F-ratio | 9.276 | 9.146 | 9.533 | 10.513 | 6.498 | 3.144 | 7.454 | 5.655 |
| $x_{23}$ | p-value | 0.000* | 0.000* | 0.000* | 0.762 | 0.000* | 0.009* | 0.000* | 0.018* |
| | F-ratio | 4.875 | 4.623 | 3.928 | 0.304 | 4.786 | 2.724 | 4.108 | 2.461 |

$\beta_i$: represent the estimated regression coefficient for main linear effects
$\beta_{ii}$: represent the estimated regression coefficient for quadratic effects
$\beta_{ij}$: represent the estimated regression coefficient for interaction effects
1: time, 2: temperature and 3: silver concentration in the composite
* Significant ($p<0.05$)

### B. Silver-Ion Migration into Apple Juice

The effect of the three independent variables (x1: time contact, x2: temperature, and x3: silver concentration in the composite) on silver-ion migration into apple juice can be expressed using (2) for melt-blended nanocomposites and (3) for LBL-deposited nanocomposites with the use of the coefficients of the second-order polynomial regression model (Table II).

$$Y = 0.56413 + 0.18059x_1 + 0.6932x_2 + 0.12602\,x_3 - 0.14111x_1^2 + 0.00428x_3^2 + 0.03295x_1x_2 + 0.10600x_1x_3 + 0.00204x_2x_3 \quad (2)$$

$$Y = 0.73439 + 0.23710x_1 + 0.10348x_2 + 0.07809\,x_3 - 0.16599x_1^2 - 0.0308628x_3^2 + 0.05389x_1x_2 + 0.07163x_1x_3 + 0.02075x_2x_3 \quad (3)$$

The results indicated that silver-ion migration into apple juice was most significantly affected by the main effect of time contact for all of the nanocomposites (p<0.05), followed by silver concentration for melt-blended nanocomposites and temperature for LBL-deposited nanocomposites (Table III). In addition, the quadratic effect of silver concentration and the interaction between silver concentration and temperature were found to be insignificant for melt-blended nanocomposites. As stated in a previous study (Song *et al.*, 2011b), silver-ion migration from polyethylene silver nanocomposites is influenced by the type of food simulant, migration time, and temperature. They stated that temperature has an insignificant effect for alkaline food simulants.

The negative significant sign (p<0.05) of the quadratic effect of time can be interpreted by the equilibrium of silver migration from nanocomposites after an extended period of time [24]. A 3D surface plot of the silver migration from melt-blended nanocomposite (Fig. 1) and LBL-deposited nanocomposite (Fig. 2) into apple juice shows the visual representation of the effects of the independent variables on silver-ion release. A negative effect of square time on silver-ion migration into apple juice is found in Fig. 1 and Fig. 2.

However, the quadratic effect of silver concentration into apple juice for LBL-deposited nanocomposites was found to be significantly negative (p<0.05), even though such effect cannot be considered strong in terms of the regression coefficient (0.03086) and F ratio (2.113).

This result can be expressed clearly by comparing the surface plot of ion release as a function of time and concentration between melt-blended (Fig. 1) and LBL-deposited (Fig. 2) nanocomposites. The deposition of too many layers of silver nanoparticles onto LDPE films may not result in enhanced silver-ion release. This phenomenon may be interpreted by a strongly electrostatic interaction of opposite charged layers of LBL-deposited films, which results in a more difficult silver-ion migration from interior layers. The results indicated that silver-ion migration into apple juice was most significantly affected by the main effect of time contact for all of the nanocomposites (p<0.05), followed by silver concentration for melt-blended nanocomposites and temperature for LBL-deposited nanocomposites

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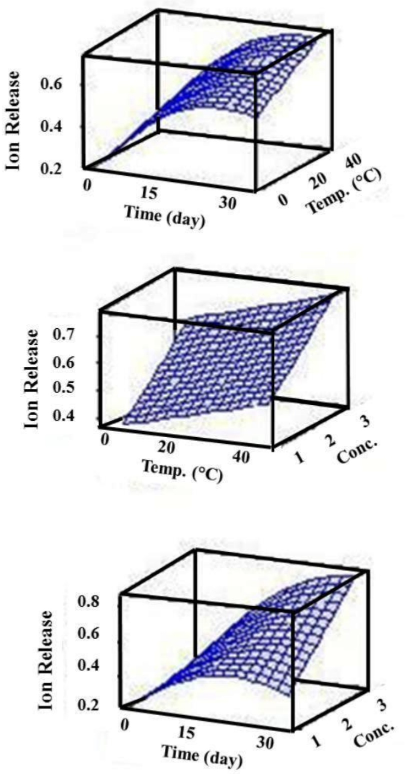


Figure 1. Response surface plots of silver ion migration from melt blended nanocomposites into apple juice as a function of time, temperature and silver concentration in the composite

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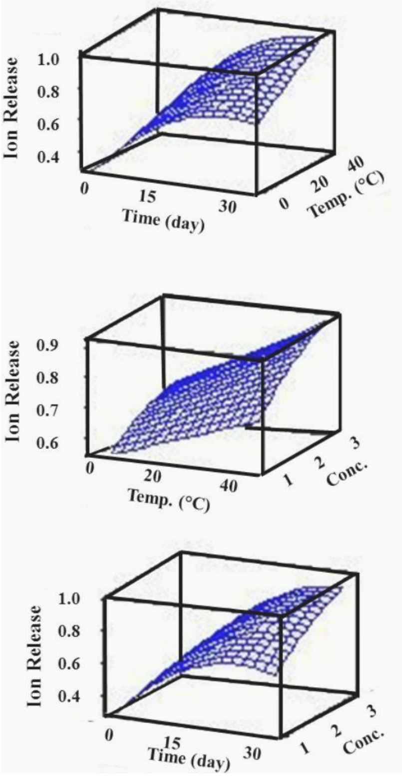


Figure 2. Response surface plots of silver ion migration from LBL deposited nanocomposites into apple juice as a function of time, temperature and silver concentration in the composite

## IV. CONCLUSION

In this study, RSM was used to develop empirically significant ($p<0.05$) models for estimating the variations in silver-ion migration from either melt-blended or LBL-deposited nanocomposites into food simulants and apple juice. The silver-ion migration was evaluated as a function of silver concentration in nanocomposite, migration time, and temperature. The results indicated that RSM was a helpful tool for determining the effects of processing and migration conditions on silver-ion release. The results of this study showed that silver-ion migration was significantly influenced by the processing and migration conditions. This study concludes that the duration of contact is the most effective variable that affects silver-ion migration in food simulants and apple juice from both melt-blended and LBL-deposited nanocomposites.

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