Cleaning Kinetic Model for Carbohydrates- and Protein-based Stains in Automatic Dishwasher

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Abstract

A mechanistic model capable of describing the cleaning mechanism of protein-based and carbohydrate-based stains in an automatic dishwasher (ADW) is proposed. The effect of several factors such as pH, temperature, water hardness, bleaching and chelating agents, surfactants, builder, and functional polyacrylate in different cycles of dishwashers were studied. A three – stage procedure is used. First, a statistical analysis based on response surface methodology (RSM) was conducted to identify the impact of the most significant variables in the cleaning of each stain. Both stains cleaning was highly dependent by enzymatic action. However, protein-based stain was the only where its colour was compromised by the action of bleaching agents. Next, the kinetic mechanisms of the significant technologies, were proposed and integrated in a unique dynamic model based on non-linear differential equations, including the stability of enzymes and bleaching compounds. Subsequently, the parameter estimation was done employing Levenberg-Marquardt nonlinear least squares algorithm. Finally, a validation of the mechanistic model for each stain was carried out, getting a determination coefficient higher than 0.8 for carbohydrate-based and protein-based stains respectively, capturing most of the variation in stain cleanliness.

**Keywords**: Stain Removal, Automatic Dishwasher, Cleaning Model.

* 1. Introduction

Millions of people every day clean dishes, being the dishwashing a common practice around the world. Automatic dishwasher contributes with a significant reduction of water and energy consumption (75% and 25% respectively) compared to hand washing (Berkholz et al., 2010). The cleaning inside an ADW involves complex physical and chemical processes which affect the cleaning performance being highly linked between (Pérez-Mohedano et al., 2017). The optimization of cleanliness, sustainability and operating costs is only possible by understanding the cleaning mechanisms involved. Several techniques have been used to analyze the stain removal behavior during cleaning such as micromanipulation technique based on a stainless-steel probe to measure the adhesive forces (Liu et al., 2002), millimanipulation technique to study highly adhesive soils (Ali et al., 2015) or Fluid Dynamic Gauging (FDG) to explore the thickness evolution of the stain (Gordon et al., 2010). The change in the thickness of the stain, as well as the forces that condition its structure and adhesion to the surface where it is found, are highly dependent on the chemical conditions present in the wash. In this way, detergent’s ingredients such as enzymes, bleaches, surfactants, buffers, and builders are key factors in stains cleaning. Enzymes promote a more environmentally friendly washing by the reducing the wash time, pH, and temperature. Bleaches provide a germicidal action together with a stain color reduction. Surfactants aim to reduce the surface tension, increasing the wettability of the stain and its dissolution in the washing media. On the other hand, the control of pH and water hardness is an important factor that is carried out by buffers and builders. Currently, the combination of activated bleaching systems and enzymes such as amylases and proteases are highly employed since the hydrolysis and bleaching of stains as well as disinfection during washing is possible at low temperatures without compromising the stability of the active compounds present (Bianchetti et al., 2015).

In this way, a detailed understanding of the cleaning mechanism of each of the key ingredients on the different types of stains is crucial to improve the cleaning performance and reduce the environmental impact, promoting the achievement of the objectives set by United Nations in terms of sustainability and responsible consumption and production (United Nations, 2023). For these reasons, the present work is focused on the identification of the most important factors and mechanisms involved in carbohydrate – based and protein-based stains, proposing a cleaning model for each stain where it is included the stability of the key cleaning ingredients such as enzymes and bleaching compounds. The validation of the models was carried out using experimental data.

* 1. Material and Experimental Procedure
		1. Stain technical samples

Sprayed layers of starch and minced meat on a melamine base were considered as stain technical samples, acquired from Centre for Testmaterials. The dimensions of samples were 12 cm x 10 cm x 0.12 cm.

* + 1. Detergent formulation

Amylase and protease enzymes with an activity of 4% and 9.71% respectively were considered. The activated bleaching system was composed by TAED as bleach activator, manganese - based bleaching catalyst and sodium percarbonate with an activity of 92%, 2% and 100% respectively. Insoluble precipitate formation and pH were controlled by chelating, builder, sodium carbonate and silicate – based compound. Additionally, polymers and non – ionic surfactants were also considered in the study.

* + 1. Apparatus

A Miele GSL200 dishwasher was considered to run all the experiments. In this appliance 8 different cycles were conducted. All cycles have the same stages, a main wash, cold rinse, and hot rinse. For main wash, a time distribution of 17 – 69 min and temperature levels of 40 - 50 ºC were considered. In the case of hot rinse, durations between 23 – 26 min and target temperatures range of 55 - 65 ºC were performed. The duration of the cold rinse is the same for all cycles and its temperature profile is set by the temperature of the main wash stage.

* + 1. Experimental procedure

Initially, the water supply tanks are filled, spiking the corresponding levels of water hardness for each experiment. Then, a pair of tiles are located inside an ADW, one on the left and the other on the right – hand, placing a blank tile at the front. To mime the soil found in the domestic ADWs, a defrosted ballast soil is added using the same level for all experiments. Next, the pH meters are located inside an ADW. Once the corresponding cycle is running, the pH and temperatures profiles are recording over time by pH meters. Once the cycle finishes, the stain removal index (SRI) is measured as response variable. SRI is computed by the color difference between the stain before and after washing, employing the eq (1), (Copley, 2017; Neiditch et al., 1980) where $IN\_{i}$and $FN\_{i}$ are the initial and final noticeability for the stain i. The execution of the experiments was carried out based on a design of experiments (DOE) provided by the custom design platform of JMP Pro 16. A total of 217 experiments were conducted, employing a 10 % for validation.

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| $$SRI\_{i}=\frac{IN\_{i}-FN\_{i} }{IN\_{i}}$$ | (1) |

* 1. Modelling Methodology

A three – step methodology was considered to build a non – linear differential model to describe the cleaning mechanism of protein-based and carbohydrate – based stains in ADWs. Figure 1 describes the steps of the methodology followed. Once all the experiments were conducted based on the design of experiments, a response surface methodology was employed to identify the most significant variables at their effects on the cleaning of each stain, considering a statistical significance of 0.01 as reference. Based on the statistical analysis, a kinetic mechanism for each key factor is proposed, formulating a non-linear differential model for each stain. Subsequently, an estimation of the adjustable parameters of the main cleaning mechanisms was done employing Levenberg-Marquardt nonlinear least squares algorithm. Finally, a validation of the mechanistic model for each stain was carried out by correlating the estimated and measured SRIs.



**Figure 1**: Cleaning modelling methodology for carbohydrate – based and protein – based stains.

* + 1. Mechanistic Cleaning Modelling

During the cleaning, a combination between the physical removal and bleaching of the stain takes place. Physical removal by enzymatic action promotes a loss of color since a fraction of the components that provide the color is solubilized. Simultaneously, the bleaching compounds act on the remaining fraction of the stain removing the color. Assuming a homogeneous composition distribution of the stain, the total physical stain removal can be computed by eq (2), where is included the easy and difficult rate of removal due to the transition from a fast-cleaning stage at the beginning of the cycle to a slower one experimentally witnessed. This curvature change in the cleaning is considered by $μ\_{i}$, a fitting parameter. Additionally, $k\_{i}^{Phys}$is the cleaning constant which depends on the main factors involved in the physical removal. The union between the physical removal and bleaching from bleaches is showed by eq (3), where $SRI\_{i}^{Total}$represents the total stain removal including physical removal and loss of color and $m\_{i}^{d}$is the color remaining fraction of the stain. This fraction can be computed as the difference between the total reaming fraction and the bleached fraction of the stain $i$.

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| $$\frac{dSRI\_{i}^{Phys}}{dt}=μ\_{i}·k\_{i}^{Phys}·\left(f\_{i}^{E}-SRI\_{i}^{E,Phys}\right)+k\_{i}^{Phys}·\left(f\_{i}^{D}-SRI\_{i}^{D,Phys}\right)$$ | (2) |

|  |  |
| --- | --- |
| $$\frac{dSRI\_{i}^{Total}}{dt}=-\frac{dm\_{i}^{d}}{dt}$$ | (3) |

* 1. Results and Discussion
		1. Cleaning factors selection for carbohydrate – and protein – based stains.

From the response surface methodology, the most important variables in carbohydrate – based and protein – based stains removal are identified. Table 1 summarizes the results. The statistical analysis shows that time and enzymatic action by amylase are the main two drivers for cleaning of the carbohydrate – based stain. However, bleaching compounds provide a negative impact in the cleaning of this stain because they decompose the amylase, not impacting on the stain bleaching. Additionally, water hardness also gives a negative impact on the cleaning of this stain since deposits on stain surface by metal ions from water hardness may hinder the amylase action. For the protein-based stain, the cleaning is highly dependent of time, protease, amylase, and bleaching compounds concentrations.

* + 1. Cleaning model formulation and validation for carbohydrate – based and protein – based stains.

The statistical analysis reduces the complexity in identifying the mechanisms involved in the removal of each stain and their corresponding differential model parameters. For carbohydrate – based stain, the model parameters selected were those related to the amylase effect on the physical removal, employed to calculate the kinetic constant of physical removal. For the protein – based stain, the fitting parameters related to physical removal by amylase and protease as well as bleaching effect by peracetic acid and hydrogen peroxide were considered. A total of 8 and 11 parameters coming from the cleaning mechanistic models of carbohydrate - and protein - based stain were fitted, respectively. For both stains, their corresponding differential cleaning models have a high statistical significance since p - values lower than 0.01 were obtained in the ANOVA of the regressions.

After the fitting parameter estimation, a validation of the mechanistic model for each stain was carried out comparing the estimated and measured SRIs. Figure 2 shows a scatter plot made up by the predicted stain removal index versus the experimental ones for both stains. The models can capture the most part of the variation in the SRI since determination coefficient of 0.93 and 0.89 were obtained for carbohydrate – based and protein – based stain respectively. However, the reduced amount of experimental data between 30 and 50 % of the SRI in Figure 2a provides outliers in this region.

**Table 1**: Selected factors for differential models of carbohydrate – and protein – based stains from statistical analysis.

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| --- | --- | --- |
|  | **Represented Factors** | **p -value > F** |
| **Carbohydrate - based stain** | TAED | 0.0003 |
| Amylase | <0.0001 |
| Water Hardness | 0.0007 |
| Main wash time | <0.0001 |
| Amylase – Amylase | <0.0001 |
| **Protein - based stain** | Sodium percarbonate | <0.0001 |
| Protease | <0.0001 |
| Amylase | <0.0001 |
| Non - ionic surfactants mixture | 0.044 |
| Main wash time | <0.0001 |
| Sodium percarbonate - Protease | <0.0001 |
| Protease – Protease | <0.0001 |
| Protease – Amylase | <0.0001 |
| Protease – Main wash time | <0.0001 |
| Amylase – Main wash time | 0.002 |



**Figure 2:** Validation cleaning models 95 % of confidence: (a) Carbohydrate – based stain, (b) Protein – based stain.

* 1. Conclusions

A three – stage methodology is employed to build a dynamic cleaning mechanistic model for carbohydrate – based and protein – based stains. Initially, a statistical analysis based on response surface methodology allowed the identification of the main factors involved on the removal of the stains. Enzymatic action was the main route in the decomposition of both stains. However, only in the protein – based stain, color removal by bleaching agents was observed. The statistical analysis allowed the identification of kinetic cleaning mechanism, allowing the formulation of a non – linear differential model for both stains. High statistical significance and adequate accuracy of the models were obtained, concluding that the use of the previous statistical study helps in the identification of mechanisms and fitting complex models for ADW cleaning process.

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