Evaluation of Absorption Kinetics of Oxygen Scavenger Sachets Using Response Surface Methodology

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SUMMARY

The performance of oxygen scavengers can be influenced by several conditions, such as temperature (T) and relative humidity (RH), which are considered to be the two major factors. Therefore, the development of new scavengers requires the study of their performance, with these conditions varied. In this paper, the response surface methodology (RSM) was used to study the performance of a newly developed oxygen scavenger sachet and to model the influences of T and RH and their interaction on the absorption capacity and rate constant of the developed sachet. Commercial oxygen scavenger sachets were used for comparison purposes. The oxygen absorption capacity and rate constant were evaluated with a 2² factorial design with a central point. The results showed that each absorber sachet presented a different behaviour and there were significant interactions between T and RH; so, the RSM was the most appropriate for these studies. The developed sachet presented a better performance compared with the commercial ones at 23°C and 53% RH, which represents the condition for commercialization at room temperature of foods of intermediary water activity, while in the extreme conditions (100% RH and 37°C) all sachets present a similar absorption capacity. Copyright © 2010 John Wiley & Sons, Ltd.

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INTRODUCTION

Many packaged foods are sensitive to oxygen (O_2), which can cause oxidation, change in flavour, colour and odour, and nutrient loss. Indeed, oxygen also facilitates the growth of aerobic bacteria, moulds and insects.¹ In order to minimize these problems, many technologies have been developed to eliminate or reduce the levels of O_2 inside packs. Modified atmosphere packaging and vacuum packaging have been widely adopted to exclude oxygen from the headspace. However, the efficiency of these methods is limited,² and O_2 residual concentrations from 2 to 3% are commonly observed.³ More appropriate approaches are the use of O_2 scavengers in the package that are able to reduce and maintain the O_2 concentration to levels lower than 0.01%, if the package remains intact.^{4,5}

Structurally, the O_2 scavenging component of a package can take the form of a sachet, a label, a film (incorporation of scavenging agent into the packaging material), a card or a closure liner.^{1,6} Nowadays, most of the commercially available O_2 scavengers are based on iron oxidation. The main reactions involved in this process can be expressed in Equations 1–4.⁷ The importance of relative

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humidity (RH) on iron oxidation can be observed directly in reactions 2 and 4. It should be noticed that despite reactions 1 to 4 being relatively simple, the mechanism of the O_2 scavenging is complex and involves phase transitions, oxidation-reduction reactions and moisture transfer of other components to iron powder.

$$Fe \to Fe^{+2} + 2e^{-} \tag{1}$$

$$1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$$
⁽²⁾

$$\operatorname{Fe}^{+2} + 2\operatorname{OH}^{-} \to \operatorname{Fe}(\operatorname{OH})_{2}$$
 (3)

$$2Fe(OH)_2 + 1/2O_2 + H_2O \rightarrow 2Fe(OH)_3 \tag{4}$$

To prevent the food contamination by different constituents of the sachet, such as active agent (powder iron, zinc powder, copper powder or mixture thereof), particulate matter (diatomaceous earth, perlite, zeolite, activated alumina, silica gel, activated carbon, activated clay, sand, pebble and mixtures thereof) and other components of the mixture, it is recommended that the material of the sachet present a high mechanical strength, good sealing and consistent pore structure in each layer of the sachet. The high permeability film to oxygen and water vapour, as well as pore structure, allow oxygen and moisture flow from the headspace of the packaging to the components of the sachet so that they can act, adsorbing the oxygen.⁸⁻¹¹ These sachets are available in a variety of O_2 absorbing capacities, varying from 20 to 2000 ml.⁴ According to Miltz and Perry,¹² the commercial scavengers present an absorption capacity much higher than the nominal capacity provided by the manufacturers. Brandon et al.¹³ verified that the low oxygen concentration present in the packed product is an important factor that can influence the absorption capacity of O_2 and the reproducibility of the sachet. Although O_2 scavengers are commercially available and commonly used, information on their absorption characteristics is still limited in the literature. The works of Galdi et al.¹⁴ and Foltynowicz et al.¹⁵ are examples of development and study of active agents iron based on oxygen scavengers, respectively. Scavengers can be characterized by their two main properties: absorption capacity and rate constant. The absorption capacity is the maximum quantity of O_2 that can be absorbed, and is a property usually well documented for commercial scavengers, because these systems are generally designed to remove a specific amount of O_2 from the packages. The rate constant of absorption is inversely related to the elapsed time to reach the absorption capacity, and few studies have been performed to evaluate this property and the effects of temperature (T) and RH in the scavenger performance - parameters of prime importance for food applications. Tewari *et al.*¹⁶ and Charles *et al.*¹⁷ discussed the capacity and O₂ absorption kinetics at different T and RH. However, the T and RH relation to the rate constant and absorption capacity was not clear for the different scavengers studied.

The study and optimization of multiple variables that affect a system or processes are one of the main research fields of chemometrics, where experimental design, genetic algorithms and response surface methodology (RSM) are examples of optimization methods applied in many research areas.^{18,19} The application of these methods for packaging development and optimization can be observed in several papers. Peng *et al.*²⁰ applied RSM for the optimization of the feed compositions of biodegradable packaging foams, where the authors conclude that the radial expansion ratio, bulk density, compressibility and spring index of biodegradable cushioning extrudates can be effectively optimized using RSM with a minimum number of experiments.^{20,21} Limbo and Piergiovanni²² applied a central composite design and RSM to study the influence of high oxygen partial pressures in combination with ascorbic and citric acid on loss of some quality attributes of sliced potatoes. The study was able to show that the respiration rate and the volatile compounds production of sliced potatoes were strongly influenced by the initial level of O₂.²²

In this paper, the development of an oxygen scavenger sachet for applications in food products with intermediate water activity, such as cured meat products, is described. The performance of the developed sachet and two commercial sachets usually applied for foods presenting these characteristics are discussed. For a better characterization and comparison of the three sachets evaluated, the absorption capacity and the rate constant for oxygen absorption were evaluated at different T and RH

and a detailed study to model the influence of these factors and their interaction was also described. Kinetics curves were fitted to O_2 absorption during time, making it possible to predict the absorption capacity and rate constant in the conditions established by a 2^2 factorial design with a central point. RSM was used to model the behaviour of each response variable (absorption capacity and rate constant) from the factors T and RH.

MATERIALS AND METHODS

The commercial oxygen scavengers used as reference sachets were O-Buster (Hsiao Sung Non-Oxygen Chemical, Taichung, Taiwan) and Oxyfree 504 A (TIANHUA SCIENCE, Nanjing, China), commonly used in Brazil to preserve cured meat. The nominal capacities of each sachet according to the manufacturers were 20 and 30 ml of oxygen, respectively. Both sachets were based on iron powder and donated by DIDAI Technology Ltd, a product distributor in Brazil.

The sachet developed at the university laboratory was designed to have a nominal capacity of 20 ml and after preparation it presented approximately the same weight as O-Buster (approximately 1.50 g). It is based on iron powder as the active agent (as are the commercial sachets) with a controlled particle size of 325 Mesh. The other constituents used for the sachet preparation were: the active agent iron powder (Aksell Química, Indaiatuba, Brazil), particulate matter constituted by a synthetic zeolite (W.R. Grace Davison Chemical Division, Baltimore, Maryland, USA), NaCl, CaCO₃. The final mixture (1.5 g) was packed in an envelope consisted of a film composed by PET/PE/Paper/PE 110 μ m thick. The PET and PE in the outer and inner layers were microperforated, presenting 25 and 50 holes per square centimetre, with hole sizes of 400 and 250 μ m in diameter, respectively.

The preparation of the oxygen scavenger was done in two steps. First, component A was prepared by weighing a mass of reduced iron powder, and the equivalent of 2% of this mass was added to the NaCl aqueous solution, at a concentration of 20% (w/v). Then, the mixture was homogenized and placed in an oven at 80°C for 3 h for the removal of all water content. After that, a mass of 2% calcium carbonate was added to the mixture, which was dried later. The mixture was homogenized and was placed again in an oven for at least 1 h. After this step, component B was prepared by weighing a mass of the synthetic zeolite, and a sufficient volume of distilled water was added for the immersion of the particulate matter. Subsequently, the suspension was stirred and filtered. Afterwards, the filtered component B was placed in an oven at 60°C until it achieved the desired 50%(w/w) of moisture content in relation to the initial mass of particulate matter.

After the preparation of components A and B, 0.75 g of each component was separately weighed, and then mixed in an inert environment of nitrogen gas. Then, 1.50 g of the mixture was placed inside a sachet of dimensions 3×4 cm, which was then sealed. The sachets were vacuum packaged and stored in high barrier multilayer film (PET/PE/PAPER/PE) using a Selovac 200 vacuum (Selovac, São Paulo, Brazil) sealer to prevent contact with oxygen from the air before performing tests.

In the oxygen absorption tests, each sachet was set within a leak-free absorption cell (Figure 1), consisting of a 600 ml glass jar hermetically closed with metal cap, fitted with a septum in order to collect the gas samples.

The RH inside the absorption cells was generated by saturated solutions of lithium chloride, magnesium nitrate and potassium sulphate (ASTM E 104 - 02), which corresponds to 11, 53 and 98% of RH, respectively with temperatures varying from 0 to 50°C. The RH in the glass containers was confirmed through analyses of the water activity in a Decagon CX-2T (Pullman, WA, USA) operating at $20 \pm 2^{\circ}$ C in quadruplicate. In these analyses, a small volume of each saturated solution was added to the Decagon cell and the water activity was determined after the equilibrium had been reached in the equipment.

Sachets (commercial or developed) were placed inside adsorption cells containing each salt solution and kept at temperatures of 4, 23 and 37°C. The tests were performed in duplicate according to a 2^2 factorial design with central point for evaluation of the influence of the RH and T.

The volume of O_2 absorbed by the sachet was determined by a gas chromatography (GC) system (Shimadzu, Tokyo, Japan) consisted of a equipped with a molecular sieve 5A column (Supelco, Bellefonte, PA, USA) and a thermal conductivity detector with the follows conditions: injector (84°C),



Figure 1. Hermetic absorption cell with a saturated salt solution for relative humidity control.

oven (82°C), detector (140°C) and argon used as the carrier gas. The GC determination was accomplished with three certified standards obtained from White Martins (Praxair, Campinas, Brazil) with 1.01, 4.99 and 20.00% of O_2 . By injecting 0.400, 0.300, 0.200 and 0.400 ml of the certified standards with 1.01, 4.99, 20.00 and 20.00% of O_2 , respectively, four different concentrations of O_2 were obtained (0.002, 0.015, 0.040 and 0.080 ml, respectively). A linear regression relating the peak area of each standard sample and the amount of O_2 in ml present in each aliquot injected was performed daily. The correlation coefficients of the regressions were often 0.999 or better. The analysis of the amount of O_2 present in the absorption cell was performed by injecting 0.300 ml of the gas present in the cell. To evaluate the absorption kinetic of the sachet, aliquots were withdrawn at pre-established times. Most of the experiments were performed during 50 h or less until the residual O_2 inside the cell reached a constant value. Response variables were defined as the absorption capacity (ml) and rate constant estimated after 24 h of analyses.

DATA ANALYSIS

The results obtained by GC were units of percentage of O_2 into the absorption cell over time. Since the rate constant is determined by the relation of the absorbed volume of O_2 in ml over time, these percentages should be appropriately converted to ml before the analyses of the absorption kinetics. This conversion was accomplished by Equation 5:

$$V_{02} = [(\%O_2)_i - (\%O_2)_i] \times 0.01 V_L$$
(5)

where: V_{O2} is the volume of oxygen absorbed by the sachet (ml) at time t; (%O₂)_i is the initial concentration of O₂ in the cell (%); (%O₂)_t is the concentration of O₂ in the cell (%) after a *t* time that the sachet is in the cell; 0.01 is a factor for conversion percentage to volume; and V_L is the free volume in the cell (ml) discounting the volume of saline solution and the volume occupied by the sachet. According to Tewari *et al.*⁸ and Charles *et al.*,⁹ a kinetic curve expressed by Equation 6 can efficiently explain the experimental results for the absorption of O₂ over time for the sachets.

$$(V_{O_2}) = (V_{O_2})_{Max} - (V_{O_2})_{Max} \cdot e^{-kt}$$
 (6)

where: (V_{O_2}) is the volume of oxygen absorbed by the sachet (ml) at time t; $(V_{O_2})_{Max}$ is the maximum volume of oxygen absorbed (ml); k is constant rate of absorption (h⁻¹) and t is the time (h). Charles *et al.*⁹ indicate that the absorption process expressed by Equation 6 may be considered a first-order reaction. To find the best kinetic curve that fits the data, Equation 6 was fitted in each experiment using Matlab[®] 7.0 and the optimization toolbox.

The variation of the O_2 absorption capacity and rate constant as a function of T and RH were modelled by the RSM. Different models were fitted for each kind of sachet studied and response (absorption capacity or rate kinetic). This procedure was necessary because of the complexity of each model, and the number of significant parameters in each situation may be different. The statistical data treatment was accomplished with the Software Statistica version 7.0. Following the standard procedure of the RSM, linear models were fitted and their performance evaluated by the analysis of variance (ANOVA). If the linear model did not present satisfied results, then a more complex model (i.e. a quadratic model) could be tested and the results would be evaluated.

The statistical significance and lack of fit in the models were assessed by *F*-tests with the mean square determined in ANOVA. For the significance of the model, the $F_{calculated}$ was determined by ratio of the mean square of the regression and mean square of the residue (MS_R/MS_r), while the test for lack of fit the $F_{calculated}$ was determined by the ratio of the mean square of the lack of fit and the mean square of the pure error (MS_{lof}/MS_{pe}), respectively. These calculated *F*-values were compared with the $F_{tabulated}$ values at 95% confidence level and the appropriate number of degrees of freedom.¹⁴

RESULTS AND DISCUSSION

Table 1 presents the results obtained for O_2 absorption capacity and rate constant (estimated with Equation 6). It can be observed that the three sachets presented different behaviours from the environmental factors T and RH over the first 24 h of analysis. The results for absorption capacity show that only O-Buster reached the nominal capacity in all studied conditions. The Oxyfree 504 A at the lower RH (11%) and extremes temperatures (4 and 37°C) did not reach its nominal capacity. Considering the developed sachet only at the lower condition of both T and RH, 4°C and 11%, the nominal

Sachet (NC) ^a	Variable – T (°C)		Variable – RH (%)			
	Actual	Coded	Actual	Coded	$V_{02} \ (ml)^b$	$k (h^{-1})^b$
O-Buster	4	_	11	_	28.7 (±2.7)	0.15 (±0.05)
^a (20 ml)	37	+	11	_	40.4 (±1.5)	0.92 (±0.09)
	4	_	98	+	45.7 (±7.7)	0.07 (±0.00)
	37	+	98	+	95.0 (±0.3)	0.34 (±0.01)
	23	0	53	0	45.6 (±8.3)	0.48 (±0.04)
Oxyfree 504 A	4	_	11	_	8.7 (±0.0)	0.50 (±0.09)
^a (30 ml)	37	+	11	-	16.6 (±4.2)	1.50 (±0.01)
	4	_	98	+	69.5 (±7.4)	0.03 (±0.00)
	37	+	98	+	99.0 (±0.0)	0.47 (±0.00)
	23	0	53	0	45.7 (±0.4)	0.16 (±0.06)
Developed	4	_	11	_	13.7 (±0.0)	0.05 (±0.00)
^a (20 ml)	37	+	11	_	20.3 (±1.5)	0.09 (±0.00)
	4	_	98	+	26.4 (±3.8)	0.03 (±0.01)
	37	+	98	+	100.6 (±6.1)	0.07 (±0.05)
	23	0	53	0	85.5 (±2.3)	0.10 (±0.04)

Table	1. Values	of actual	and coded	variables	: Temper	rature (T)) and :	relative	humidity	(RH)	and re	sults
for the	response	variables	oxygen ab	sorption a	capacity	$(V_{O2.})$ and	d rate	constan	t (k) after	24 h	of ana	lyses

^aNominal capacity.

^bEstimation of the standard deviations of the duplicate measurements presented in parenthesis.

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capacity was not achieved. It is important to notice that the results obtained for central point of the experimental design (23°C and 53%) show that the developed sachet presented a capacity of O_2 absorption almost twice of those for the commercials sachets. This is a desirable characteristic of O_2 scavengers used for preservation of foods presenting intermediate water activity at ambient conditions. At the higher T and RH conditions, 37°C and 98%, respectively, it was observed that the three sachets presented approximately the same volume of O_2 absorbed, which correspond to about 5 times the nominal capacity for O-Buster and the developed sachet and approximately 3.3 times for Oxyfree 504 A.

The ANOVA results for the linear models of the absorption capacity of the commercial sachets O-Buster and Oxyfree 504A are presented in Tables 2 and 3, respectively. Since the explained variances were very close to the maximum explained variances, the linear models explain almost all systematic variation of the results for the commercial sachets. Significance tests for regression and lack of fit also demonstrate the good performance of the linear models in these cases, where the estimated *F*-values for the significance of the regression and lack of fit were, as expected, respectively larger and lower than the critical values of the tabulated distribution.

The results of the linear model for the developed sachet are presented in Table 4. It can be observed that in this case, the linear model did not present good results, since the explained variance was

Table 2. Analysis of variance (ANOVA) for the results of the linear model for the absorption capacity of O_2 of the O-Buster sachet.

Source of variation	SS ^a	DF^{b}	MS ^c	$F_{calculated}$	F _{Tabulated}
Regression	5137.68	3	1712.56	47.92	5.14
Residuals	214.42	6	35.74		
Lack of fit	75.35	1	75.45	2.71	6.61
Random error	139.07	5	27.81		
Total	5352.11	9	_	_	-
Explained variance: 95.99	9%	Maximum explai	ned variance: 97.40%		

^a square sum, ^b degrees of freedom and ^c mean square.

Table 3. Analysis of variance (ANOVA) for the results of the linear model for the absorption capacity of O_2 of the Oxyfree 504 A sachet.

Source of variation	SS ^a	DF^{b}	MS ^c	F _{calculated}	F _{Tabulated}
Regression	11181.40	3	3727.13	264.71	5.14
Residuals	84.46	6	14.08		
Lack of fit	12.25	1	12.25	0.85	6.61
Random error	72.21	5	14.44		
Total	11265.86	9	_	_	_
Explained variance: 99.25	5%		Maximum explai	ned variance: 99.36%	

^a square sum, ^b degrees of freedom and ^c mean square.

Table 4. Analysis of variance (ANOVA) for linear and quadratic model (parenthesis values) for the absorption capacity of O_2 of the developed sachet.

Source of variation	SS ^a	DF^{b}	MS ^c	$F_{calculated}$	F _{Tabulated}
Regression	9877 (13153)	3 (4)	3292 (3288)	5.9 (277)	4.76 (5.19)
Residuals Lack of fit Random error	3336 (59) 3276 (—) ^d 60 (60)	6 (5) 1 (0) 5 (5)	556 (12) 3276 (—) ^d 12 (12)	273 (—)	6.61
Total	13213	9 (9)	_	_	_
Explained variance: 74.	75% (99.55%)	Maximum expla	ined variance: 99.5	5%	

^a square sum, ^b degrees of freedom, ^c mean square and ^d undetermined values.

74.75%, while the maximum explained variance was 99.55%. The estimated *F*-values for regression and lack of fit significance tests were lower and larger than the tabulated values, respectively, confirming the inadequacy of the linear model in this system. To circumvent this problem and to obtain a model that describes this data satisfactorily, a quadratic model was fitted in the results for the development sachet and its performance also evaluated by ANOVA (values between parentheses in Table 4). Since the quadratic model presents five parameters in its equation, which is equal to the number of different experiments of the experimental design used, it was not possible to evaluate the lack of fit of the model. For the same reason, it can be observed that the maximum explained variance (99.55%) was equal to the explained variance by the model, indicating that this model fits all systematic variation of the data.

The fitted models for the absorbed volume of O_2 for O-Buster, Oxyfree 504A and the developed sachet are represented by Equations 7–9, respectively:

$$V_{0_2} = 51.07 + (15.28 \times T) + (17.90 \times RH) + 9.41(T \times RH)$$
(7)

$$V_{0_2} = 47.91 + (9.34 \times T) + (35.8 \times RH) + 5.39(T \times RH)$$
(8)

$$V_{02} = 85.49 + (20.21 \times T) + (23.25 \times RH) + 16.92(T \times RH) + 45.26(Q)$$
(9)

where V_{O_2} is the absorbed volume of O_2 in ml, *T* and *RH* are the coded values of T and RH, respectively; and *Q* is the quadratic term that models the nonlinear information of both T and RH in the developed sachet. It is interesting to note that all the obtained equations showed a significant interaction coefficient.

It can be observed in Equation 9 that the coefficient of Q presented the largest value, confirming the non-linear behaviour of T and RH for the developed sachet. It is interesting to see from the obtained values for the coefficients in Equations 7–9 that contributions of T and RH in the three systems are significantly different.

For O-Buster (Equation 7) and the developed sachet (Equation 9), the values for the coefficients of *T* and *RH* are close, while for Oxyfree 504 A (Equation 8), the coefficient for *RH* is significantly larger than for *T*, indicating that the absorption capacity of Oxyfree 540A presents a higher dependence for RH than T. This distinct behaviour can be attributed to the different composition, preparation method, raw materials, particle size and nominal capacities of the three kinds of sachets. These results indicated that in the development process of new sachets for O_2 scavenger, the study of the influence of T and RH should be performed for each different sachet.

The responses surfaces obtained by Equations 7–9 are presented in Figure 2. It can be observed in Figure 2b that the maximum absorption of oxygen for the commercial sachets was obtained when the two variables are in their maximum levels, 37° C and 98% (Figures 2a and b). However, high T and RH conditions are not suitable for nutritious products, since an acceleration of the microbiologic, enzymatic and chemical degradation of the foods are induced. These conditions were applied just to evaluate the influence of these factors in the O₂ absorption capacity and the rate constant of the sachets. Note that for the developed sachet (Figure 2c). the maximum O₂ absorption occurs at 98% RH and approximately 27°C, showing that this sachet presents, a better performance than commercials at lower values of T.

Figure 2b also shows that Oxyfree 504 A is less dependent of T than RH, since at high RH, high O_2 absorptions are obtained even at lower values of T.

O-Buster (Figure 2a) presented a similar influence of T and RH and a linear behaviour over the capacity of absorption, while for the developed sachet, it was clearly verified as a non-linear behaviour demonstrated by the curvature of the surface (Figure 2c). It is important to observe that for the developed sachet, the region where the largest values of absorption were obtained, was next to the central region of the surface, indicating a better performance around 23°C and 53% when compared to the commercial sachets. A possible explanation for the best performance of the developed sachet at 23°C and 53% is the moisture already present in the sachet, since in the preparation procedure of the experimental sachet one of the two components mixed already presents 50% (w/w) of moisture. This is probably one of the main reasons that explains the significant better performance of this sachet in



Figure 2. Responses surfaces of absorption capacity VO_2 for O-Buster (a), Oxyfree 504 A (b) and developed sachet (c).

the environmental conditions, since the sachet is less dependent of the humidity of the packed product. Considering the extreme conditions (100% of humidity and 37°C), it was observed that both the commercial and the experimental sachets present a good performance for the absorption capacity. Figure 2 shows that almost 120 ml of O_2 were absorbed with all sachets.

The statistical analysis of the O_2 absorption rate constant data showed that only for O-Buster it was possible to obtain a fitted response surface model (Figure 3). For the other sachets, even considering quadratic models, poor results were observed. The explained variances obtained for the linear models were 97.0, 82.0 and 42.0%, while the maximum explained variances were 98.2, 91.5 and 59.9%, respectively for O-Buster, Oxyfree 504 A and the developed sachet.



Figure 3. Responses surfaces of O₂ absorption rate constant (k) for O-Buster sachet.

Equation 10 represents the fitted linear model for the O-Buster O_2 absorption rate constant, k. The response surface obtained is presented in Figure 3.

$$\mathbf{k} = 0.39 + (0.26 \times T) + (0.16 \times RH) + 0.12(T \times RH)$$
(10)

Figure 3 and Equation 10 show that the O_2 absorption rate constant for O-Buster is more dependent on T than RH, which was different from the one observed for O-Buster O_2 absorption capacity.

Furthermore, as in the absorption capacity modelling, Equation 10 shows a significant interaction coefficient. It is interesting to note that the larger values of rate constant were obtained at higher T and lower RH values, which can be explained by the fast reaching of a constant level of O_2 absorption in this condition (easier observed in Figure 4a). This result shows that the optimum condition for the rate constant is located in a different region of the response surface from the observed for absorption capacity. For O-Buster, the increase in RH causes a decrease in the rate constant but improves the absorption capacity.

Figure 4a–c show the O_2 absorption data as a function of time at the five conditions of the experimental design and their respective kinetic curves determined by Equation 6, for O-Buster, Oxyfree 504 A and the developed sachet, respectively. Through these graphs, the variation of both absorption capacity and the rate constant between sachets can be observed, even for Oxyfree 504 A and the developed sachet, for which good results with the RSM were not obtained.

It can be observed that the commercial sachets presented a higher absorption rate than the developed one at high RH. Comparing the kinetic curves of the three sachets, it can be observed, at central point conditions (T = 23° C and RH = 53%), that the developed sachet presented not only a higher absorption capacity, but also a lower absorption rate compared with the commercial sachets. However, the absorption rate was high enough to reach the minimum capacity of 20 ml in the first 3 h, which ensures a fast consumption of the residual oxygen and its proper application for extending the shelf life of intermediate water activity foods.

CONCLUSION

The results indicated that the response surface methodology can be an efficient tool to investigate the behaviour of rate constant and absorption capacity for O_2 scavenger sachets from T and RH, making it possible to obtain the conditions that optimize the performance of these scavengers. The equations

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Figure 4. Kinetic curves for the absorption of O-Buster (a), Oxyfree 504 A (b) and developed sachet (c). Conditions of T (°C) and RH (%) were: 4°C and 11% (+), 37°C and 11% (o), 4°C and 98% (*), 37°C and 98% (\diamond) and 23°C and 53% (\blacklozenge).

obtained for the surfaces also showed that significant interactions between T and RH were presented in all studied sachets, showing that univariate methods usually used in evaluating these systems could not be appropriate.

The responses surface obtained for the absorption capacity suggested that significant different behaviours may be expected even with scavengers based on the same active agent, with similar

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nominal capacities, which can be attributed to the different formulations, raw materials and size of particles, among other factors involved in sachets development. Therefore, the modelling of the influence of T and RH over the rate constant and absorption capacity should be performed for each different sachet.

At high RH and T, the developed O_2 scavenger presented a better absorption capacity and an inferior (but not impeditive) absorption rate when compared to the commercial ones. However, the developed sachet showed superior results to both parameters at environment conditions around 23°C and 53% RH. Thus, the developed sachet could be indicated for a wider number of food products than the commercial ones, especially for foods presenting intermediate water activity, such as cured meat and products stored at ambient conditions. The paper also confirms that the correct choice of the type of sachet should take into account the water activity of the food and the temperature of transport, storage and distribution.

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