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MATHEMATICAL MODELS ON MILK, COFFEE AND BEER

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Abstract. The simple differential equation $y' = ky, k \in \mathbb{R}$ is an important mathematical model. It is well known in Population Dynamics as the *Malthusian Equation* and it is familiar to food technologists as *Bigelow's First Law*, which describes the microbial mortality at constant lethal temperatures. In the paper we focus on the process of thermal sterilization of milk. The Malthusian Equation is also a mathematical model for Newton's law of cooling or heating. The rate of heat loss of a cooling body is proportional to the difference in temperatures between the body and its surroundings. In the paper we analyze the data of an experimental study on the cooling of coffee conduced by "Mathematics & Real Life" Project. The measurements of the temperature were taken using a centesimal temperature sensor connected to a computer for automatic data capture.
Another simple differential equation is Darcy's equation, a fundamental mathematical model in the filtration theory. In the paper we are interested in mathematical models derived from Darcy's law, which are applied to the cross flow microfiltration at constant pressure of beer. These models are then tested using experimental data provided by the Italian Brewing Research Centre of the University of Perugia.

Keywords: Malthusian Equation, Darcy's Equation, Newton's law of cooling, First Bigelow model, cross flow microfiltration

Mathematics subject classification: Primary 97M10; Secondary 97M50, 34A34

1 Introduction

The *Malthusian Equation* $y' = ky, k \in \mathbb{R}$ and *Darcy's law* $Q = \frac{PA}{R\mu}$ are important mathematical models in Food Technologies.
Microbial mortality at constant lethal temperatures is traditionally considered a process following a first-order constant rate kinetics reaction (*First Bigelow model*). According to this model the organism's survival can be described by the Malthusian Equation where $y(t)$ is the microbial population survived after t seconds of thermal process and $k < 0$ is the constant rate of microbial destruction relating to homogeneous microbial population. During heat treatment several food compounds undergo changes. In the specific case of thermal sterilization of milk an usual side-effect is the production of *furosine*, a typical *Maillard reaction* that induces a yellow-brown colour and smell of cooked milk.

The Italian law sets the limit at 2.9 mg/ls for the furosine in the milk. Luckily, the formation of furosine follows a linear growth production. According to the Collision Theory, the constant rate k of each reaction increases with temperature. The results of our models prove that the optimization of sterilization effect, i.e the sanitization of the product with minimizing the degradation of milk quality, is achieved by increasing the temperature and reducing time, in agreement with the acronyms found in products on the market: UHT (Ultra High Temperature) and HTST (High Temperature Short Time).
The Malthusian equation is also a mathematical model for Newton's law of cooling or heating, which is applied in the processes of pasteurization and sterilization to evaluate the temperature during the heating of the product. Newton's law can be described by the equation $T' = k(T - T_a), k < 0$, where T_a is the temperature of the surrounding environment. The constant rate depends on physical and environmental factors. In the paper we calculated the value of the constant rate using the data from an experimental test on cooling of a cup of coffee. The measurements of the temperature were taken using a centesimal temperature sensor connected to a computer for automatic data capture.
Darcy's equation is a fundamental mathematical model in the filtration theory. In the cross flow microfiltration, Darcy's equation $Q = \frac{PA}{R\mu}$ describes the flow rate Q as a function of resistance R and membrane area A where P is the trans-membrane pressure and μ is the viscosity of the solution, which are constant values. In the paper we studied some of the prominent mathematical models derived from Darcy's law that are proposed in the literature. Precisely we focused on the classical four-constant pressure Hermia's models (basic models) [7] and their feasible combinations (combined models). These models are typically used to describe fouling. We validated the models with experimental trials of the cross flow microfiltration of beer monitoring the filtrate volume and the flow rate by a pilot plant equipped with a ceramic membrane. The data were provided by the Italian Brewing Research Centre of the University of Perugia. None of the basic models has been able to explain fouling. This indicates that multiple mechanisms participate in the fouling process and suggests the development of the combined models. The combination of two basic models, the standard pore blocking model and the complete pore blocking, yields the better fit in the first phase of the process. This result can be explained considering the beer composition that consists of different dimensions particles. In the second phase of the process, the CPB+SPB model does not fit the experimental data because it does not take in account the back-flush washing performed during the experimental trials. Regarding the flow rates, the results obtained by the basic models are more encouraging.
Our research project is to continue these studies, improve the combined mathematical models and evaluate other experimental tests, even considering filtration of different fluids or other types of membranes.

2 Malthusian equation

The equation

$$y' = ky, \;\; k \in I\!R$$

whose solution is

$$y(t) = y(0)e^{kt}, \;\; y(0) \text{ initial data at } t = 0$$

is an important dynamic model. It is known as the Malthusian equation by the name of the English economist Thomas Malthus (1766 - 1834). What was commonly accepted in Malthus's analysis was the idea that in the absence of external constraints (food or environmental constraints, pollution, social-economic constraints, economic constraints) populations tend by nature to unlimited growth, directly proportional to the number of the population, with a constant growth rate. In many cases the equation appears in the discrete formulation, as a difference equation.

The finite difference method is a technique used to obtain numerical solutions to Differential Equations, i.e. solutions that are known only at a finite number of points. In general, increasing the number of points increases the accuracy of the numerical solution.
The solution of the discrete formulation of Malthusian equation $y_{n+1} - y_n = ky_n$ is the geometric sequence $y_n = y(0)(1 + k)^n$, with mesh $\triangle t = 1$.
If the mesh is reduced $\triangle t = 1/r, r > 0$ the geometric sequence becomes $y_n = y(0)(1 + k/r)^{rn}$ from which it is deduced that the corresponding continuum of the geometric sequence is the exponential law as shown in the following Figure 1:

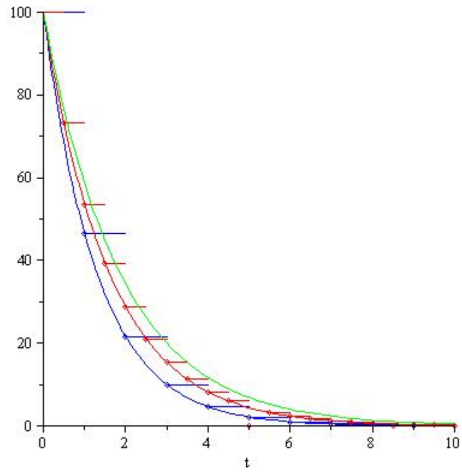

Fig. 1.

- $y_n = y(0)(1 - k)^n, \ \ k = 0.536, \ \ y(0) = 100, \ \ \triangle t = 1$.
- $y_n = y(0)(1 - k/2)^{2n}, \ \ k = 0.536, \ \ y(0) = 100, \ \ \triangle t = 0.5$.
- $y(t) = y(0)e^{-kt}, \ \ k = 0.536, \ \ y(0) = 100$.

If k_F is the constant rate of difference equation, then the constant rate k of related differential equation is $k = \ln(k_F + 1) \simeq k_F$ $[k_F = e^k - 1 \simeq k]$ for values of the constant rate close to zero. So if the differential equation $y'(t) = 0.02y(t), \ \ t$ years, describes the growth of a population, with a good approximation we can say that the population grows by 2% a year.

2.1 First Bigelow model

In food technologies the equation $y' = -ky, \ \ k > 0$ is knows as *First Bigelow model* and describes the microbial mortality at constant lethal temperatures [9]. $y(t) = y(0)e^{-kt}$ is the microbial population survived after t seconds of thermal process and k is the constant rate of microbial destruction in relation to a homogeneous microbial population. In the specific case of thermal sterilization of milk the constant rate (at $120\ ^0C$) is $1.10 \cdot 10^{-2}$ (s^{-1}), and the commercial sterility is estimated at 10^{-4} (spore/l). According to the Collision Theory, the constant rate k of each reaction depends on the temperature. Raising the temperature, the rate of reaction increases [6].
The temperature dependence of the kinetic parameters is adequately described by the *Arrhenius model*. In Table 1 we can read the values of the constant rates when the temperature of the treatment is varied [10]. The same table also shows the data on the formation of furosine, a negative side effect that occurs during the heat treatment of the milk. The formation of furosine is a typical *Maillard reaction* that follows a linear growth and leads to the production of compounds that gives the yellow-brown colour and smell of cooked milk ([1, 12]).

temperature	k (s^{-1}) First Bigelow model	k (mg/(l s)) kinetics of furosin production	seconds of treatment for commercial sterility	mg/l of furosine produced
120 °C	0.011	0.126	1249.03	157.37
125 °C	0.041	0.172	332.91	57.412
130 °C	0.141	0.234	91.19	21.359
135 °C	0.415	0.315	25.78	8.141
140 °C	0.841	0.422	7.51	3.176
141 °C	0.904	0.447	5.89	1.628

Tab.1. Constant rates values as a function of temperature.

The Italian law sets to 2.9 mg/l the limit for furosine in the milk, hence the optimization of the sterilization effect is achieved by increasing the temperature and reducing time. These results are in agreement with the acronyms found in products on the market: UHT (Ultra High Temperature) and HTST (High Temperature Short Time) [3].

2.2 Newton's law of cooling

The Malthusian equation is a mathematical model for Newton's law of cooling or heating. The rate of cooling or heating of a body is proportional to the difference in temperatures between the body and its surroundings. Newton's law can be described by the equation $T' = k(T - T_a), k < 0$, whose solutions are $T(t) = Ce^{kt} + T_a$ (for cooling) and $T(t) = T_a - Ce^{kt}$ (for heating), where T_a is the temperature of the surrounding environment.
The discrete formulation of Newton's law of cooling is $T_{n+1} - T_n = k(T_n - T_a)$.
Put $S_n = T_n - T_a$ the thermal jump, we find the discrete formulation of Malthusian equation $S_{n+1} - S_n = kS_n$.
Clearly, the rate constant depends on many factors, both physical and environmental. We calculated the value of the rate constant using the data from an experimental test on cooling of a cup of coffee conduced by "Mathematics & Real Life" Project, July 2006.
In July, a cup of coffee at the initial temperature of $70 - 75\ ^0C$ was placed in an environment at the temperature of $29\ ^0C$ and by using a centesimal temperature sensor connected to a computer for automatic data capture, the temperature was measured as shown in Table 2.

Room temperature	29 °C
Duration of each test	45 minutes
Number of readings per test	4500
Estimation of reading error	0.01 °C
Initial coffee temperature	70 -75 °C
Final measured temperature	34 -38 °C

Tab.2. Experimental trials on the cooling of a cup of coffee.

The graph in Fig.2 shows the temperatures measured every twelve seconds starting from $61.36\ ^0C$ i.e. the temperature measured 2.45 minutes after the beginning of the experiment.

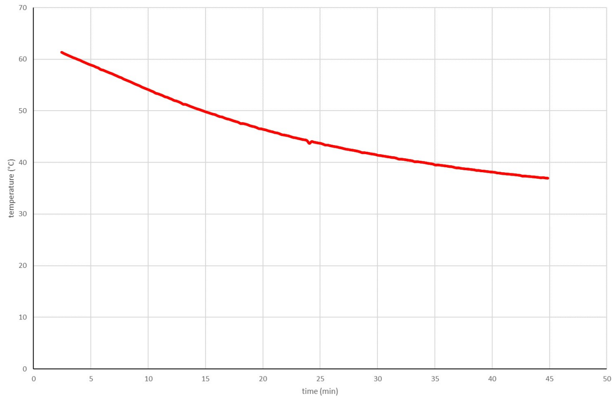

Fig. 2. Experimental temperature data.

By using the semilogarithmic coordinates in Fig.3, we can estimate the value of the relative cooling rate: $k = -0.0338\ \ (\text{min}^{-1})$

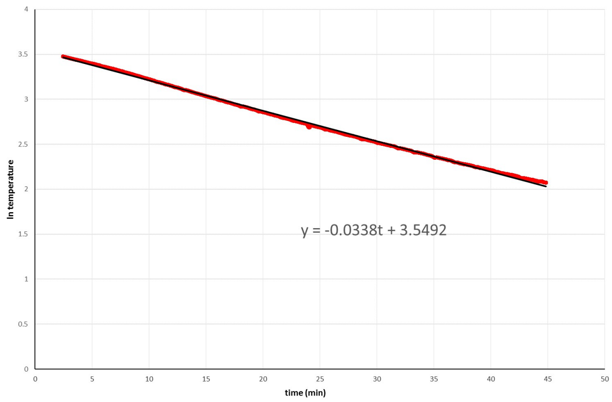

Fig. 3.

The solution $T(t) = 29+(61.36-29)e^{-0.0338t}\ (^0C)$ of the mathematical model $T' = -0.0338(T-29)$ is a good approximation of the experimental data (see Fig.4).

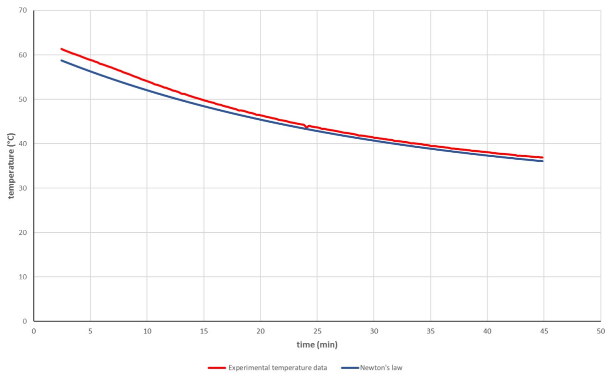

Fig. 4. Validation of the model.

3 Darcy Equation

Darcy's law is a fundamental mathematical model in the cake filtration theory. In this paper we will be focused in the filtration of beer. The brewing industry has an ancient tradition and is a dynamic sector open to modern technology and scientific progress. Clarification of the beer is an important operation during the brewing process. Rough beer is filtered in order to eliminate yeast cells and colloidal particles responsible for haze. The conventional beer clarification process employs filter press or pressure vessel filters and these systems are based on the employ of diatomaceous earth. This type of process, though, presents significant problems because the diatomaceous earth is a non-renewable material which is difficult and expensive to dispose of. Environmental pressure on the use of diatomaceous earth has forced the industry to investigate new and alternative technologies. The membrane separation process with the filtration carried out in cross flow is a promising alternative to the traditional clarification process because it eliminates the residues generated by the conventional treatment and the need for filter aids.

An important research topic related to the cross flow microfiltration processes is the study of the flux decline due to membrane fouling and many different models have been proposed in the literature [2, 4, 5, 7, 8, 11]. It may be useful to classify fouling as in-depth pore fouling, pore plugging and cake formation. In this context, prominent models are the classical four - constant pressure Hermia's models, that are typically used to describe fouling : standard blocking model, intermediate blocking model, cake filtration model, and complete blocking model [7]. These models derive from Darcy's law.

In the crossflow microfiltration Darcy's equation

$$Q = \frac{PA}{R\mu}$$

describes the flow rate Q (m^3/s) as a function of resistance R (m^{-1}) and membrane area A (m^2) where P (N/m^2) is the trans-membrane pressure and μ (Ns/m^2) is the viscosity of the solution, which are constant values.

In the first two models, Complete and Intermediate pore blocking, the study of the fouling depends mainly on the reduction of the surface filtration in time. Denoted by Q_0, A_0, R_0 the initial data, we can assume $\frac{Q}{Q_0} = \frac{A}{A_0}$. In the other two models the increasing of the resistance assumes greater importance and they are based on the assumption $\frac{Q}{Q_0} = \frac{R_0}{R}$.

Complete pore blocking model (CPB model) is based on the premise that the particles are larger than the pore size of the membrane and this results in the particles sealing off the membrane and preventing the flow.

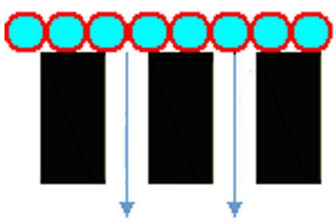

Fig. 5. Complete pore blocking model.

The available membrane area decreases with respect to permeate volume according the equation $A = A_0(1 - \frac{k_b}{Q_0}V)$ that combined with Darcy's law gives $Q = \frac{dV}{dt} = Q_0 - k_bV$ from which it is derived

$$V(t) = \frac{Q_0(1 - e^{-k_bt})}{k_b} \quad \text{and} \quad Q(t) = Q_0e^{-k_bt}$$

where $k_b = \frac{P\sigma}{R\mu}$ (s^{-1}) and σ (m^{-1}) is the blocked area per unit filtrate volume.

Intermediate pore blocking model (IPB model) assumes that a portion of the particles seal off pores and the rest accumulate on top of other deposited particles.

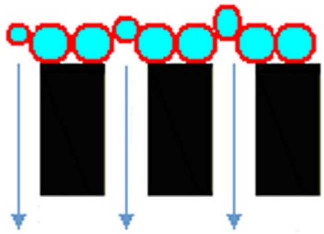

Fig. 6. Intermediate pore blocking model.

This model uses a successive approximation method to membrane area reduction and to permeate volume. The reduction of the available membrane with respect to the permeate volume can be expressed as a function of volume by $A = A_0e^{-k_iV}$. By Darcy's law we obtain $Q = \frac{dV}{dt} = Q_0e^{-k_iV}$ from which

$$V(t) = \frac{\ln(1 + k_iQ_0t)}{k_i} \quad \text{and} \quad Q(t) = \frac{Q_0}{1 + k_iQ_0t}$$

where $k_i = \frac{\sigma}{A_0}$ (m^{-3}).

Cake filtration model (CF model) occurs when particles accumulate on the surface of a membrane in a permeable cake of increasing thickness that adds resistance to flow.

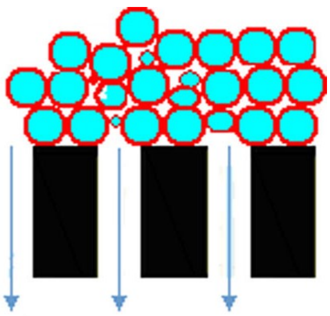

Fig. 7. Cake filtration model.

The total resistance R is the sum of the membrane resistance and the cake resistance; it can be expressed by the function $R = R_0(1 + k_cQ_0V)$ that together with Darcy's law gives

$Q = \frac{dV}{dt} = \frac{Q_0}{1+k_c Q_0 V}$. As a result, the permeate volume and the flow rate as a function of the time is

$$V(t) = \frac{\sqrt{1+2k_c Q_0^2 t} - 1}{k_c Q_0} \quad \text{and} \quad Q(t) = \frac{Q_0}{\sqrt{1+2k_c Q_0^2 t}}$$

where $k_c = \frac{S}{AR_0 Q_0}$ (sm^{-6}), S (m^{-2}) depends on the cake specific resistance and on filtrate density.

Standard pore blocking model (SPB model) assumes that particles accumulate inside membranes on the walls of straight cylindrical pores.

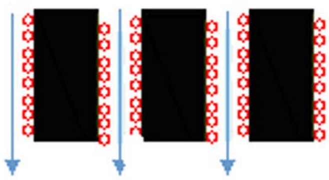

Fig. 8. Standard pore blocking model.

The rays of the pores decrease due to the solid matter that accumulates on the pore walls, so the growth of resistance as a function of the permeate volume can be expressed by $R = R_0(1 - \frac{k_s V}{2})^{-2}$ and, from Darcy's law, $Q = \frac{dV}{dt} = Q_0(1 - \frac{k_s V}{2})^2$. Through the integral we have

$$V(t) = (\frac{k_s}{2} + \frac{1}{Q_0 t})^{-1} \quad \text{and} \quad Q(t) = \frac{Q_0}{(1 + \frac{k_s Q_0 t}{2})^2}$$

where $k_s = \frac{2C}{LA}$ (m^{-3}) and C is the volume of solid particles retained per unit filtrate volume, L (m) is the membrane thickness.

Combining the previous basic models, other models can be developed which describe the fouling taking into account both membrane area reduction and increasing of resistance [2, 4]. Darcy's law, in these models, describes the flow rate as a function of the resistance and the membrane area that vary with permeate volume, under constant pressure conditions

$$\frac{Q}{Q_0} = \frac{R_0 A}{R A_0}.$$

In the various combinations, the permeate volume as function of the time is described by

$V(t) = \frac{Q_0}{k_b}(1 - e^{\frac{-k_b \sqrt{1+2k_c Q_0^2 t - 1}}{k_c Q_0^2}})$ (CPB and CF models)

$V(t) = \frac{1}{k_i} ln(1 + \frac{k_i}{k_c Q_0}(\sqrt{1+2k_c Q_0^2 t} - 1))$ (IPB and CF models)

$V(t) = \frac{Q_0}{k_b}(1 - e^{\frac{-2k_b t}{2+k_s Q_0 t}})$ (CPB and SPB models)

$V(t) = \frac{1}{k_i} \ln(1 + \frac{2k_i Q_0 t}{2+k_s Q_0 t}$ (IPB and SPB models).

In the present paper, basic models as well as combined models have been used to explain experimental observations.

3.1 Experimental trials

The technological trials of cross flow microfiltration of beer were conducted using a pilot plant equipped with a ceramic membrane. The membrane presented the following characteristics (Tab.3):

Material	Aluminium Oxide ceramic fiber
Structure	symmetric
Porosity	$0.80\mu m$
Filtration surface	$0.8m^2$
Transmembrane pressure	5.5 bar
Number of capillaries	290
Internal diameter of capillary	3.0 mm

Tab.3. Constructive characteristics of the ceramic membrane.

Two technological replications of the cross flow microfiltration of beer were conducted monitoring the filtrate volume (m^3) (Fig. 9) and the volumetric flow rate (m^3/s) (Fig.10) every five minutes for a total filtration cycle of 180 minutes and performing back-flush washing each three minutes.

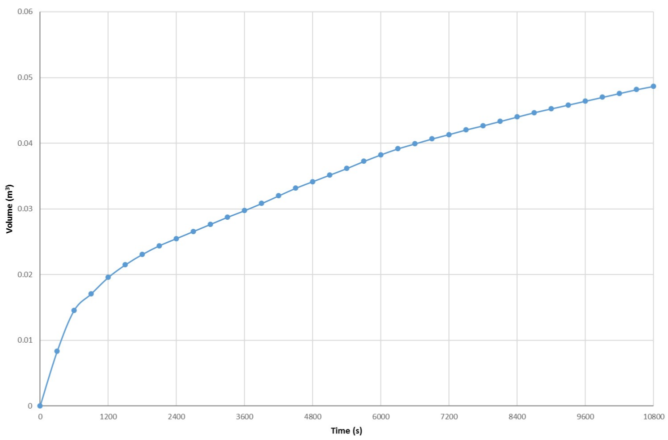

Fig. 9. Experimental data of the cumulate volume.

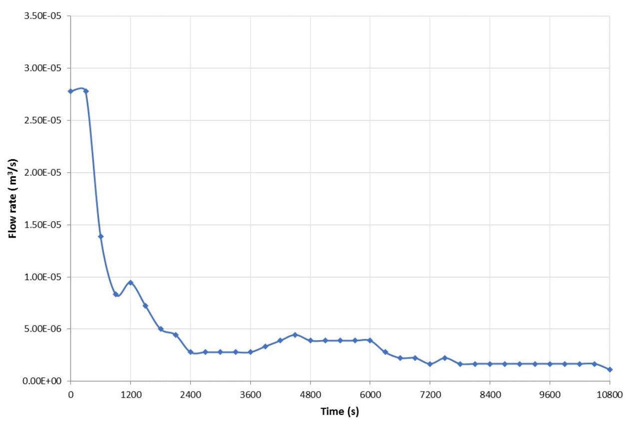

Fig. 10. Experimental data of the volumetric flow rate.

The experimental data were used for the estimate of the parameters k_b, k_i, k_c, k_s related to the previous described models. The values of these parameters depend on the type of membrane and the composition of beer (see Tab.4).

$k_b(s^{-1})$	$4.84 \cdot 10^{-4}$
$k_i(m^{-3})$	58.56
$k_c(sm^{-6})$	$11.01 \cdot 10^{6}$
$k_s(m^{-3})$	30.17

Tab.4. Empirical parameters associated to the models.

The results related to the filtrate volume described by the basic models are not satisfactory (Fig. 11). None of the basic models is able to explain fouling. The intermediate pore blocking model provided the best fit for the data in the first thirty minutes. However, significant deviations are observed in the following minutes. This indicates that multiple mechanisms participate in the fouling process and suggests the development of the combined models.

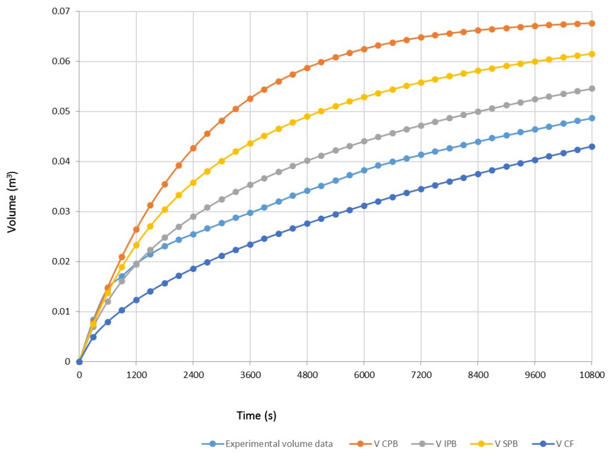

Fig. 11. Experimental cumulate volume and estimated volume by basic models.

As can be seen in Fig. 12, the combination of the standard pore blocking model and the complete pore blocking model yields the better fit in the first ninety minutes of the process.

This result can be explained considering the beer composition. Beer is a complex matrix containing different dimension particles as yeast cells, proteins, no starch polysaccharides as beta-glucan and arabinoxylan, and other compounds that derived from raw materials. The larger particles are subjected to superficial retention on the membrane while the smaller particles cause the occlusion of the membrane pores. The combined model CPB+SPB simultaneously takes into account the reduction of the filter membrane surface and the increase in resistance and describes in a more appropriate manner the experimental studied process. In the second phase of the process, the model CPB+SPB does not fit the experimental data because it does not take in account the back-flush washing performed during the experimental trials.

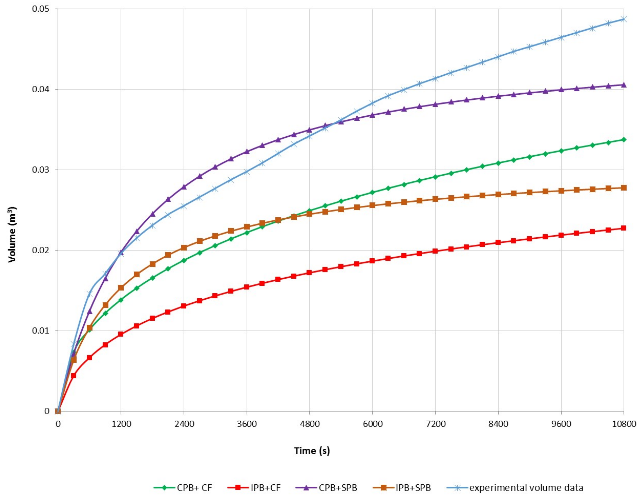

Fig. 12. Experimental cumulate volume and estimated volume by combined models.

Regarding the flow rates, the results obtained by the basic models are more encouraging. In particular, except for the CPB model, the other functions describe the experimental data with a good approximation (see Fig. 13).

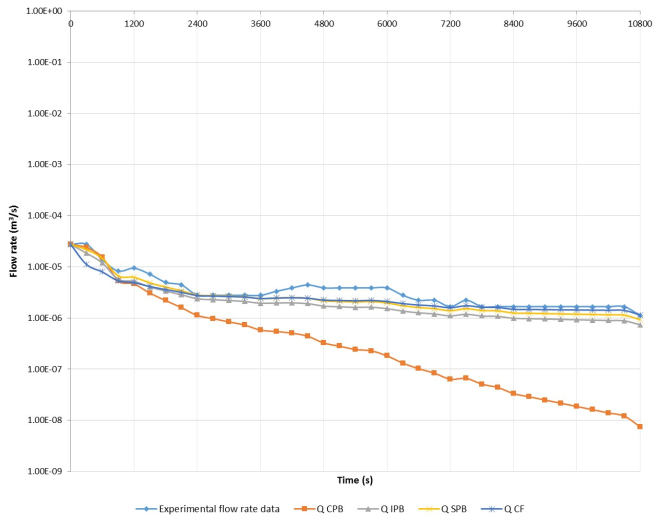

Fig. 13. Experimental flow rate data and estimated flow rate by basic models.

In the brewing industry the cross flow filtration technique is a valid alternative to traditional filtration processes. The application of this technology is still under study and development and further research and experimentation are needed to optimise the production process and obtain the best performance. The formulation of mathematical models that interpret these processes is a valid aspect of research in this area.

Our research project is to continue these studies, improve the combined mathematical models and evaluate other experimental tests, even considering filtration of different fluids or other types of membranes.

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