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A STUDY OF THE MECHANISMS OF CHEMICAL CLEANING OF MILK PROTEIN FOULING DEPOSITS USING A MODEL MATERIAL (WHEY PROTEIN CONCENTRATE GEL)

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A thesis submitted for the fulfillment of the requirements for the degree of Doctor of Philosophy

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ABSTRACT

It is crucial to understand the fundamental mechanisms of cleaning milk protein fouling to optimise Cleaning-in-place (CIP) process. Using Whey Protein Concentrate (WPC) gel as a model material and a rapid ultraviolet (UV) spectrophotometry, a comprehensive laboratory study on the cleaning of the WPC gel deposits from hard surface with alkaline cleaning solutions has been conducted. The kinetics of the cleaning process has been established and mathematical models have been developed in order to elucidate the influences of various parameters on cleaning process.

This study has provided sound evidence that whey protein concentrate gel is a reliable simulation of the whey protein fouling deposits used in most milk protein fouling and cleaning studies. Based on treating denatured whey protein gels as biopolymers, a chemical reaction controlled polymer dissolution cleaning mechanism has been proposed. The polymer dissolution plays a major role of removing proteinaceous deposits when treated with alkaline solutions under the flow conditions tested. Similar to the diffusion of cleaning chemicals and chemical reactions, the reptation (induction) is also one of essential steps for the dissolution of WPC gels in alkaline solutions. The disengagement of intermediate reaction products (altered protein molecules) from a gel-solution interface and subsequent mass transfer of these reaction products to the bulk cleaning solutions are the rate-limiting steps for the cleaning process.

The typical dissolution cleaning rate curve of WPC gels in alkaline solutions includes swelling, uniform and decay cleaning stages. This study on cleaning kinetics shows that increasing the cleaning temperature can improve the cleaning efficiency. The apparent activation energy for these three stages is 32.6, 40.5, and 38.3 kJ/mol, respectively, which is in agreement with previous research works. Increasing flow velocity enhances the cleaning process. However, this effect could be reduced when and the cleaning process gradually changes from a mass transfer-controlled process to a disengagement-controlled process, where the flow velocity is very high.

The introduction of the hydrolysis, \( \beta \)-elimination reactions and some competing chemical reactions have highlighted the complex of chemical reactions involved in cleaning of proteinaceous fouling using alkaline solutions. The changes in molecular mass distribution and
SH content of WPC gel dissolved at various temperatures observed has confirmed the assumption that all these chemical reactions are temperature dependent. The investigation on the swelling, microstructural and mechanical properties of WPC gels treated with alkaline solutions also illustrates the concentration dependency of these chemical reactions. The mechanical property studies demonstrate that the chemical treatment could make WPC gel weaker and easier to be destroyed. However, the relationship between the mechanical properties and the cleaning process needs to be further studied.

Based on the polymer dissolution and mass transfer theory, a mathematical model of chemical cleaning has been proposed. Various parameters, such as $t_r$ (reptation time), $R_m$ (constant cleaning rate), $m_c$ (the critical mass), $\xi$ (rate constant in swelling stage), $k_d$ (rate constant in decay stage) and $\psi$ (a dimensionless parameter) have been used to characterise the whole cleaning process. Among the parameters used in the cleaning model, the constant cleaning rate ($R_m$) is the most important one and determines the overall efficiency of a cleaning process, which has been further predicted and expressed as a product of mass transfer coefficient and solubility of disengaged protein molecules. The successful model formulations for the cleaning rate and cleaning time under various operation conditions are a good outcome of the rational mechanisms proposed for the removal of proteinaceous fouling. This research has provided a good foundation for further fundamental research in this area and for optimising the cleaning processes.
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TABLE OF CONTENTS

LIST OF FIGURES IX
LIST OF TABLES XIV
NOMENCLATURE XV
ABBREVIATIONS XIX

CHAPTER 1. INTRODUCTION

1.1 Introduction to Cleaning Research 1
1.2 Chemical Cleaning Mechanisms 2
1.3 Aims of the Thesis 4
1.4 Thesis Outline 5
1.5 Summary 7

CHAPTER 2. LITERATURE REVIEW

2.1 Introduction 8
2.2 Fouling Deposit of Dairy Materials 8
  2.2.1 Classification of milk fouling deposits 8
  2.2.2 Formation mechanisms of milk fouling deposit 10
  2.2.3 Low temperature milk deposits 11
2.3 Cleaning Procedures 11
  2.3.1 CIP schedules 11
  2.3.2 Typical cleaning rate curve 12
  2.3.3 Visualisation of protein deposit removal 12
2.4 Cleaning Mechanisms 13
  2.4.1 Mechanical action 15
  2.4.2 Chemical reactions 16
    2.4.2.1 Cleaning chemicals 17
    2.4.2.2 Protein-chemical reactions in high pH environments 18
  2.4.3 Mass transfer 24
2.5 Influences of the System Parameters 25
CHAPTER 4. DISSOLUTION AND MECHANICAL PROPERTIES OF WPC GELS

4.1 Introduction

4.2 Dissolution of WPC Gels in NaOH solutions
   4.2.1 Experimental method
   4.2.2 Effect of temperature and concentration on dissolution rate
   4.2.3 Effect of stirring speed on dissolution rate
   4.2.4 Effect of pH on dissolution rate
   4.2.5 Consumption of NaOH during dissolution process
   4.2.6 Effect of contamination of NaOH cleaning solution on dissolution rate

4.3 Dissolution of WPC gels in Different Cleaning Solutions
   4.3.1 Experimental method
   4.3.2 NaOH-NaClO solutions
   4.3.3 NaOH-H₂O₂ solutions
   4.3.4 NaOH-Na₂SO₃ solutions
   4.3.5 Discussion

4.4 Mechanical Properties of WPC Gel
   4.4.1 Dynamic oscillatory shear testing
   4.4.2 Indentation test

4.5 Penetration Rate of NaOH Solution in WPC Gel

4.6 Swelling Experiments

4.7 Microstructure Changes
   4.7.1 Particulate and Fine-Stranded Gel
   4.7.2 Microstructure of WPC gels

4.8 Discussion

4.9 Conclusions

CHAPTER 5. CLEANING KINETICS AND A MATHEMATICAL MODEL

5.1 Introduction

5.2 Polymer Dissolution Based Cleaning Mechanism
   5.2.1 Background of polymer dissolution
5.2.2 Physical picture of dissolution WPC gel film

5.3 Cleaning Model
   5.3.1 Swelling and uniform stage
   5.3.2 Decay stage

5.4 Experimental Procedure

5.5 Results and Discussion
   5.5.1 Typical cleaning rate curve
   5.5.2 Mass recovery ratio as a function of Reynolds number
   5.5.3 Identification of model parameters
   5.5.4 Effect of temperature on cleaning
   5.5.5 Effect of flow velocity on cleaning
   5.5.6 Effect of initial amount of deposits on cleaning
   5.5.7 Effect of concentration of cleaning solutions upon cleaning

5.6 Prediction of Cleaning Results
   5.6.1 Relationship of the model parameters with temperature and fluid velocity
   5.6.2 Previous cleaning results
   5.6.3 Comparison of the cleaning properties for various proteinaceous fouling deposits

5.7 Conclusions

CHAPTER 6. PREDICTING THE CONSTANT CLEANING RATE USING A MASS TRANSFER THEORY

6.1 Introduction

6.2 Model Development

6.3 Solubility and Viscosity of WPC gel in NaOH solutions
   6.3.1 Solubility measurement
   6.3.2 Viscosity measurement

6.4 Comparisons between the Predicted and Experimental $R_m$ Results

6.5 Molecular Mass (Size) Change
   6.5.1 Sulfhydryl group (SH) content measurement
   6.5.2 Determination the molecular mass distribution by size exclusion chromatography (SEC) method

VIII
### 6.6 Effect of Solid Content and Composition of WPC Gel on Cleaning

#### 6.6.1 Experimental procedure

#### 6.6.2 WPC gel solids content
- **6.6.2.1** Effect of gel solids content on cleaning
- **6.6.2.2** Mechanical properties of WPC gel with different solid contents

#### 6.6.3 WPC gel with various pH values

#### 6.6.4 High calcium content WPC gel
- **6.6.4.1** Cleaning results
- **6.6.4.2** Microstructure of high calcium content WPC gel
- **6.6.4.3** Discussion

#### 6.6.4 High calcium content WPC gel

#### 6.7 Other Important Factors Influencing Cleaning Results
- **6.7.1** Disengagement and mass transfer controlled cleaning process
- **6.7.2** Cleaning behaviour of 2.0 wt% NaOH solutions at high flow velocity

#### 6.8 Conclusions

### CHAPTER 7. GENERAL CONCLUSIONS AND RECOMMENDATIONS

#### 7.1 Summary
- **7.1.1** Improvements of the experimental methods
- **7.1.2** The role of chemicals in cleaning processes
- **7.1.3** Polymer dissolution controlled cleaning procedure
- **7.1.4** Influence of operation conditions on cleaning efficiency
- **7.1.5** Influence of the nature of the soil on cleaning kinetics
- **7.1.6** Prediction of cleaning processes

#### 7.2 Recommendations for Future Work
- **7.2.1** Methodology of cleaning study
- **7.2.2** Modeling the cleaning process
- **7.2.3** Optimisation of the CIP process
- **7.2.4** Minimisation of the environmental impacts

### APPENDICES

### BIBLIOGRAPHY
LIST OF FIGURES

1.1 Schematic illustration of the forces involved in cleaning and related cleaning procedures (a) forces involved in cleaning; (b) removal of large pieces of reacted and/or unreacted deposits; (c) removal of small lumps; (d) dissolution process.

2.1 Literature results of the effects of velocity on cleaning time (Timperley and Smeulders 1988).

2.2 A typical modelling result for a WPC deposit cleaned with NaOH solutions (Bird, 1993).

3.1 Schematic illustration of the mechanism of whey protein fouling and gelation.

3.2 Microstructure of thermally-induced (a) whey protein fouling (Schraml and Kessler, 1994); (b) regular β-lactoglobulin gel; (c) irregular β-lactoglobulin gel (Hermansson and Langton, 1994).

3.3 Schematic diagram of the rotation device used to prepare WPC gel deposits.

3.4 Absorption spectra of standard whey protein concentrate solutions at pH 13 buffer solutions with disposable cuvette (OPS).

3.5 Linear correlation of whey protein concentration to UV absorption at 290 nm.

3.6 Absorption spectra difference of standard whey protein concentrate solutions with flow quartz cuvette and disposable cuvette (OPS).

3.7 Absorption spectra of standard whey protein concentrate solutions at 0.5 wt% NaOH solutions with flow quartz cuvette.

3.8 Linear correlation of absorption at 248-256 nm to whey protein concentration.

4.1 Dissolution curves of WPC gels in the cleaning solutions with various NaOH concentrations at 65 °C.

4.2 Changes in the surface area of the WPC gels treated with the cleaning solutions of various NaOH concentrations at 65 °C. (S₀ is the initial surface area of the WPC gels).

4.3 A typical dissolution rate curve for WPC gels in NaOH solutions.

4.4 Effects of NaOH concentration and temperature of the cleaning solutions upon the dissolution rate of WPC gels (the cleaning rates for Bird’s experiments are presented as the total mass removal rate (whey protein + 30 wt% water)).

4.5 Arrhenius plots (ln (R₀) versus 1/T) for the WPC gels treated with the cleaning solutions with 0.1, 0.3, 0.5, 1.0, 2.0 wt% NaOH.
4.6 Influence of stirring speed on the dissolution of the WPC gels. ($m_0$ is the initial mass of the WPC gel).

4.7 Effects of pH of WPC gels on dissolution.

4.8 Comparing the dissolution results based on 290 nm absorption of whey protein and 552 nm absorption of phenolphthalein.

4.9 A schematic drawing of dissolution apparatus.

4.10 Influence of whey protein contaminated 0.5 wt% NaOH solutions on the dissolution of the WPC gels.

4.11 The dissolution results of the WPC gel in NaClO-NaOH solutions.

4.12 The dissolution results of the WPC gels in H$_2$O$_2$-NaOH solutions.

4.13 The dissolution results of the WPC gel in Na$_2$SO$_3$-NaOH solutions.

4.14 Schematic illustrations for the puncture and indentation hardness tests.

4.15 Typical strain sweep curves for WPC gels treated with various NaOH concentration solutions.

4.16 Influence of NaOH concentration on the storage modulus of WPC gels as a function of temperature.

4.17 The storage modulus changes of 2 wt% NaOH treated WPC gels as a function of temperature.

4.18 The compliance curves for WPC gel sample treated with and without alkaline solutions.

4.19 Typical load versus deformation curves from a puncture test.

4.20 Schematic representation of penetration of NaOH solution into the WPC gel.

4.21 The thickness changes of unreaction zone of WPC gels at various NaOH concentrations.

4.22 Effect of NaOH concentration upon its penetration rate in 25 wt% WPC gel.

4.23 Swelling of WPC gel in alkaline solutions at 4 °C.

4.24 Schematic representation of microstructure changes of proteinaceous fouling in high pH environment.

4.25 Cryo-SEM microstructure of WPC gels treated with NaOH solutions: (a) initial WPC gel; (b) treated with 0.5 wt% NaOH; (c) treated with 2.0 wt% NaOH.
5.1 A schematic diagram of the dissolution process of a WPC gel film.

5.2 A schematic diagram of the cleaning apparatus.

5.3 A typical cleaning rate-time curve.

5.4 Mass recovery ratio as a function of Reynolds number.

5.5 The estimation of the reptation time at various temperatures from the cleaning rate-time plots using 0.5 wt% NaOH solutions.

5.6 A typical plot of \( \ln\left(\frac{wR}{R_m - R}\right) \) versus time used to identify the values of \( \xi \) and \( t_r \) from the experimental results.

5.7 The comparison of the experimental and predicted cleaning results at different temperatures at a constant Reynolds number (\( Re = 6080 \)) using 0.5 wt% NaOH cleaning solutions.

5.8 Arrhenius plots (\( \ln\xi, \ln R_m, \ln k_A, \ln\left(\frac{1}{t_r}\right) \)) versus \( 1/T \) respectively) for the WPC gel films treated with 0.5 wt% NaOH solutions.

5.9 The comparison of the experimental and predicted cleaning results at different flow velocities at 65 °C using 0.5 wt% NaOH cleaning solutions.

5.10 The cleaning rate versus time plots for the WPC gel films with various initial masses at a flow velocity of 0.25 m/s and 65 °C using the 0.5 wt% NaOH cleaning solutions.

5.11 The experimental cleaning results at different temperatures at 0.25 m/s using 2.0 wt% NaOH cleaning solutions.

5.12 \( y \cdot \exp\left(\frac{E_a}{RT}\right) \) versus Reynolds number plots at 65 °C for (a) \( y=R_m \), (b) \( y=\xi \), (c) \( y=k_A \), and (d) \( y=1/t_r \).

5.13 The predicted and experimental total cleaning times for the WPC gel films with various initial masses.

5.14 The comparison of the experimental and predicted cleaning results at various temperatures at a flow velocity of 0.25 m/s.

5.15 Arrhenius plots (\( \ln\xi, \ln R_m, \ln k_A, \ln\left(\frac{1}{t_r}\right) \)) versus \( 1/T \) respectively) for the WPC gel films treated with 0.5 wt% NaOH cleaning solutions at different Reynolds number.

5.16 The model predictions together with the experimental results reported by Gallot-Lavallee and Lalande (1985).
The model predictions together with the experimental results reported by Bird and Fryer (1995).

The model predictions together with the experimental results reported by Gillham et al. (1999).

The comparison of the constant cleaning rate of WPC gel and real fouling under the same cleaning conditions.

Effect of temperature on WPC solubility in 0.5 wt% NaOH solutions.

Arrhenius correlation of viscosity and temperature of WPC-0.5 wt% NaOH solutions with various concentrations.

Comparisons between the predicted and experimental results of $R_m$ at different temperatures.

Comparisons between predicted and experimental results of $R_m$ with different flow velocities.

A schematic drawing of the molecular size (weight) reduction in high pH environment.

Effects of dissolution and temperature on SH content.

The repeatability of the SEC experimental results.

Typical SEC profiles of WPC gel dissolved by NaOH solution.

Effect of WPC gel solid content on cleaning rate.

Comparison between the predicted and experimental results of the constant cleaning rate with different solid contents.

Indentation compliance curves for WPC gels with different solid contents.

Storage modules as a function of frequency for WPC gels with different solid contents.

Effect of pH of gel formation on the cleaning rate of the WPC gel.

Effect of pH on the mechanical property of β-lactoglobulin gel (Stading and Hermansson, 1991).

Effect of calcium chloride on cleaning rate of the WPC gel.

Effect of pH on the cleaning rate of 2 wt. % CaCl₂-WPC gel.

Microstructure of 25 wt% WPC gel: (a) pure WPC gel; (b)&(c) 2 wt% CaCl₂-WPC gel.
6.18 Cleaning results using 0.5 wt% NaOH solutions with high flow velocities.

6.19 Comparison of the predicted and experimental results of the constant cleaning rates.

6.20 The effects of flow velocity on the cleaning rate of WPC gels using 2.0 wt% NaOH cleaning solutions (ϕ=10 mm tube).
LIST OF TABLES

2.1 Types of milk deposits formed at different processing temperature ranges.

3.1 Typical protein compositions of WPC powder, proteinaceous fouling and fresh milk.

4.1 Indentation hardness results for WPC gels treated with NaOH cleaning solutions.

5.1 The experimental conditions and model parameters obtained from the analyses of the experimental results given in Figure 5.7.

5.2 The experimental conditions and model parameters obtained from the analyses of the experimental results given in Figure 5.9.

5.3 The model parameters used in the model predictions for the removal of WPC gel fouling.

5.4 The comparison of the model parameters identified from analysing the cleaning results using 0.5 and 2.0 wt% NaOH cleaning solutions (see Figure 5.11 and 5.14).

5.5 The formation conditions and properties of the proteinaceous fouling used in different cleaning studies.

5.6 The experimental conditions and the model parameters obtained from the analyses of experimental results given in Figure 5.16 and 5.18.

5.7 The experimental conditions and model parameters obtained from the analyses of the experimental results given in Figure 5.17.

5.8 The parameters used in model prediction for previously published cleaning results.

6.1 Parameters used in the prediction of \( R_m \).

6.2 The efflux time of various solutions measured at 25 °C.

6.3 Mechanical properties of WPC gels with different water contents.
## NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>$A$</td>
<td>surface area of deposits, m$^2$</td>
</tr>
<tr>
<td>$A_{L}$</td>
<td>deposit surface area remained in decay stage, m$^2$</td>
</tr>
<tr>
<td>$A_p$</td>
<td>projected contact area of indenter, m$^2$</td>
</tr>
<tr>
<td>$A_{10}$</td>
<td>total surface area covered by the protein film, m$^2$</td>
</tr>
<tr>
<td>$A_{248}$</td>
<td>value of UV absorbance at the wavelength of 248 nm</td>
</tr>
<tr>
<td>$A_{256}$</td>
<td>value of UV absorbance at the wavelength of 256 nm</td>
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<tr>
<td>$A_{290}$</td>
<td>value of UV absorbance at the wavelength of 290 nm</td>
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<tr>
<td>$A_{412}$</td>
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<tr>
<td>$B$</td>
<td>reaction frequency factor, s$^{-1}$</td>
</tr>
<tr>
<td>$C$</td>
<td>mass concentration, kg/m$^3$</td>
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<tr>
<td>$C_b$</td>
<td>mass concentration of reaction products in cleaning solution, kg/m$^3$</td>
</tr>
<tr>
<td>$C_{OH}$</td>
<td>the concentration of hydroxyl ions, g/L</td>
</tr>
<tr>
<td>$C_s$</td>
<td>saturation concentration of disengaged protein chains in boundary layer, kg/m$^3$</td>
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<tr>
<td>$C_s^*$</td>
<td>solubility value based on the whey protein content, kg/m$^3$</td>
</tr>
<tr>
<td>$C_{SH}$</td>
<td>SH content, µM/g</td>
</tr>
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<td>$d$</td>
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<tr>
<td>$D$</td>
<td>mass diffusivity, m/s$^2$</td>
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<tr>
<td>$D_c$</td>
<td>diameter of the capillary, m</td>
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<td>$D_F$</td>
<td>dilution factor</td>
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<td>$E_k$</td>
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<tr>
<td>$f$</td>
<td>frictional coefficient of the fluid flow</td>
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<td>$f_r$</td>
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<tr>
<td>$G''$</td>
<td>lost modulus, Pa</td>
</tr>
<tr>
<td>$h$</td>
<td>depth of penetration in indentation test, m</td>
</tr>
<tr>
<td>$h_p$</td>
<td>depth of contact in indentation test, m</td>
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</table>
$h_r$  residual value of penetration depth in indentation test, m

$h_0$  zero offset of penetration depth in indentation test, m

$H$  hardness, Pa

$I_E$  elasticity index

$J_R$  removal rate, kg/m$^2$.s

$k$  proportionality constant, s$^{-1}$

$k_1$  first order rate constant for the surface area reduction, s$^{-1}$

$k_B$  Boltzmann constant, $10^{-23}$ J/K

$k_d$  disengagement rate constant, s$^{-1}$

$k_{DO}$  the deposit mass transfer coefficient, m/s

$k_m$  mass transfer coefficient, m/s

$k_{OH}$  the hydroxyl ion mass transfer coefficient, m/s

$k_p$  penetration velocity of NaOH solution in WPC gel, m/s

$k_r$  reaction rate constant, s$^{-1}$

$k_x$  a rate constant, m$^3$/kg.s

$k_X$  a first order rate constant, s$^{-1}$

$k_Y$  a zero order rate constant, m/s

$k'_Y$  a first order rate constant, s$^{-1}$

$k_\phi$  a mass transfer coefficient, g/m$^2$.s

$l$  length of the capillary, m

$l_b$  thickness of the boundary layer, m

$l_d$  thickness of the deposit layer, m

$l_f$  deposit of initial thickness, m

$l_s$  upper layer of swelled deposit thickness, m

$l_y$  lower layer of unswollen deposit thickness, m

$L$  average distance between the upper and lower menisci, m

$L_u$  thickness of the unreaction zone, m

$m$  mass removed per unit area, g/m$^2$

$m_c$  critical mass per unit area, g/m$^2$

$m_d$  deposited mass per unit area, g/m$^2$

$m_i$  initial deposit mass per unit area, g/m$^2$

$m_u$  mass removed during uniform cleaning stage, g/m$^2$

$m_{su}$  total mass removed during swelling and uniform cleaning stage, g/m$^2$
$m_{uv}$ dissolved mass calculated using the UV absorbance data, g/m$^2$

$m_1$ a coefficient for an indentation loading curve

$m_2$ a coefficient for an indentation unloading curve

$M$ molecular weight, Dalton

$M_{NaOH}$ molecular weight of NaOH, u

$M_X$ the mass of the initial deposits, kg

$M_Y$ the mass of the intermediate reaction products of deposits, kg

$M_Z$ the mass of the final form of deposits, kg

$n_1$ a loading index for an indentation loading curve

$n_2$ a loading index for an indentation unloading curve

$N$ equivalent concentration, eq/L

$N_{HCl}$ the equivalent concentration of hydrogen chloride acid, eq/L

$P$ force, N

$P_1$ applied force in an indentation loading curve, N

$P_2$ applied force in an indentation unloading curve, N

$P_t$ maximum applied load in an indentation test, N

$Q$ mass of the fluid flown through the capillary, kg

$r$ radius, m

$r_d$ solid content of the WPC gel, wt%

$R$ cleaning rate, g/m$^2$s

$R'$ cleaning rate expressed as the mass loss of whey protein, g/m$^2$s

$R_d$ average dissolution rate, g/m$^2$s

$R_D$ cleaning rate during decay cleaning stage, g/m$^2$s

$Re$ Reynolds number

$R_g$ molar gas constant, J/mol·K

$R_m$ constant cleaning rate, g/m$^2$s

$R_{m-real}$ literature result of constant cleaning rate, g/m$^2$s

$R_{m-WPC}$ model prediction of constant cleaning rate, g/m$^2$s

$R'_m$ constant cleaning rate expressed as the mass loss of whey protein, g/m$^2$s

$S$ elastic contact stiffness, N/m$^2$

$Sc$ Schmidt number

$S_d$ deposit strength, N/m$^2$

$S_o$ initial surface area of the WPC gel, m$^2$
\[ S(t) \] surface area of the WPC gel at time \( t \) during the dissolution process, \( \text{m}^2 \)

\( t \) time, s

\( t_c \) time needed to cleaning the deposits at certain flow velocity, s

\( t_d \) cleaning time in decay stage, s

\( t_e \) efflux time, s

\( t_{es} \) solvent efflux time, s

\( t_p \) penetration time, s

\( t_r \) reptation time, s

\( t_t \) total cleaning time, s

\( t_{su} \) sums of cleaning times in swelling and uniform stage, s

\( t_u \) cleaning time during uniform cleaning stage, s

\( t^* \) the time when all the deposit was changed to a removable form, s

\( \tan\delta \) loss factor

\( T \) temperature, K

\( u \) flow velocity, m/s

\( V \) volume of solution, \( \text{m}^3 \)

\( V_B \) timed volume of liquids passing through the capillary, \( \text{m}^3 \)

\( V_{HCl} \) volume of HCl solution, L

\( V_{NaOH} \) volume of NaOH solution, L

\( W_e \) elastic work of indention, J

\( W_t \) total work of indentation, J

\( W_{NaOH} \) consumption of the NaOH, g/L

\( X \) initial form of deposits

\( y \) model parameter

\( Y \) intermediate form of deposits

\( Z \) final form of deposits
Greek letters

\( \alpha \) a constant
\( \beta \) a constant
\( \delta \) phase shift angle, \(^{\circ}\)
\( \varepsilon \) viscometer constant
\( \eta \) viscosity, Pa.s
\( \eta_b \) viscosity of the boundary layer, Pa.s
\( \eta' \) ratio of swollen to unswollen deposit thickness
\( \phi \) volume fraction of the disengaged protein molecules in the boundary layer, \%. 
\( \phi_m \) maximum volume fraction of the disengaged protein molecules, \%.
\( \phi_v \) volume fraction of the tangling protein chains at the solution side of gel-solution interface at the time \( t = t_r \)
\( \gamma \) strain
\( \nu \) kinematic viscosity, mm\(^2\)/s
\( \nu_p \) Poisson’s ratio
\( \theta \) a half angle of indenter, \( ^{\circ} \)
\( \rho \) density, kg/m\(^3\)
\( \rho_s \) swollen deposit density, kg/m\(^3\)
\( \rho_Y \) intermediate reaction products density, kg/m\(^3\)
\( \tau \) mean shear stress, Pa
\( \sigma \) angular frequency, s\(^{-1}\)
\( \psi \) dimensionless parameter
\( \xi \) kinetic constant, s\(^{-1}\)
ABBREVIATIONS

ASTM  American standard test method
BSA  bovine serum albumin
CIP  cleaning-in-place
COD  chemical oxygen demand
CSEM  cryogenic scanning electron microscope
DOS  degree of swelling
EDTA  ethylene diamine tetra-acetic acid
ID  inside diameter
HILLS  hygienic industrial live line sampler
HPLC  high performance liquid chromatography
LAL  lysinoalanine
LVR  linear viscoelastic region
MEK  methyl ethyl ketone
NTA  nitrilo-tri-acetic acid
OH⁻  hydroxyl ions
PDI  protein dispersibility index
SDS-PAGE  sodium dodecyl sulfate-polyacrylamide gel electrophoresis
SEC  size exclusion chromatography
SEM  scanning electron microscope
SH  sulphydryl group
S-S  disulphide bond
TS  total solids percentage
UHT  ultra high temperature
UV  ultraviolet
WHC  water holding capacity
WPC  whey protein concentrate
WPI  whey protein isolate

XXI