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Kinetic desorption models for the release of nanosilver from an experimental nanosilver coating on polystyrene food packaging

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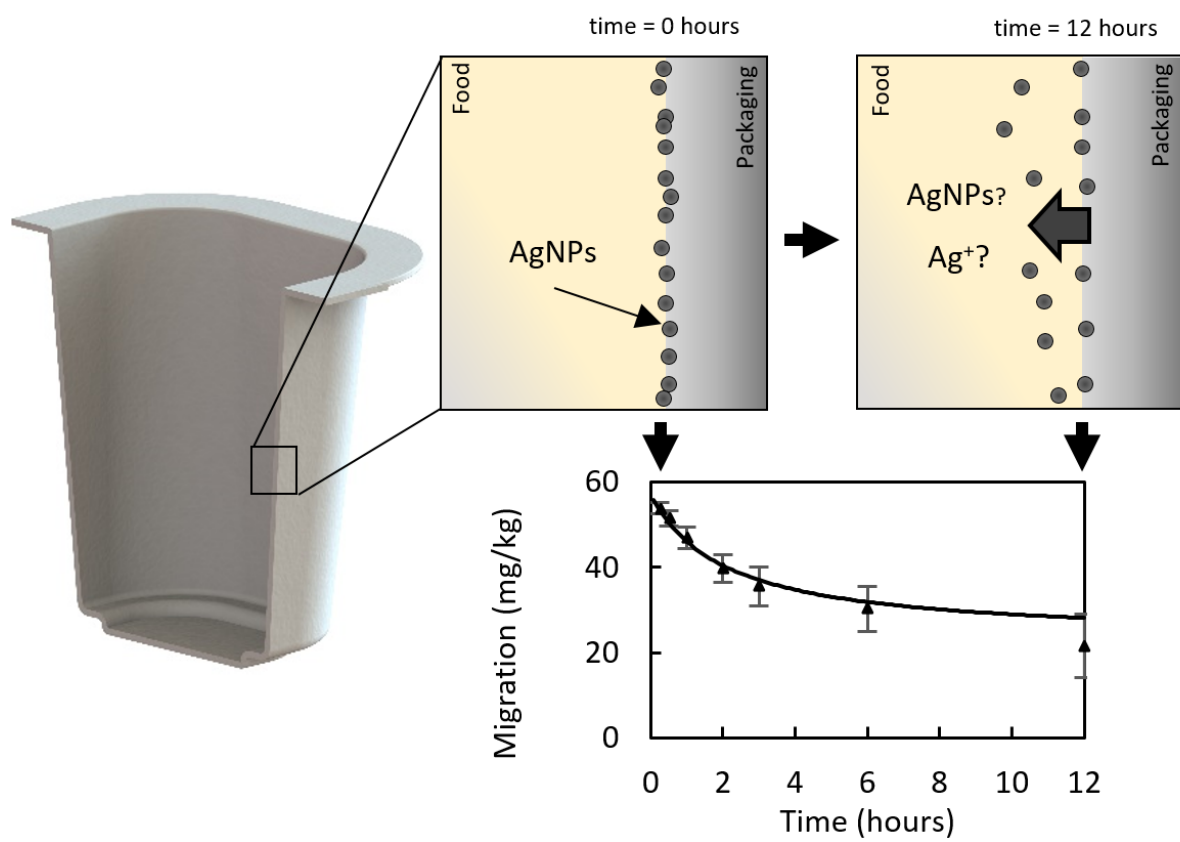
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Graphical Abstract

Abstract

To predict the kinetic desorption of silver from an experimental nanosilver coated polystyrene food packaging material into food simulants (0, 1, 2 and 3% acetic acid (HAc) in distilled water (dH$_2$O)) at 4 temperatures (10, 20, 40 and 70 °C), 5 sorption models were examined for their performance. A pseudo-second order kinetic sorption model was found to provide the best prediction of an unseen desorption validation dataset with R^2 = 0.90 and RMSE = 3.21. Poor predictions were witnessed for desorption at 70 °C, potentially due to re-adsorption of the silver back onto the polystyrene substrate, as shown in the kinetic migration experiments. Similarly, the temperature dependence of the desorption rate constant was satisfactorily described using the Arrhenius equation with the exception of the 70 °C scenario. The use of sorption models identified scenarios that may limit human exposure to nanosilver migrating from this experimental nanocoating, i.e. low temperature applications.

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1. **Introduction**

Each year roughly one third of all food produced is lost due to food waste (FAO 2011). A large portion of these losses are accrued during transport and storage due to microbial spoilage. Active nanopackaging incorporating antimicrobial nanoparticles having dimensions in the size range 1-100 nm, are providing a solution to this issue by improving food shelf life through inactivation of spoilage microorganisms. Silver nanoparticles (AgNPs) have been the subject of many research studies due their antimicrobial efficacy against both gram negative and gram positive bacteria (Azlin-Hasim, Cruz-Romero, Cummins, Kerry, & Morris, 2016), yeast and mould (Mohammed Fayaz, Balaji, Girilal, Kalaichelvan, & Venkatesan, 2009). In recent years, a number of antimicrobial nanosilver food contact materials have appeared on the global market such as; food storage boxes, food storage bags, children's sippy cups, cutting boards and refrigerators (Maynard and Michelson 2016).

Despite the use of nanosilver for food contact applications in many countries, there are concerns that have been raised related to the potential size driven increase in nanoparticle mobility within food, food packaging and the human gastro-intestinal tract, with potential bioaccumulation and toxic effects (Souza & Fernando, 2016). These concerns are heightened by the lack of knowledge regarding the influence of physicochemical properties on changes in release, transport and toxicity mechanisms of nanoparticles compared to their bulk counterparts. To assess the safety of these materials and fill gaps in knowledge a case-by-case strategy has been proposed by government bodies including the European Food Safety Authority (EFSA 2011). Considering the significant uncertainty which surrounds aspects of engineered nanomaterial (ENM) safety, this strategy is considered the most responsible approach for the safe development of ENMs in the food industry. Weaknesses in this strategy can be linked to additional financial and animal costs accrued during the risk assessment of

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ENMs and this has contributed to views that a case-by-case strategy is not optimal in the long term (Amenta et al., 2015). Therefore, more efficient risk assessment approaches are necessary to reduce the burden associated with this case-by-case testing strategy. The EFSA (2011) proposed a scenario were reduced toxicity testing would be required in the event that diminished human exposure could be proven. In the European Union, a limited number of ENMs have been accepted for use as food contact materials. These ENMs, which include titanium nitride (TiN) (European Commission 2012), silicon dioxide (European Commission 2016) and three cross linked block copolymers (European Commission 2015) have been accepted for use in the EU due to migration tests and migration modelling which support a no exposure scenario. Predictive migration models for additives and contaminants from food packaging materials are well established and accepted in many regulatory jurisdictions (Begley, 1997; Baner, Brandsch, Franz, & Piringer, 1996). Predictive migration models offer a more economical and time saving approach to determine migration from packaging than experimental migration studies.

In the literature, there are limited studies that investigate the potential migration of nanoparticles from nanoparticle food packaging materials and coatings (Kuorwel, Cran, Orbell, Buddhadasa, & Bigger, 2015), and even fewer studies that have investigated predictive migration models for the release of nanoparticles from food packaging coatings (Hannon, Kerry, Cruz-Romero, Morris, & Cummins, 2015). Migration predictive models have been proposed to model the migration of nanoparticles from nanoparticle filled food packaging materials (Bott, Störmer, & Franz, 2014; Simon, Chaudhry, & Bakos, 2008; von Goetz et al., 2013). However, these migration models focus on nanopackaging were nanoparticles are immobilised within the walls of polymer substrate and diffusion is the driving mechanism for migration. These models are not suitable for the prediction of nanoparticle migration from nanocoatings, were nanoparticles are concentrated at the surface

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of the packaging and rely on desorption or dissolution as the main migration mechanism. To the best of the author's knowledge, only one study has investigated the predictive migration modelling of nanoparticles from nanocoatings (Hannon et al. 2016c). The study uses artificial neural networks to predict the migration of nanosilver from a nanosilver spray coated LDPE substrate, but provides limited mechanistic information for the desorption process due to the black box nature of the model.

The objective of this study was to investigate a number of kinetic sorption models to predict the desorption of AgNPs from a nanosilver coated polystyrene experimental food grade material into food simulants.

2. Materials and Methods

2.1. Nanocomposite manufacture

AgNPs were synthesised using a method adapted from Chen et al., (2009). An ethanolic solution of silver nitrate ($AgNO_3$) (0.1 M $AgNO_3$, Sigma Aldrich, Ireland) was heated to 30 °C and an equal amount of 0.1 M Polyvinylpyrrolidone (PVP) solution (PVP, Mw = 40,000, Sigma Aldrich, Ireland) in ethanol (>99.5% ethanol, Sigma Aldrich, Ireland) was added at a rate of 0.667 ml/min using a programmable peristaltic pump (Dose It P910, Integra Biosciences AG Switzerland). The solution was stirred at a rate of 800 rpm for 2 h on a hot plate magnetic stirrer device (MSH-20D,Wise Stir, Korea), and the solution had turned a stable orange-brown colour. AgNPs were separated by addition of acetone (Sigma Aldrich, Ireland) at a volume ratio of approximately 1:4, respectively. The solution was then sonicated using an ultrasonicator (Cole-Palmer 8891) for 10 min and centrifuged at 6000 rpm for 15 min in a Beckman J2-21 centrifuge (Beckman Instruments Inc., USA). The supernatant was discarded and the pellet was re-dispersed in ethanol. The separation step was repeated once

again, and the pellet was dried in an oven overnight at 60 °C and finally crushed into a powder.

AgNPs (0.5 wt. %) were dissolved in ethanol, sonicated for 5 min and directly poured onto a 405 mm × 305 mm high impact polystyrene (HIPS) tray (Barkstone plc, UK). HIPS trays containing AgNP solutions were then placed in an oven at 60 °C for 24 h in order to evaporate remaining solvent. The AgNP coated tray was rinsed with dH_2O to remove any unattached AgNPs and kept in an environmental chamber (T =25 °C, RH = 50%) until further analysis.

2.2. Determination of AgNP loading in coating

The total concentration of silver in the nanosilver coated polystyrene material was determined by heat assisted digestion with 10 ml HNO_3 followed by ICP-AES analysis. For each $1 \times 1 \ cm^2$ sample, the surface was sliced with a disposable scalpel and the shavings were collected in a PTFE vessel. A 10 ml volume of concentrated nitric acid (69% HNO_3, VWR International, Dublin, Ireland) was transferred to each digestion vessel which was sealed with a rupture membrane in place. The vessels were placed in an oven (Plus II Oven, Gallenkamp, Loughborough, U.K.) at 120 °C for 5 hours. Once the digestion was complete, the digestate was filtered through a 0.45 µl syringe filter and 200 µl digestate was diluted in 9.8 ml of milli-Q water (18 MΩcm, PURELAB Option-Q, Elga, U.K.) for analysis by ICP-AES.

2.3. Migration study

The release of silver from the experimental nanosilver coated polystyrene food grade material (sample size 1 cm × 1 cm) was initiated by total immersion in 10 ml of one of the food simulants (0, 1, 2 and 3% HAc in dH_2O) at a given temperature (10, 20, 40 and 70 °C)

for 5 days. Food simulants were prepared by volumetrically diluting concentrated HAc (>99% Acetic acid, Sigma Aldrich, Arklow, Ireland) in dH_2O to the desired concentration. To investigate the kinetic behaviour of silver release 200 μl aliquots, without replacement, were sampled at time points (0.25, 0.5, 1, 2, 3, 6, 12, 24, 48, 72, 96 and 120 h) up to 5 days. The silver concentration readings from ICP-AES analysis were subsequently corrected to account for the removal of small aliquots from the food simulants. Each aliquot was diluted with 9.8 ml of milli-Q water acidified with 200 μl 69% HNO_3 and 100 μl HCl (37% HCl, Sigma Aldrich, Ireland) prior to ICP-AES analysis. Each scenario of temperature/pH was tested in replicate (n = 2 samples, 6 replicate ICP-AES readings).

2.4. Inductively Coupled Plasma – Atomic Emission Spectrometry

The concentration of total silver (ionic and NP) in the coating and migrant solutions was determined using the ICP-AES technique (Vista Pro RL, CCD simultaneous ICP-AES, Varian, Victoria, Australia). The instrument was purged with argon gas for 20 min and allowed to equilibrate for 50 min prior to analysis. The ICP-AES was calibrated using four standards (0.001, 0.005, 0.01 and 0.1 mg/l) produced by serial dilution of a 1000 mg/l silver nitrate standard (1000 mg/l $AgNO_3$, Elementec, Kildare, Ireland). Samples that had silver concentrations above this range were diluted and retested accordingly. All samples tested were spiked with yttrium as an internal standard. All glassware and sample containers used in the preparation and testing of the samples were immersed overnight in 5% HNO_3 aqueous solution and then rinsed with copious amounts of dH_2O before being used in migration studies or total digestions.

2.5. Nanoparticle tracking analysis (NTA)

To obtain the size distribution of nanoparticles following migration studies, a AgNP-coated polystyrene sample (1 cm $\times$ 1 cm) was immersed in 10 ml dH$_2$O at 20 °C and after 30 min a 1 ml aliquot was removed and tested using the NTA technique (Nanosight NS300, Malvern, U.K.) as outlined by Hannon et al. (2016b).

2.6. Scanning Electron Microscopy and Transmission Electron Microscopy

Scanning electron microscopy combined with energy dispersive X-ray (FEI Quanta 3D FEG DualBeam, Hillsboro, U.S.A.) was used to identify and characterise AgNPs in the nanosilver coating and in the food simulants used for migration studies. The polystyrene substrate was immobilised coated side up on a SEM stub using double sided carbon tape and sputter coated with gold using an Emitech K575X Sputter Coating Unit (Quorum Technologies Ltd., Kent, U.K.) before being imaged using SEM. For food simulants containing migrant silver, a 5 µl aliquot was pipetted onto aluminium foil mounted on a SEM stub and dried under ambient conditions covered with a petri dish. Once dry, the food simulants were gold coated and imaged using SEM-EDX. Particle measurements were performed using the Fiji programme (Schindelin et al., 2012) following the image processing steps outlined in Hannon et al. (2016b).

Further characterisation of nanoparticles in the dH$_2$O and 3% HAc food simulants was performed by drying 5 µl aliquots of the food simulants on 200 mesh copper grids (Electron Microscopy Sciences, U.S.A.) for analysis by transmission electron microscopy (FEI Technai F30 transmission electron microscope, Hillsboro, U.S.A.).

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2.7. Statistical Analysis

Statistical analysis of the migration data was conducted in the StatTool 6.3 program (Palisade, Middlesex, U.K.). To perform a sensitivity analysis of the factors influencing the migration of AgNPs into the food simulants (temperature, time and pH) a Pearson's correlation analysis was conducted. Temperature (10, 20, 40 and 70 °C), time (at each time point) and pH (6.55, 2.75, 2.61 and 2.58) were all set as independent numeric variables and migration was set as the dependent numeric variable.

3. Desorption modelling

3.1. Kinetic desorption models

The location of the nanosilver at the coating substrate-food simulant interphase impacted on the type of migration model used to predict the release of AgNPs. In this instance, the particles are not required to diffuse through the plastic packaging but rather desorb or dissolute from the surface. Due to uncertainties regarding the rate controlling process (i.e. desorption or dissolution) responsible for AgNP migration from the polystyrene surface, a number of kinetic adsorption-desorption models were considered (Table 1). To obtain details of the sorption processes governing the migration of AgNPs, the performance of the five sorption models, which are each associated with various rate controlling migration processes and boundary conditions, was assessed.

Table 1

Kinetic sorption models used to predict the desorption of AgNPs from a nanosilver coated polystyrene material

Models	Linearized equation	Constants		Plot to determine constants	Reference
First order	$\ln(q_e - q_t) = \ln(q_e) - \left(\dfrac{k_1 t}{2.303}\right)$	k_1	First order sorption rate constant	$\ln(q_e - q_t)$ against t	(Lagergren, 1898)
		q_e	Sorption amount at equilibrium		
Second order	$\dfrac{t}{q_t} = \dfrac{1}{k_2 \cdot q_e{}^2} + \dfrac{t}{q_e}$	k_2	Second order sorption rate constant	$\dfrac{t}{q_t}$ against t	(Ho & McKay, 1999)
Intraparticle	$q_t = k_i t^{1/2} + C$	k_i	Intraparticle rate constant	q_t against $t^{1/2}$	(Weber and Morris, 1963)
		C	constant		
Elovich	$q_t = \beta \cdot \ln(\alpha \cdot \beta) + \beta \cdot \ln(t)$	α	constant	q_t against $\ln(t)$	(Low, 1960)
		β	constant		
Fractional power model	$\ln(q_t) = \ln(\alpha) + \beta \cdot \ln(t)$	α	constant	$\ln(q_t)$ against $\ln(t)$	(Dalal, 1974)
		β	constant		

For each of the models tested, there are a set of assumptions and boundary conditions which may influence their ability to effectively predict migration of silver from polystyrene (Largitte & Pasquier, 2016). The pseudo-first and second order models assume; sorption only occurs on localised sites, there are no interactions between adsorbates, the adsorbate concentration is constant, a saturated monolayer on the adsorbent corresponds to the adsorbents maximum adsorption capacity and the adsorbent surface coverage does not influence the energy of adsorption. Both models differ through their governance by a pseudo-first order and second order rate equation. Similar to the pseudo-first and second order

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models, the Elovich model assumes that sorption only occurs on localised sites and the adsorbate concentration is constant. The Elovich model accounts for interactions between adsorbates and assumes negligible adsorption prior to the exponential and a linear relationship between adsorption energy and surface coverage. The intraparticle diffusion model or Weber and Morris model (1963) assumes that the adsorption-desorption process is controlled by intraparticle pore diffusion and/or boundary layer diffusion. The model assumes that the boundary layer is constant and the thickness of the boundary layer is related to the intercept of a plot of q_t vs $t^{0.5}$ (Al-Rashdi, Tizaoui, & Hilal, 2012). The fractional power model (Dalal, 1974) which is a modified form of the Freundlich equation, is applied in systems where the adsorbent is assumed to have a heterogeneous surface and multilayer adsorption occurs.

It is important to note differences between the sorption boundary conditions in this study to those used to derive each of the kinetic sorption models presented in Table 1. For each of the kinetic sorption models, the boundary conditions assume that at the beginning of the sorption process the sorbent does not contain sorption material (t = 0, q(0) = 0). For a desorption problem, this is not the case as the sorbent contains all of the sorption material at the initial time point (t = 0, q(0) = qi). In addition, it is assumed that during the formation of the nanosilver coating, the adsorption of PVP-coated AgNPs onto polystyrene did not reach equilibrium (i.e. unsaturated surface with fractional AgNP coverage) and that a homogeneous monolayer of dispersed AgNPs was formed (Supplementary information Fig. S1), as the AgNP's PVP-coating would not be conducive to multilayer formation. To comply with the boundary conditions of each of the kinetic sorption models, the sorption process is considered for the absorption of AgNPs into the food simulants and the remaining AgNPs in the coating is determined using Eq. 1.

$$q(t)_P = q_{P,init} - q(t)_{fs} \tag{1}$$

Where $q(t)_P$ is the concentration of nanosilver in the packaging coating at time t, $q_{P,init}$ is the initial concentration of nanosilver in the coated material and $q(t)_{fs}$ is the amount of nanosilver absorbed into the food simulant at time t. It is assumed that differences in partition coefficients between the nanocoating and highly aqueous food simulants is negligible and migration processes into each of the food simulants can be described by the same model parameters (Franz & Störmer, 2008).

Each of the models is provided in a linear form that can be used to predict sorption rate constants and other sorption properties (q$_e$) by plotting different configurations of the kinetic parameters, q(t) and t. The sorption rate constants are then determined from the slope and intercept of the produced linear regression line. Each of the models was validated using leave-one-out cross validation method, which randomly selected 20% of the total migration dataset. To calibrate and validate each of the models to account for uncertainty and variability in the input datasets Monte Carlo simulations were carried out using the @Risk software (Palisade, Middlesex, U.K.) and the number of iteration runs was set to 10,000 iterations.

3.2. Arrhenius equation – influence of temperature on sorption rates

In a previous study, temperature contributed significantly to the release of silver from nanosilver food packaging coatings (Hannon et al., 2016a). Therefore, to take into account the influence that temperature has on the desorption rate of AgNPs from nanosilver coated polystyrene, the Arrhenius equation was employed (Eq. 2)

$$k = Ae^{-E_a/RT} \tag{2}$$

Where R is the ideal gas constant (8.31 J/Kmol), E_a is the activation energy, T is the absolute temperature (K), A is the exponential factor and k is the desorption rate constant. A plot of ln(k) against 1/T is used to determine the activation energy and exponential factor for the system.

3.3. Thermodynamic considerations

To gain a greater understanding of the AgNPs desorption process, thermodynamic properties of the system were determined using the Van't Hoff equation (Eq. 3).

$$\ln(k_e) = -\left(\frac{\Delta G^\theta}{RT}\right) = -\left(\frac{\Delta H^\theta}{RT}\right) + \left(\frac{\Delta S^\theta}{R}\right) \tag{3}$$

Where k_e is the equilibrium rate constant, R is the ideal gas constant, T is the absolute temperature in the system, ΔG^θ is the Gibbs free energy, ΔH^θ is the change enthalpy and ΔS^θ is the change in entropy. These parameters were determined from the slope and intercept of a plot of $\ln(k_e)$ against 1/T. k_e is a ratio of the initial concentration of silver in the coating to the equilibrium concentration of silver in the coating (Eq. 4) (El Boujaady, Mourabet, Bennani-Ziatni, & Taitai, 2014).

$$k_e = \frac{(q_i - q_e)}{q_e} \tag{4}$$

4. Results and Discussion

4.1. Characterisation of AgNPs in coating and food simulants – SEM and TEM

The identification and characterisation of nanoparticles at different stages of a food product lifecycle has been emphasised in risk assessment guidance documents for the industry (EFSA 2011). In this study, TEM and SEM-EDX were used to identify and characterise nanoparticles at each hypothetical lifecycle stage; raw materials used for manufacture, manufactured material and migration of AgNPs from the manufactured material into food. The size distribution of AgNPs used for the manufacture of the nanocoating measured using TEM had a mean size of 12.5 nm (n = 1074 at 3 locations). When immobilized on the surface of the polystyrene a size distribution measured in 5 different locations had mean size 78.9 nm and mode of 43 nm (n = 811). A potential cause of the increase in size distribution may have occurred as a result of agglomeration/aggregation during the manufacturing process. Another possible contributing factor to the increased size distribution may be due to the limited resolution provided by the SEM technique, used to characterise particles in the AgNP precursor solution used to manufacture the nanocoating and particles observed in the food simulants.

Following migration studies at 70 °C for 2 h, food simulants were imaged using TEM and SEM-EDX to obtain size distributions covering a wider size range than a single technique on its own. A noteworthy finding was the absence of nanoparticles in the 3% HAc imaged by both TEM and SEM-EDX. Nanoparticles with characteristic silver atom spacing (~0.28 nm (Desireddy et al., 2013; Ma et al. 2012)) of 0.23 nm were observed in dH$_2$O (Fig. 1g) after incubation at 70 °C for 2 h by TEM analysis and agglomerates of silver were observed by SEM, confirmed by silver element maps obtained using EDX technique that were overlaid on the SEM images (Fig. 1h). As the TEM and SEM techniques both rely on

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samples to be dried prior to analysis, the NTA technique was used to determine the hydrodynamic diameter of nanoparticles in the dH_2O following migration studies (Fig. 2). Although AgNPs were observed in dH_2O following migration studies with a mean size of 30.18 nm (Fig 1e and 1f, n = 79), it is important to note that there was a limited number of particles identified on the TEM grids. The low number of particles identified could have been due to low AgNP concentrations present in the food simulants relative to the volume of food simulant dried on the copper grid for testing using the TEM technique (~5 µl). The low number of AgNPs per µl would make their identification difficult. Therefore, the use of the NTA technique which has a high sample throughput can be advantageous in providing statistically reliable size distributions.
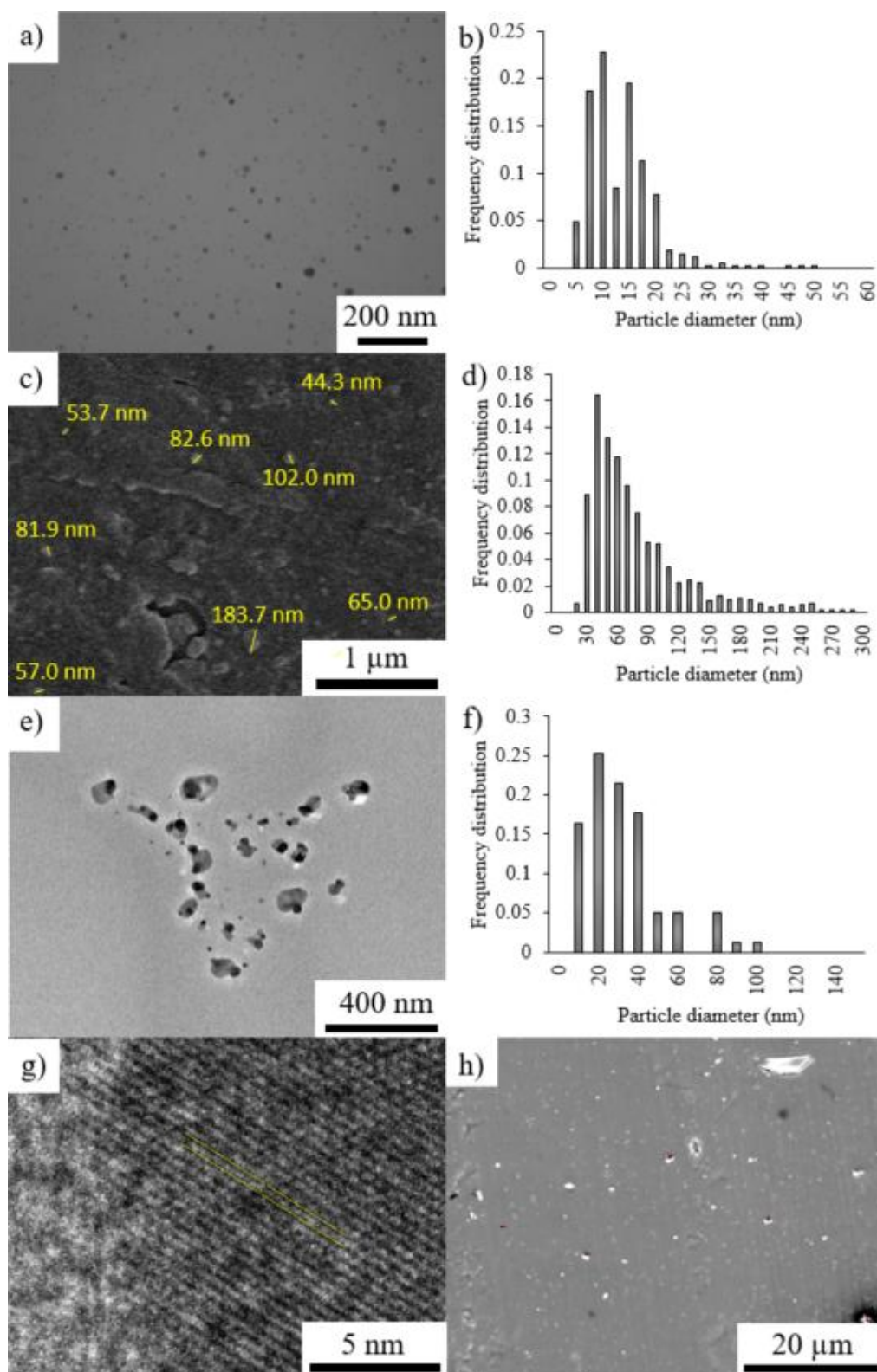
Fig. 1. TEM image of a) AgNPs used to coat the polystyrene surface and b) corresponding

size distribution, c) SEM image of nanosilver coating on polystyrene and d) corresponding

size distribution, e) TEM image of AgNPs in dH$_2$O after 2 h at 70 °C and f) corresponding

size distribution, g) high magnification TEM image of one of the particles in image e), and h)

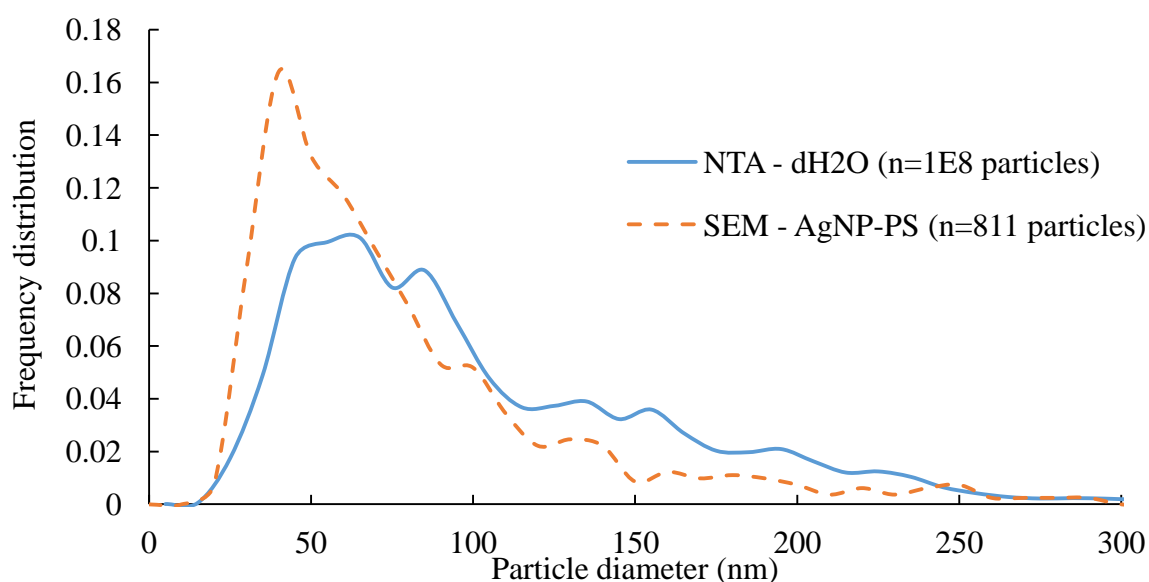SEM image of AgNPs in dH$_2$O after 2 h at 70 °C with silver element maps overlapped.

Fig. 2 Size distributions of nanoparticles identified in dH$_2$O compared to the size distribution

of nanoparticles identified on the AgNP-coated polystyrene.

4.2. Kinetic desorption model performance

The migration kinetics of nanoparticles from food contact materials is an area of

research where there is a lack of knowledge related to mechanisms of action, particularly for

nanocoatings. A number of sorption models were tested for their performance when used to

predict the desorption of AgNPs from a nanosilver coated material under ideal conditions

using food simulants. The performance of the five models is summarised in Table 2. In this

study, no adsorption-desorption isotherms were determined, due to the circumstances in

which the desorption reaction occurred. Although isotherms play a significant role in

adsorption-desorption systems, it was assumed that the maximum adsorption capacity of silver on the polystyrene surface was not reached during manufacture and that silver saturation in the food simulant did not occur at equilibrium migration. For the manufacture of the nanosilver coating, a fixed concentration of silver was used, that was optimised for antimicrobial efficacy of the final nanocoating. For the food simulants, far higher silver concentrations have been achieved in solutions without reaching saturation conditions (Loza et al., 2014). For these reasons, adsorption-desorption isotherms were not considered in this study and instead a focus was placed on kinetic desorption models to predict migration.

Table 2

Performance of the sorption models used to predict AgNP migration from a nanosilver coating on polystyrene into food simulants

Models	Calibration		Validation	
	R^2	RMS Error	R^2	RMS Error
First order	0.46	8.84	0.02	14.32
Second order	0.92	2.99	0.90	3.21
Intraparticle	0.88	3.70	0.81	4.61
Elovich	0.92	3.02	0.89	3.47
Power function	0.86	4.10	0.80	5.33

On inspection of the R^2 and RMS Error values in Table 2, the pseudo-second order sorption model was found to produce the best fit of the calibration dataset and predict the validation dataset with the least error. The Elovich, Intraparticle and Power Function also provided satisfactory fitting and prediction of the calibration and validation datasets. The superior prediction of migration provided by the pseudo-second order model implies that the

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AgNPs form a monolayer on the polystyrene surface via a chemisorption mechanism and the migration process is controlled by a second order rate equation. This finding of a chemisorption mechanism is supported by the satisfactory determination coefficient obtained for the Elovich model which is used for chemisorption systems and also suggests a heterogeneous adsorption surface. The weaker predictions provided by the intraparticle diffusion model reduces the possibility of a diffusion rate controlling mechanism existing within the system (Akpomie, Dawodu, & Adebowale, 2015). Among the five models tested the only model that did not have satisfactory performance was the pseudo-first order sorption model. This is a significant finding as it greatly reduces the likelihood of dissolution, which has been associated with the pseudo-first order rate equation (Hahn, Brandes, Wagener, & Barcikowski, 2011), being a significant rate controlling mechanism in the AgNP migration process (Supplementary information Fig. S2-5).

Representative plots showing the performance of the pseudo-second order desorption model are shown in Fig. 3. From both plots it is evident that for each of the models tested the error increased with increasing silver migration.
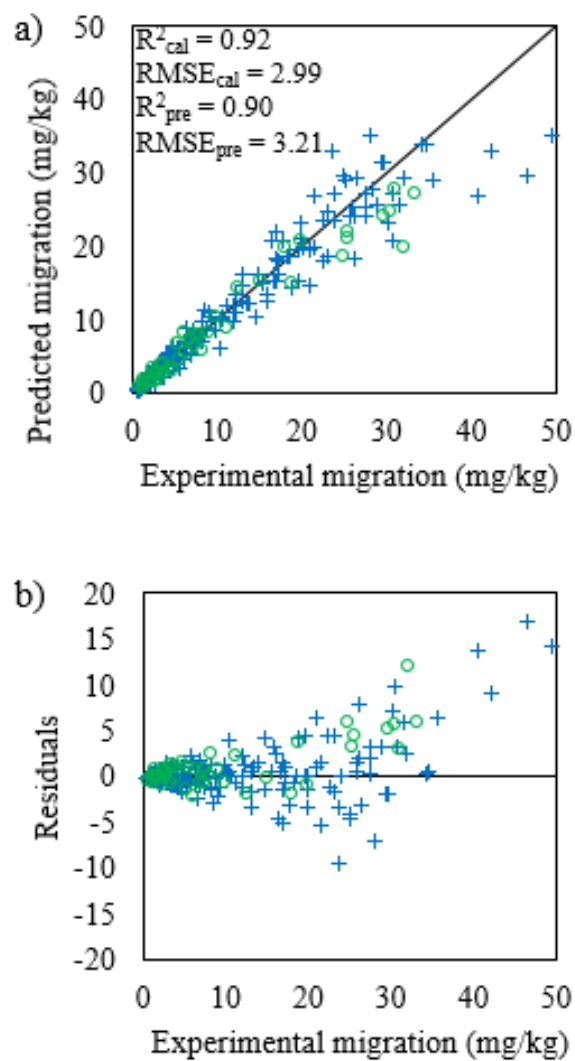
a)

R²cal = 0.92
RMSEcal = 2.99
R²pre = 0.90
RMSEpre = 3.21

b)

Fig. 3. Scatterplots showing a) experimental against predicted migration and b) experimental migration against residuals (+ = calibration dataset and ○ = validation dataset).

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4.3. Thermodynamic considerations for the desorption process

Table 3

Desorption thermodynamic parameters

% HAc	T (°C)	T (K)	q_i mg/kg	q_e mg/kg	Ke	ΔG^Θ kJ/mol	ΔH^Θ kJ/mol	ΔS^Θ J/mol
0 % HAc	10	283.15	57	52.99	0.08	6.07	38.15	115.30
	20	293.15	57	50.08	0.14	4.82		
	40	313.15	57	27.25	1.09	-0.23		
	70	343.15	57	27.75	1.05	-0.15		
1% HAc	10	283.15	57	47.69	0.20	3.85	40.17	129.49
	20	293.15	57	42.26	0.35	2.57		
	40	313.15	57	18.56	2.07	-1.90		
	70	343.15	57	13.14	3.33	-3.43		
2% HAc	10	283.15	57	50.70	0.12	4.91	50.73	162.49
	20	293.15	57	42.85	0.33	2.70		
	40	313.15	57	29.26	0.95	0.14		
	70	343.15	57	8.14	5.99	-5.11		
3% HAc	10	283.15	57	53.10	0.07	6.15	41.84	257.95
	20	293.15	57	45.27	0.26	3.29		
	40	313.15	57	19.84	1.87	-1.63		

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| 70 | 343.15 | 57 | 21.91 | 1.60 | -1.34 |

From the sensitivity analysis of migration data (Fig. 6) it was noticed that the thermodynamics of the system play a significant role in the mechanisms governing the detachment of AgNPs from the polystyrene surface. To gain a greater understanding of the energies governing the desorption process at the coating-food simulant interphase, the Arrhenius equation and Van't Hoff equation were used to determine the exponential factor, activation energy, Gibbs free energy, change in enthalpy and change in entropy (Fig. 4a and b). For each of the food simulants, the Gibbs free energy is found to be increasingly negative showing that the process is endothermic in nature. This finding is also supported by the positive values for ΔH^{Θ} obtained. The high magnitude of ΔH^{Θ} suggests that the main mechanism governing the attachment of AgNPs on the polystyrene surface is chemisorption, as the ΔH^{Θ} is in the range 40 to 800 kJ/mol, compared to the range 4 to 40 kJ/mol associated with a physisorption mechanism (Crini & Badot, 2008). It is proposed that the chemisorption mechanism governing PVP-coated AgNP attachment on the polystyrene surface is influenced by AgNP-PVP and PVP-polystyrene interactions, as the poor affinity between polar hydrophilic silver and non-polar hydrophobic polystyrene have been reported in previous studies (Youssef & Abdel-Aziz, 2013; Pongnop, Sombatsompop, Kositchaiyong, & Sombatsompop, 2011; Krystosiak, Tomaszewski, & Megiel, 2017). To facilitate the attachment of AgNPs on polystyrene, the Ag^+ ions are reduced to AgNPs in the presence of PVP. During the formation of PVP-coated AgNPs, the carbonyl group on PVP's pyrrolidone ring have a strong influence on the interaction between PVP and Ag^+ (Chen et al. 2009; Gao et al., 2014). Once the PVP-coated AgNPs are formed, their attachment to the polystyrene surface is enabled through the interaction between the amide nitrogen present on the PVP's side chains and sulphate groups on the polystyrene surface (Smith, Meadows, & Williams,

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1996). The occurrence of a chemisorption mechanism demonstrates the efficiency of the coating mechanism for the attachment of AgNPs onto the polymer for controlled release, unlike a physisorption mechanism that would provide a weak bonding of the AgNPs to the polystyrene surface. This finding also explains why the pseudo-second order kinetic sorption model provided the best fit of the experimental migration data, as this model is suited towards chemisorption systems (Febrianto et al., 2009). The high values of ΔS^{Θ} for the system are typical of a dissociative mechanism for the desorption process and indicates increasing randomness in the system (Akpomie, Dawodu, & Adebowale, 2015). This is particularly true considering the energy being introduced into the system in the form of heat.

The temperature dependence of the desorption process was described using the Arrhenius equation (Fig. 4b). An important finding observed in this plot is the increased pseudo-second order desorption rate (k_2) at the highest temperature of 70 °C. This non-linear behaviour at higher temperatures suggests that there is a change in the rate controlling process for AgNP migration. A potential rate limiting process may involve the increased dissolution of AgNPs into Ag^+ ions at higher temperatures (Kittler, Greulich, Diendorf, Köller, & Epple, 2010), which could be potentially re-adsorbed by free carbonyl groups on the PVP-AgNP coated polystyrene surface (Zhang et al., 2014; Liu & Hurt, 2010). This finding is also supported by a clear decrease in Gibbs free energy with increasing temperature which implies that adsorption is more favourable than desorption at higher temperatures. A plot of the natural logarithm of the sorption rate constants against inverse absolute temperature provided satisfactory linear relationships for each of the food simulants with R^2 of 0.78, 0.91, 0.87 and 0.66 for 0%, 1%, 2% and 3% HAc, respectively. Activation energies were in the range -61.76 to -47.31 kJ/mol.
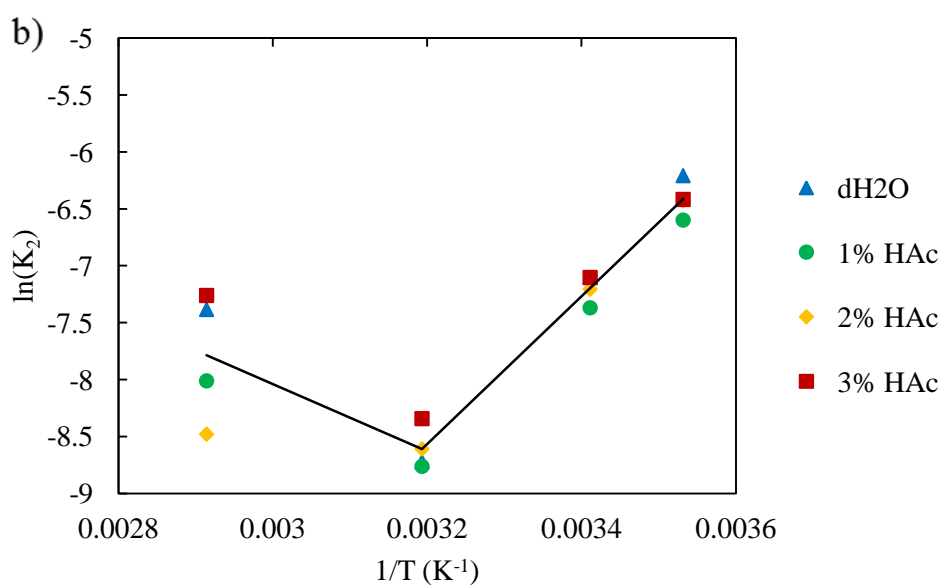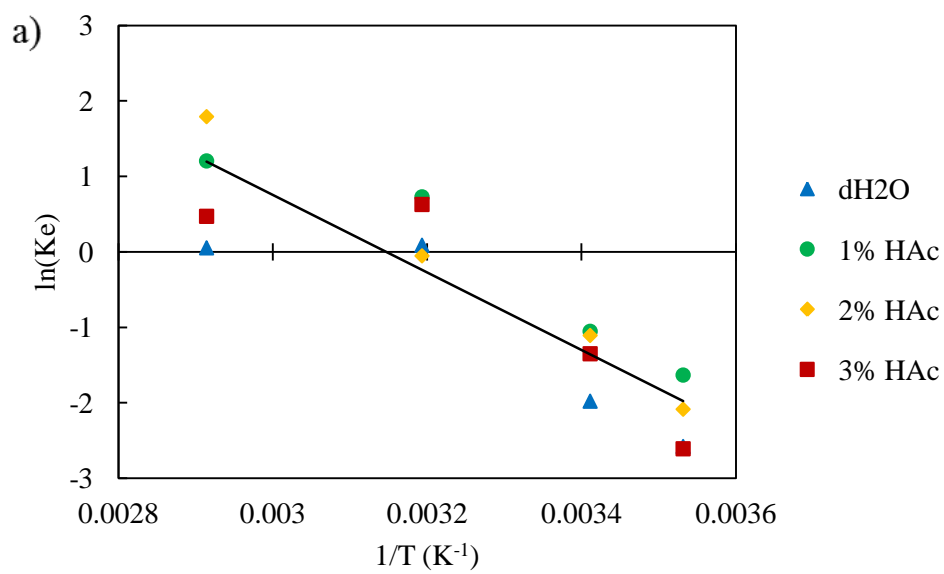
Fig. 4 a) Van't Hoff plot showing linear relationship between ln(ke) and $1/T_{abs}$ and b) plot of natural logarithmic of the second order rate constant (K_2) against inverse absolute temperature (1/T).

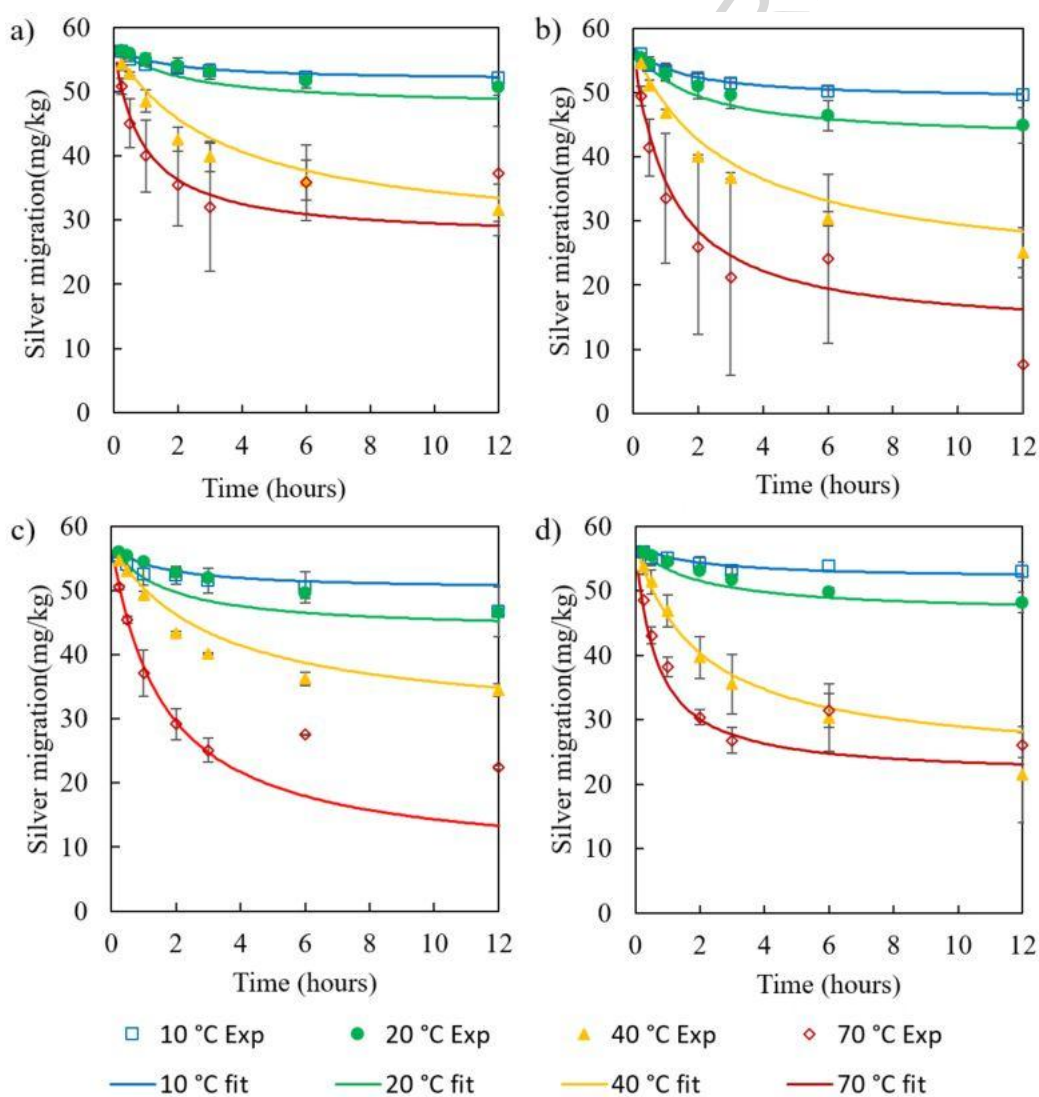## 4.4. Migration assessment of silver from the nanosilver coating

Fig. 5. Experimentally determined silver migration from nanosilver coated polystyrene and pseudo-second order model fits for food simulants a) dH_2O, b) 1% HAc, c) 2% HAc and d) 3% HAc.

The migration of nanosilver from antimicrobial coated active packaging materials provides a complex scenario were migration into the food is necessary to provide antimicrobial activity; However, migration should be controlled and limited to reduce human exposure to within safe limits. This scenario is different from materials that are under safety assessment (e.g. Zinc oxide) or have been approved for use in the EU; such as titanium nitride and cross-linked copolymers, that provide their novel function within the walls of the food packaging material and present limited or negligible migration. In this study, migration from the nanosilver coating exceeded regulatory limits of 0.01 mg/kg$_{food}$ for unauthorised substances (European Commission 2011) and more specifically the migration limits outlined by the EFSA for silver migration from food contact materials of 0.05 mg/kg$_{food}$ (EFSA 2006). It should be noted that these limits have exclusions, with ENMs explicitly mentioned. Currently, there are no nano-specific migration limits to benchmark the migration of nanoparticles from food contact materials. In this study, the equilibrium silver migration (mean value for dH_2O, 1%, 2% and 3% HAc) from the coated material reached after 12 hours was 6.40 ± 1.41 mg/kg$_{food}$, 12.01 ± 2.31 mg/kg$_{food}$, 31.98 ± 3.44 mg/kg$_{food}$ and 33.44 ± 1.41 mg/kg$_{food}$ when migration were tested at 10, 20, 40 or 70 °C, respectively (Fig. 5). In all cases, the migration of silver was a fraction of the initial silver concentration of 9.62 ± 1.45 mg/dm^2 (57.72 ± 8.71 mg/kg$_{food}$) found in the nanosilver coated material determined by total acid digestion.
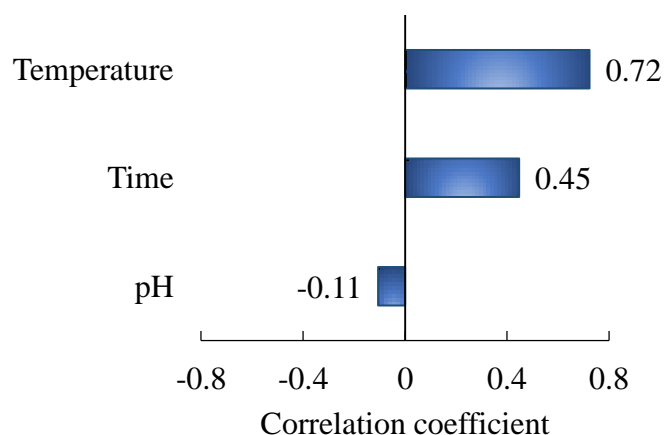
Fig. 6 Sensitivity analysis demonstrating the effect of each experimental parameter on AgNP desorption.

The sensitivity analysis (Fig. 6) indicated that temperature has the most prominent influence on the release of AgNPs from the coated material, followed by time and pH. Although pH is denoted as having a negative impact on migration of AgNPs, this may be due to the increase in migration associated with a decrease in pH from 6.55 to 2.58 with the addition of HAc to dH_2O to form more aggressive food simulants. A significant finding is the lower migration observed for lower temperatures which would suggest the potential use of the coated material for cold storage of goods to limit human exposure to AgNPs from the coated material. According to the sensitivity analysis, pH was found to have limited effect on the release of AgNPs from the nanocoating compared to temperature and time. Although time did have an impact on the release of AgNPs, equilibrium concentrations in the food simulants were reached within 24 hours and therefore limits the number of applications that could benefit from significant shelf life extension while reducing human exposure. This is provided that the coating is not used solely for food safety purposes to reduce harmful food pathogens in short shelf life products, e.g. shellfish.

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Considering the high migration observed from this nanosilver coated material into food simulants, there needs to be adjustments made to the coating manufacture process to minimise the potential risk to humans from oral exposure to AgNPs. In this study, the migration falls into a high migration bracket (5-60 mg/kg$_{food}$) established by the EFSA (2016), that requires extensive data related to human exposure and toxicology. Currently, toxicity studies in the literature for AgNPs are sparse and the limited number of studies present many contradictions. For example, a human *in vivo* 14 day oral study using 10 ppm (5-10 nm) and 32 ppm (25-40 nm) AgNP doses showed no clinically significant changes in human hematologic, urine, metabolic or physical findings (Munger et al., 2014). However, in a 14 day *in vivo* mouse oral toxicity study, 22 nm, 42 nm, 71 nm and 323 nm AgNPs at a 1 ppm dose caused size dependent transport to organs, significant increases in TGF-β levels in serum and B cell distribution (Park et al., 2010). There are also uncertainties surrounding the toxic mechanisms of AgNPs which include; the contribution of ionic and nanoform silver to silver toxicity, the relationship of AgNP coating on toxicity and the main signalling pathways and enzymes responsible for AgNP toxicity (McShan, Ray, & Yu, 2014). Based on the uncertainty with regard to AgNP toxicity, it is difficult to conclude on the potential toxicity to humans from exposure to migrant AgNPs from this experimental nanosilver coated polystyrene material.

In order to minimise human exposure to migrating AgNPs, a reduction in the initial concentration of silver attached in the coating during the manufacture process could be performed. Alternatively, adjustments to the coating manufacture process through coating treatments could improve chemisorption behaviour between the AgNPs and polystyrene substrate, subsequently reducing migration.

5. Conclusions

The momentous task set forth by government agencies to provide a case-by-case testing of ENMs used in food contact materials has the potential to hinder the development and uptake of these ENMs. Predictive migration models are invaluable tools for the safety assessment of nanoparticle food contact materials, as they can be used to bridge gaps in experimental data and provide information on the mechanisms driving nanoparticle migration. In this study, the desorption of AgNPs from a nanosilver coating on polystyrene into food simulants was successfully predicted using a pseudo-second order kinetic sorption model, providing satisfactory determination coefficients ($R^2_{prediction}$ = 0.90) and RMSE = 3.21. The temperature dependence of the rate of desorption was accounted for using the Arrhenius equation up to a temperature of 40 °C. Beyond this temperature, re-adsorption of the silver onto the polystyrene substrate was proposed as a cause for the non-log linear change in desorption rate constant. Using the Arrhenius equation the pre exponential factor and activation energies were determined for the system ranging from 1×10^{-12} to 1×10^{-17} and -38.11 to -68.07 kJ/mol, respectively. Thermodynamic parameters determined using the Van't Hoff equation show that the desorption process is endothermic in nature, is controlled by chemisorption mechanisms and becomes more spontaneous at higher temperatures. These findings indicate that the coating process improves the attachment of AgNPs through chemisorption mechanisms. Therefore, despite the high migration of nanosilver from the coating, there is potential to limit human exposure to nanosilver by enhancing chemisorption behaviour during the nanosilver coating manufacture, subsequently improving AgNP attachment.

Following migration studies, spherical AgNPs were discovered in dH_2O by TEM analysis, however, this could be as a result of formation of AgNPs during the drying process.

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No nanoparticles were found in the 3% HAc food simulant following migration studies. Considering gaps in knowledge related to AgNP toxicity in the human body it is difficult to conclude on the safety of the AgNP coated polystyrene material.

In this work only one AgNP size, shape and surface coating was used in the production of the nanocoating. It is recommended that future studies investigate any potential size, shape and surface coating dependent changes in desorption rates by applying nanoparticles with a combination of these parameters in the nanocoating manufacture. In addition, the desorption model should be investigated for its applicability to predict the migration of nanoparticles from nanocoatings into real food matrices, to identify possible interactions between nanoparticles and components of food.

Conflict of Interest

The authors declare that they have no conflict of interest.

References

Akpomie, K. G., Dawodu, F. A., & Adebowale, K. O. (2015). Mechanism on the sorption of heavy metals from binary-solution by a low cost montmorillonite and its desorption potential. *Alexandria Engineering Journal, 54*(3), 757-767.

Al-Rashdi, B., Tizaoui, C., & Hilal, N. (2012). Copper removal from aqueous solutions using nano-scale diboron trioxide/titanium dioxide (B2O3/TiO2) adsorbent. *Chemical Engineering Journal, 183*, 294-302.

Amenta, V., Aschberger, K., Arena, M., Bouwmeester, H., Botelho Moniz, F., Brandhoff, P., Peters, R. J. (2015). Regulatory aspects of nanotechnology in the agri/feed/food sector in EU and non-EU countries. *Regulatory Toxicology and Pharmacology, 73*(1), 463-476.

Azlin-Hasim, S., Cruz-Romero, M. C., Cummins, E., Kerry, J. P., & Morris, M. A. (2016). The potential use of a layer-by-layer strategy to develop LDPE antimicrobial films coated with silver nanoparticles for packaging applications. *Journal of Colloid and Interface Science, 461*, 239-248.

Baner, A., Brandsch, J., Franz, R., & Piringer, O. (1996). The application of a predictive migration model for evaluating the compliance of plastic materials with European food regulations. *Food Additives & Contaminants, 13*(5), 587-601.

Begley, T. (1997). Methods and approaches used by FDA to evaluate the safety of food packaging materials, *Food Additives & Contaminants*, 14(6-7), 545-553.

Bott, J., Störmer, A., & Franz, R. (2014b). A model study into the migration potential of nanoparticles from plastics nanocomposites for food contact. *Food Packaging and Shelf Life, 2*(2), 73-80.

33

Chen, D., Qiao, X., Qiu, X., & Chen, J. (2009). Synthesis and electrical properties of uniform silver nanoparticles for electronic applications. *Journal of Materials Science, 44*(4), 1076-1081.

Crini, G., & Badot, P.-M. (2008). Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature. Progress in Polymer Science, 33(4), 399-447.

Dalal, R. C. (1974). Desorption of soil phosphate by anion- exchange resin. *Communications in Soil Science and Plant Analysis, 5*(6), 531-538.

Desireddy, A., Conn, B. E., Guo, J., Yoon, B., Barnett, R. N., Monahan, B. M., . . . Bigioni, T. P. (2013). Ultrastable silver nanoparticles. *Nature, 501*(7467), 399-402.

EFSA (2006). Opinion of the Scientific Panel on food additives, flavourings, processing aids and materials in contact with food (AFC) on a request related to a 12th list of substances for food contact materials. *The EFSA Journal*. 2(11), 1-21.

EFSA (2011). Scientific Opinion. Guidance on the risk assessment of the application of nanoscience and nanotechnologies in the food and feed chain. *The EFSA Journal*. 5(5), 1-36.

EFSA (2016). Safety assessment of the substance zinc oxide, nanoparticles for used in food contact materials. *The EFSA Journal*. 14(3), 1-8.

EI Boujaady, H., Mourabet, M., Bennani-Ziatni, M., & Taitai, A. (2014). Adsorption/desorption of Direct Yellow 28 on apatitic phosphate: Mechanism, kinetic and thermodynamic studies. *Journal of the Association of Arab Universities for Basic and Applied Sciences, 16*, 64-73.

European Commission (2011). Commission Regulation (EU) No. 10/2011 of 14th January 2011 on plastic materials and articles intended to come into contact with food. *Official Journal of the European Union*. 1-132.

European Commission (2012). Commission Regulation (EU) No. 1183/2012 of 30th November 2012 amending and correcting Regulation (EU) No. 10/2011 on plastic materials and articles intended to come into contact with food. *Official Journal of the European Union*. 1-5.

European Commission (2015) Commission Regulation (EU) No 2015/174 of 5 February 2015 amending and correcting Regulation (EU) No 10/2011 on plastic materials and articles intended to come into contact with food. *Official Journal of the European Union*. 1-8.

European Commission (2016) Commission Regulation (EU) No 2016/1416 of 24 August 2016 amending and correcting Regulation (EU) No 10/2011 on plastic materials and articles intended to come into contact with food. *Official Journal of the European Union*. 1-21.

FAO (2011). Global food losses and food waste – Extent, causes and prevention. Rome.

Febrianto, J., Kosasih, A. N., Sunarso, J., Ju, Y.-H., Indraswati, N., & Ismadji, S. (2009). Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: A summary of recent studies. *Journal of Hazardous Materials, 162*(2–3), 616-645.

Franz, R., & Störmer, A. (2008). Migration of Plastic Constituents. In Otto, P., & Baner, A., (Eds.), *Plastic Packaging: Interactions with Food and Pharmaceuticals*. (pp. 349-409). Weinheim, Wiley-VCH Verlag GmbH & Co.

Gao, Y., Jiang, P., Liu, D. F., Yuan, H. J., Yan, X. Q., Zhou, Z. P., . . . Shen, D. Y. (2004). Evidence for the Monolayer Assembly of Poly(vinylpyrrolidone) on the Surfaces of Silver Nanowires. The Journal of Physical Chemistry B, 108(34), 12877-12881.

Hahn, A., Brandes, G., Wagener, P., & Barcikowski, S. (2011). Metal ion release kinetics from nanoparticle silicone composites. *Journal of Controlled Release, 154*(2), 164-170.

Hannon, J. C., Kerry, J., Cruz-Romero, M., Morris, M., & Cummins, E. (2015). Advances and challenges for the use of engineered nanoparticles in food contact materials. *Trends in Food Science & Technology, 43*(1), 43-62.

Hannon, J. C., Kerry, J. P., Cruz-Romero, M., Azlin-Hasim, S., Morris, M., & Cummins, E. (2016a). Assessment of the migration potential of nanosilver from nanoparticle-coated low-density polyethylene food packaging into food simulants. *Food Additives & Contaminants: Part A, 33*(1), 167-178.

Hannon, J. C., Kerry, J. P., Cruz-Romero, M., Azlin-Hasim, S., Morris, M., & Cummins, E. (2016b). Human exposure assessment of silver and copper migrating from an antimicrobial nanocoated packaging material into an acidic food simulant. *Food and Chemical Toxicology, 95*, 128-136.

Hannon, J., Azlin-Hasim, S., Cruz-Romero, M., Kerry, J., Morris, M., & Cummins, E. (2016) Artificial Neural Networks as a tool to predict the migration of silver from antimicrobial nano-coated films. In Gerrille, P. (Ed.) FOODSIM'2016 Conference Proceedings, Eurosis, Belgium (pp. 38-43).

Ho, Y. S., & McKay, G. (1999). Pseudo-second order model for sorption processes. *Process Biochemistry, 34*(5), 451-465.

Kuorwel, K. K., Cran, M. J., Orbell, J. D., Buddhadasa, S., & Bigger, S. W. (2015). Review of Mechanical Properties, Migration, and Potential Applications in Active Food Packaging Systems Containing Nanoclays and Nanosilver. *Comprehensive Reviews in Food Science and Food Safety, 14*(4), 411-430.

Krystosiak, P., Tomaszewski, W., & Megiel, E. (2017). High-density polystyrene-grafted silver nanoparticles and their use in the preparation of nanocomposites with antibacterial properties. *Journal of Colloid and Interface Science, 498*, 9-21.

36

Lagergren, S. (1898). Zur theorie der sogenannten adsorption gelˆster stoffe, Kungliga Svenska Vetenskapsakademiens. *Handlingar.* 24(4), 1-39.

Largitte, L., & Pasquier, R. (2016). A review of the kinetics adsorption models and their application to the adsorption of lead by an activated carbon. *Chemical Engineering Research and Design, 109*, 495-504.

Liu, J., & Hurt, R. H. (2010). Ion Release Kinetics and Particle Persistence in Aqueous Nano-Silver Colloids. *Environmental Science & Technology, 44*(6), 2169-2175.

Low, M. J. D. (1960). Kinetics of Chemisorption of Gases on Solids. *Chemical Reviews, 60*(3), 267-312.

Loza, K., Diendorf, J., Sengstock, C., Ruiz-Gonzalez, L., Gonzalez-Calbet, J. M., Vallet-Regi, M., . . . Epple, M. (2014). The dissolution and biological effects of silver nanoparticles in biological media. *Journal of Materials Chemistry B, 2*(12), 1634-1643.

Ma, R., Levard, C., Marinakos, S. M., Cheng, Y., Liu, J., Michel, F. M., . . . Lowry, G. V. (2012). Size-Controlled Dissolution of Organic-Coated Silver Nanoparticles. Environmental Science & Technology, 46(2), 752-759.

Maynard, A., & Michelson, E. (2014). The Nanotechnology Consumer Products Inventory. http://www.nanotechproject.org/cpi/ Accessed 15 September 2016.

McShan, D., Ray, P. C., & Yu, H. (2014). Molecular toxicity mechanism of nanosilver. *Journal of Food and Drug Analysis, 22*(1), 116-127.

Mohammed Fayaz, A., Balaji, K., Girilal, M., Kalaichelvan, P. T., & Venkatesan, R. (2009). Mycobased Synthesis of Silver Nanoparticles and Their Incorporation into Sodium Alginate Films for Vegetable and Fruit Preservation. *Journal of Agricultural and Food Chemistry, 57*(14), 6246-6252.

Munger, M. A., Radwanski, P., Hadlock, G. C., Stoddard, G., Shaaban, A., Falconer, J., . . . Deering-Rice, C. E. (2014). In vivo human time-exposure study of orally dosed

commercial silver nanoparticles. *Nanomedicine: Nanotechnology, Biology and Medicine, 10*(1), 1-9.

Park, E.-J., Bae, E., Yi, J., Kim, Y., Choi, K., Lee, S. H., . . . Park, K. (2010). Repeated-dose toxicity and inflammatory responses in mice by oral administration of silver nanoparticles. *Environmental Toxicology and Pharmacology, 30*(2), 162-168.

Pongnop, W., Sombatsompop, K., Kositchaiyong, A., & Sombatsompop, N. (2011). Effects of incorporating technique and silver colloid content on antibacterial performance for thermoplastic films. Journal of Applied Polymer Science, 122(5), 3456-3465.

Samadi, N., Hasanzadeh, R., & Rasad, M. (2015). Adsorption isotherms, kinetic, and desorption studies on removal of toxic metal ions from aqueous solutions by polymeric adsorbent. *Journal of Applied Polymer Science, 132*(11),

Schindelin, J., Arganda-Carreras, I., Frise, E., Kaynig, V., Longair, M., Pietzch, T., Preibisch, S., Rueden, C., Saalfeld, S., Schmid, B. (2012). Fiji: an open-source platform for biological-image analysis. Nature Methods, 9(0), 676-682.

Simon, P., Chaudhry, Q., & Bakos, D. (2008). Migration of Engineered Nanoparticles from Polymer Packaging to Food - A Physicochemical View. *Journal of Food and Nutritional Research, 47*(3), 105 - 113.

Smith, J. N., Meadows, J., & Williams, P. A. (1996). Adsorption of Polyvinylpyrrolidone onto Polystyrene Latices and the Effect on Colloid Stability. Langmuir, 12(16), 3773-3778.

Souza, V. G. L., & Fernando, A. L. (2016). Nanoparticles in food packaging: Biodegradability and potential migration to food—A review. *Food Packaging and Shelf Life, 8*, 63-70.

von Goetz, N., Fabricius, L., Glaus, R., Weitbrecht, V., Günther, D., & Hungerbühler, K. (2013). Migration of silver from commercial plastic food containers and implications for

consumer exposure assessment. *Food Additives & Contaminants. Part A: Chemistry, Analysis, Control, Exposure & Risk Assessment, 30*(3), 612-620.

Weber, W.J. and Morris, J.C. (1963). Kinetics of adsorption carbon from solutions. Journal Sanitary Engeering Division Proceedings. *American Society of Civil Engineers.* 89, 31-6

Youssef, A. M., & Abdel-Aziz, M. S. (2013). Preparation of Polystyrene Nanocomposites Based on Silver Nanoparticles Using Marine Bacterium for Packaging. Polymer-Plastics Technology and Engineering, 52(6), 607-613.

Zhang, Y., Chi, H., Zhang, W., Sun, Y., Liang, Q., Gu, Y., & Jing, R. (2014). Highly Efficient Adsorption of Copper Ions by a PVP-Reduced Graphene Oxide Based On a New Adsorptions Mechanism. Nano-Micro Letters, 6(1), 80-87

Industrial Relevance

The use of antimicrobial packaging has the potential to reduce food spoilage and risk from pathogenic microorganisms while reducing food waste by extending the shelf life of food products. Coating of antimicrobial silver nanoparticles (AgNPs) to polymer surfaces is a highly advantageous technology as microbial contamination predominantly occurs on the surface of fresh and processed food products. However, uncertainty related to the potential release of nanoparticles from food packaging materials, subsequent potential human exposure and toxicology is a barrier to the uptake of these novel materials. In the European Union, where the safety assessment of these materials is stringent, mathematical models used to predict the worst case migration of nanoparticles from food packaging materials have supported the acceptance of some nanomaterials for use in food packaging. The performance of a number of desorption models was evaluated to predict the release of AgNPs from AgNP coated polystyrene. The model identified factors that influenced migration and possible industrial applications for the developed material to minimise human exposure. The study highlights the potential benefits of using predictive models to assess migration of NPs from polymers into food simulants instead of time consuming and expensive migration studies.

Highlights

- Nanoparticles were identified exemplarily in distilled water after migration studies at 70 °C for 2 h.

- Pseudo-second order sorption model provided best prediction of silver desorption.

- Temperature had the most significant effect on silver migration, followed by time and pH.