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A Criteria for Evaluating the Microbiological Contamination of Acrylic Paints

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The acrylic paint can be contaminated by bacteria (and rarely fungi), due to the presence of microbiological residuals on the container, that are responsible for the degradation of the paint chemical and physical characteristics. Hence, as stated by the EU regulation of May 2015, it is mandatory to provide an in-can preservation of the paint. When subject to different temperatures, the in-can product could evaporate and then condense under the cover of the can. Since biocides are not volatile substances, they are present in very small quantities in the cover phase setting the bacteria free to proliferate. This research group is working on the modelling of the microbiological evolution of in-can systems with the aim of predicting the contamination extent and of obtaining proper design procedures to guarantee the protection (of both the can and the cover phase). The thermofluid-dynamic model implemented on gPROMS software is validated through the comparison with literature experimental data. In this paper we present the criteria at the basis of the cited system modelling. More in detail, this work reports the thermodynamic (phase equilibria using NRTL model) and the kinetic fundamentals, the estimation of the kinetic parameters through a literature comparison and a case study (considering MIT biocide) considered for the model validation.

Keywords: acrylic paints; microbiological contamination, gProms, model validation.

1. Introduction

Biocides should provide both an in-can protection and the protection of the layer of paint once applied to the surface (Contant et al., 2010). The presence of microorganisms on the surface layer of the paint is undesirable since it may damage the paint considerably by causing even the discoloration. Moreover, the presence of microorganisms causes the increase of the porosity of the paint layer, a decrease in physical resistance and allows the moisture to penetrate the treated surface with, for example, consequent corruption issues in case of wood surface (Unger at al., 2013).
The organic solvents used in the formulation of paints are increasingly replaced by water-based systems to meet the more stringent environmental regulations. As a matter of fact, when subject to different temperatures, the in-can product could evaporate and then condense again under the cover of the can. Since biocides are not volatile substances, they are present in very small quantities in the cover phase and the bacteria are therefore free to proliferate.
The microorganism contamination may occur during the manufacturing stages of paint production and during the storage as packaged product (La Rosa et al., 2008). The use of effective broad-spectrum biocides, together with good manufacturing processes and plant hygiene, may ensure the long-term microbiologically trouble-free production to take place (Karsa and Ashworth, 2007). The right choice of a preservative system depends on the kind of microorganism, the physicochemical compatibility, the toxicity of the biocidal product and its final characteristics to be obtained. The biocides to be commercialized must satisfy the EU regulations for limiting the growth of microorganisms by means of the destruction of the cell membrane, the inhibition of metabolic reactions, the variation of intracellular pH and the accumulation of toxic anions. Among available molecules, typically used biocides as for in-can protection are: 1,2-Benzisothiazolin-3-one (BIT), 5-chloro-2-methyl-isothiazolin-3-one/2-methyl-isothiazolin-3-one (CMIT,MIT); Formaldehyde donors. Biocides used for

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film protection are: Zinc pyrithione, Carbendazim, Octilisotiazolin-3-one (OIT). All these compounds are classified as sensitizing substances and there are restrictive concentration limits to regulate their presence in paints and coatings, according to EUH208 valid from June 2015 (Chemap 2015).
In this framework, a correct process modelling must take into account the chemical and biological kinetics characterizing the system as well as the equilibrium thermodynamics for simulating the phase partitioning inside the can. In this work, the equilibrium between liquid and vapor phases is considered by using NRTL model. Hence the modelling considers the kinetics of the condensed film bioreactor (the microbial growth and substrate consumption) for evaluation of the biocide effectiveness as a function of time as well as the effect of temperature on bacteria proliferation inside the can. MIT-based biocide (2-Methyl-4-isothiazolin-3-one) has been chosen to simulate the biocide hindering of microorganism proliferation inside a paint can.
The kinetic parameters have been estimated by fitting some experimental results from the literature. Once the model has been trained (once the kinetic parameters have been calculated and validated), it can be implemented for predicting the biomass and substrate evolution in the paint at different temperatures. This paper reports the criteria used for setting up, training and validating the mathematical model.

Figure 1. Sketch of the system under consideration: a) liquid paint phase; b) air and vapor phase; c) condensed phase.

2. Thermodynamic and Kinetic Modelling

The system object of the theoretical insight is shown in Figure 1 and consists of three phases: a liquid phase (a), representing the paint contained in the can, a vapor phase (b) and a condensed liquid phase (c). The bacterial growth occurs in the two liquid phase a and c; the liquid-vapor balance of paint determines the different biocide concentration in the two phases. Consequently, the bactericidal action as well as the initial biocidal concentration of biocide depend on the system temperature. The presence of air is considered in the phase b; no chemical reactions are considered in the vapor-phase b and the temperature difference between phases c and a is ΔT=5 °C. The composition of phase a and c is determined by the thermodynamic equilibrium calculated with the NRTL model (Renon and Prausnitz, 1968). The model parameters related to the MIT and the binary interaction coefficients of the various subsystems have been defined by means of a group contribution model, UNIFAC (Pöllmann and Löbbecke, 1996). The mass balance equations for enzymes, substrates and biocide (Eq. 1-5) represent the the kinetic model implemented for both liquid phases a and c.

$$\frac{de_1}{dt} = \frac{\alpha_1 S_1 u_1}{k_{s1} + S_1} - \beta e_1 - \frac{dX}{dt}\frac{e_1}{X} \quad (1)$$

$$\frac{de_2}{dt} = \frac{\alpha_2 S_2 u_2}{k_{s2} + S_2} - \beta e_2 - \frac{dX}{dt}\frac{e_2}{X} \quad (2)$$

$$\frac{dS_1}{dt} = -\frac{\mu_1 v_1}{Y_{xs1}} X \quad (3)$$

$$\frac{dS_2}{dt} = -\frac{\mu_2 v_2}{Y_{xs2}} X \quad (4)$$

$$\frac{dI}{dt} = o \quad (5)$$

where X is the biomass concentration, u_i and v_i are cybernetic variables used to model the intracellular autoregulation devoted to the enzyme synthesis and cellular activity control, respectively, I is the biocide concentration and K_{ei} is the biomass dead constant. The model equations for biomass growth are reported below (Eq. 6-9) where Y_{xs1} and Y_{xs2} are the yield growth factors are based on the work of Bailey and Ollis, (1986) and Villadsen et al., 2011.

$$\frac{dX}{dt} = \left(\frac{\mu_{max1} S_1}{k_{s1} + S_1 + \frac{S_1^2}{k_{i1}}} \right) X \tag{6}$$

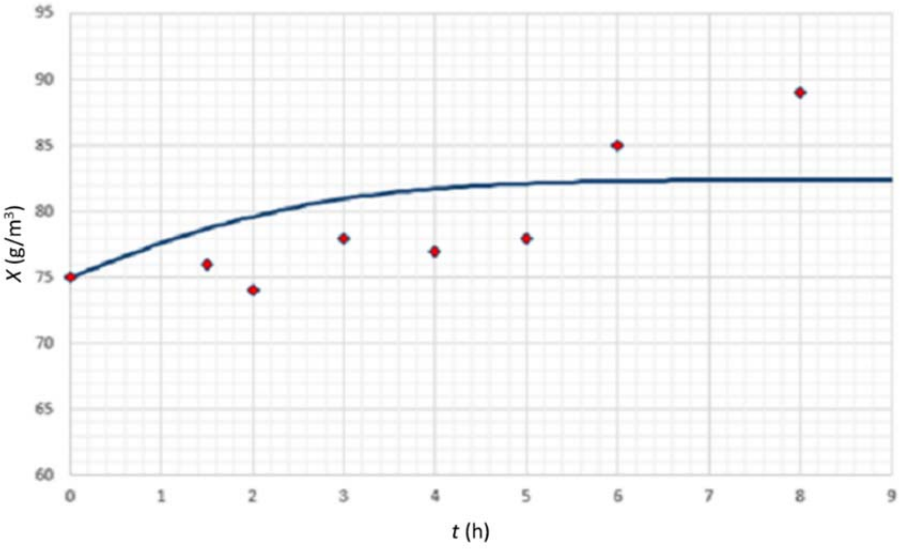
$$\frac{dS_1}{dt} = -\left(\frac{\mu_{max1} S_1}{k_{s1} + S_1 + \frac{S_1^2}{k_{i1}}} \right) \frac{X}{Y_{xs1}} \tag{7}$$

$$\frac{dX}{dt} = \left(\frac{\mu_{max2} S_2}{k_{s2} + S_2} \right) X \tag{8}$$

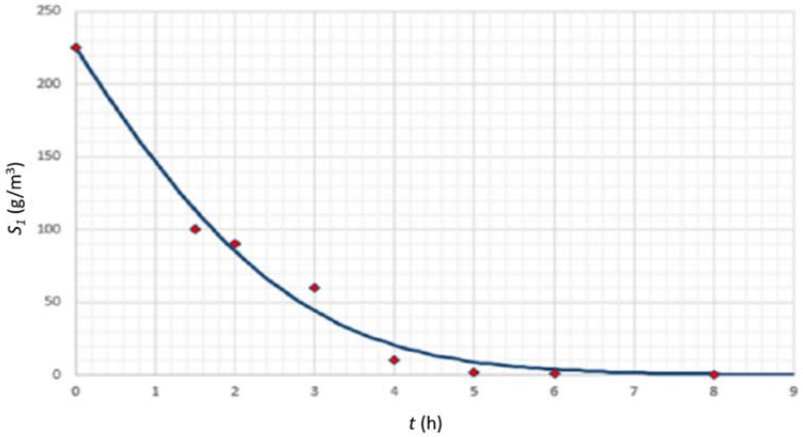
$$\frac{dS_2}{dt} = -\left(\frac{\mu_{max2} S_2}{k_{s2} + S_2} \right) \frac{X}{Y_{xs2}} \tag{9}$$

3. Model Training and Validation

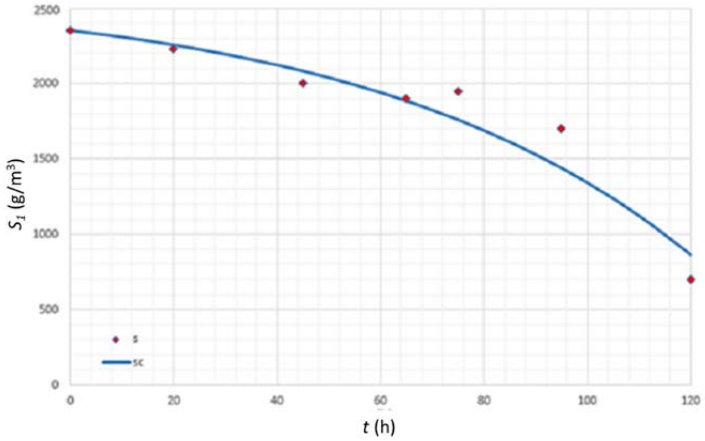
Primarily, the model has been validated by fitting experimental results relative to the two substrates S_1 (data from Kasperczyk et al., 2007) and S_2 (data from Obidi et al., 2009) for estimating the values of the kinetic parameters where α and β are the synthesis and degradation key enzyme constants and k_{i1} the substrate inhibition constant and the substrate inhibitory effect has been taken into account for the degradation kinetic of substrate S_1 (not for S_2) according to the Eq. (6-9) (Kompala, 2013). The considered paint composition is the following: vinyl acetate (S_1): 6% weight; monopropylene glycol (S_2): 2 weight%; calcium carbonate: 6% weight; water (W): 85,99% weight; MIT (I): 0,01% weight=100ppm. The contribution of pigments (calcium carbonate) to the calculation of the equilibrium phase was neglected. Considering the specific weight of painting equal to 1,66g/cm^3, it is: S_1^0 = 99597.4 g/m^3, S_2^0 = 33200 g/m^3, W^0 = 1427000 g/m^3, I^0 = 165.9 g/m^3. Results of curve fitting are shown in Figures 2-5.



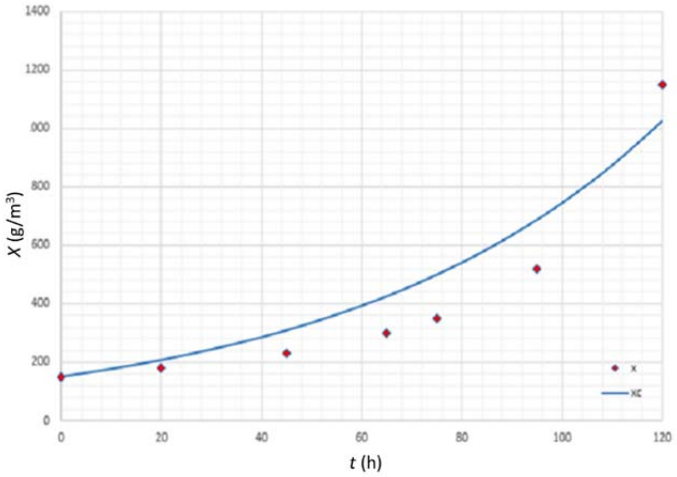
Figures 2. Kinetic parameter estimation for Eq (6). Line: model equations; symbols: experimental results (Kasperczyk et al., 2007).



Figures 3. Kinetic parameter estimation for Eq. (7). Line: model equations; symbols: experimental results (Kasperczyk et al., 2007).



Figures 4. Kinetic parameter estimation for Eqs (8). Line: model equations; symbols: experimental results by (Obidi et al., 2009).



Figures 5. Kinetic parameter estimation for Eqs (9). Line: model equations; symbols: experimental results by (Obidi et al., 2009).

The modelling criteria, here implemented, is synthetized in Figure 6. The thermodynamic analysis allows to account for the phase partitioning. The kinetic modelling has to be validated with experimental data enabling the estimation of the reaction parameters. Once the kinetic parameters have been estimated, the model is implemented to simulate the system of Figure 1 reproducing the the experimental points (symbols), derived from literature (Urška, 2011) that used a mixture MIT/BIT. Figure 7 shows some preliminary results of this simulation as the biomass *X* growth (in a) as a function of time with MIT as biocide (upper orange curve) and a mixture MIT/BIT (blue lower curve).

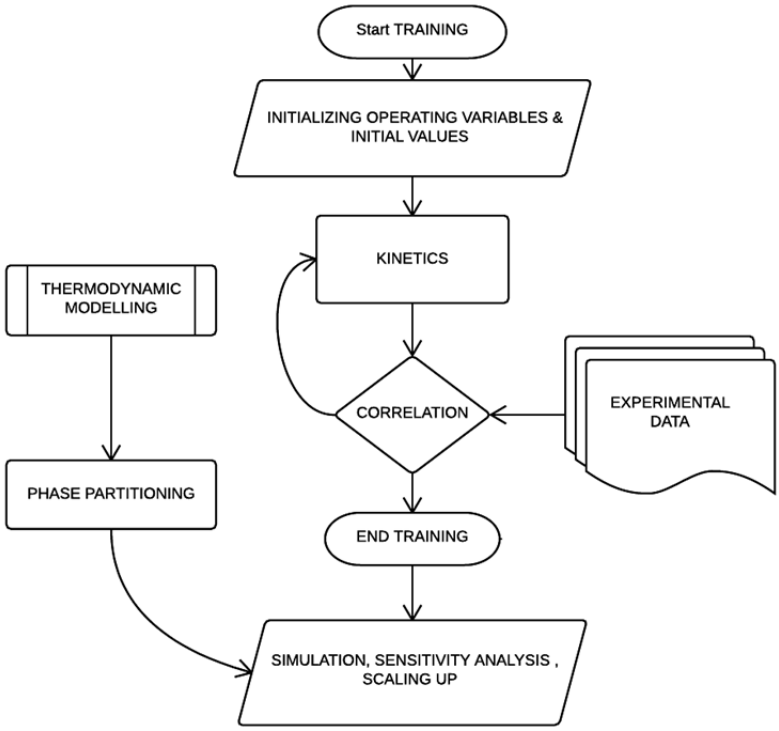


Figure 6. Logical scheme of the procedure implemented for simulating the system

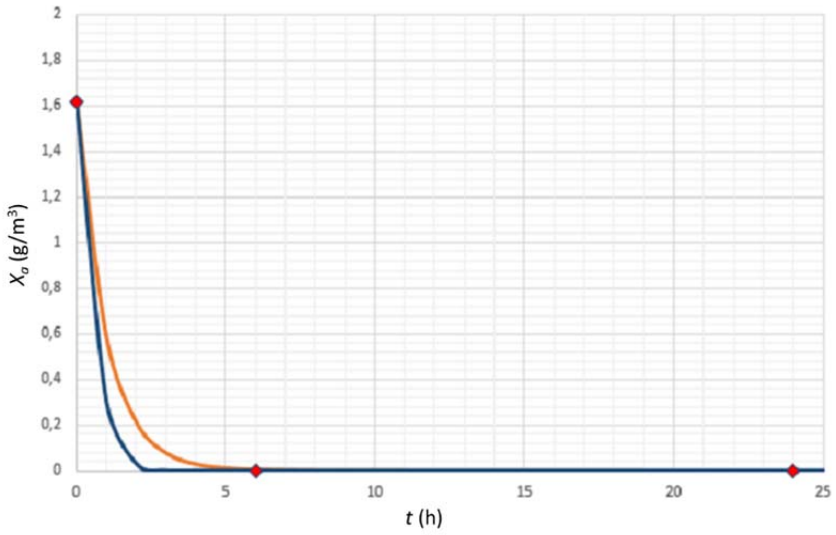


Figure 7. Comparison between model and experimental results as for MIT biocide (orange line) and MIT/BIT biocide (blue line): Biomass X_a vs. time; symbols: experimental results (Urška, 2011); I^0=199 g/m^3 and X_a^0= 1,62 g/m^3

4. Conclusions

In this paper, a criterion for modelling the microbial contamination of acrylic paint is described. The thermodynamic and kinetic fundamentals highlighting the effect of a biocide (MIT) on a water-based paint have been presented. The model is trained with experimental results (correlation with experimental data) and implemented for the three in-can system simulations. The initial biocidal concentration considered in this study is that maximum allowed by the limits of the law, that is, 165.9 g/m^3= 100 ppm. The preliminary results well reproduce the data in case of MIT biocide experiments of *Urška (2011). T*he presented model allows to consider the bacterial growth on the cover of paint can, underestimated in the experimental tests focusing primarily on bacterial behavior in the bulk of the painting. Future works will be aimed at verify the effect of other process parameters, such as initial biocide concentration, and to test the efficacy of different biocides or a mixture of them. Once tested the model reliability, a sensitivity study can be carried out for individuating the critical external temperature profile and the the proper biocide type and concentration for the protection of painting for long periods in relation to the environment conditions.

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