

DESIGN AND DEVELOPMENT OF NANOPARTICLE COATED ANTI-FOULING HEAT EXCHANGER FOR MILK PROCESSING



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IN
DAIRY ENGINEERING**

By

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M. Tech. (Dairy Engineering)**

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MAJOR ADVISOR

DEDICATED TO
MY
BELOVED FAMILY
AND
Well WISHERS

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Bengaluru

Manjunatha B.M.

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ABSTRACT

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## ABSTRACT

Plate heat exchanger (PHE) is the most popular equipment in dairy industries due to its ease of maintenance, cleanability, compactness, higher heat transfer coefficients and other features desirable in milk processing. However, fouling of its plates is a severe problem that impedes heat transfer, endangers the product quality and demands costly and time-consuming cleaning techniques. Among the number of techniques attempted to mitigate fouling of PHE, the modification of heat transfer surfaces by applying non-sticky materials like Teflon is a recent and potential technique. Present study was undertaken to design and develop a nanoparticle coated PHE for fouling mitigation by using polytetrafluorethylene (PTFE) and titanium dioxide (TiO<sub>2</sub>) as coating materials. A skid mounted module with two PHE units, balance tank, PID-controlled hot water generator, piping and pumping systems for milk and hot water was developed and evaluated. The PTFE and TiO<sub>2</sub> in the ratio of 84:16 with a coating thickness of 20  $\mu\text{m}$  were selected based on the thermal conductivity of the coated SS 316 plates. The PTFE-TiO<sub>2</sub> coating was done by spraying method on the plates of one PHE unit and the other PHE was left uncoated (control). Characterization of the coated surfaces was done by SEM-EDS, XRD, water contact angle, AFM and profilometer. Experimental trials were conducted for heat treatment of milk and paneer whey for 8 h using hot water as heating medium. Performance of the developed unit was evaluated in terms of overall heat transfer coefficients, foulants deposition and fouling resistance. The coating on testing for its adhesion strength using the cross-cut tape test was found to confirm to 5B grade as per ASTM-D3359. Average roughness of the SS 316 (uncoated) and PTFE-TiO<sub>2</sub> surfaces measured with the profilometer were  $0.2\pm0.02$  and  $0.74\pm0.09$   $\mu\text{m}$ , respectively. The contact angles for uncoated and PTFE-TiO<sub>2</sub> coated surfaces with distilled water, milk and paneer whey were  $66.8\pm6.3^\circ$  and  $112.8\pm0.8^\circ$ ,  $61\pm6.1^\circ$  and  $97.5\pm1.1^\circ$ , and  $82.44\pm2.1^\circ$  and  $103.8\pm1.03^\circ$ , respectively. It indicated successful induction of hydrophobicity on the plate surface by coating. X-ray diffraction analysis indicated that the crystallite size ranged from 56.25 to 135.51 nm on SS 316 surface and from 4.19 to 173.10 nm for the coated surface. The EDS analyses revealed that the coated composite was distributed over entire surface of the substrate (SS 316) with 65.42% fluorine and 6.31% titanium by weight of the surface constituents, which came from the PTFE and TiO<sub>2</sub> nanoparticles, respectively. The XPS of dried foulant deposits suggested the absence of PTFE and TiO<sub>2</sub>. Evaluation of the thermal performance of the developed PHE for processing of milk and paneer whey indicated mean overall heat transfer coefficients for uncoated surfaces ranged from 361.36 to 969.26 W/m<sup>2</sup>K, whereas for coated surfaces, it was from 314.46 to 352.45 W/m<sup>2</sup>K. The foulant deposition, analyzed using independent t-test, revealed that the coated surfaces realized significantly lesser ( $P<0.05$ ) foulant deposition than by the uncoated surfaces for milk as well as whey. Thus, the evaluation established the anti-fouling properties of the PTFE-TiO<sub>2</sub> coated surface.



## सारांश

प्लेट हीट एक्सचेंजर (पीएचई) रखरखाव, साफ-सफाई, सघनता, गर्मी हस्तांतरण गुणांक और दूध प्रसंस्करण में वांछनीय गुणवत्ता के कारण डेयरी उद्योगों में सबसे लोकप्रिय उपकरण है। हालांकि, इसकी प्लेटों की फाउलिंग एक गंभीर समस्या है, जो गर्मी हस्तांतरण को बाधित करती है तथा उत्पाद की गुणवत्ता को खतरे में डालती है। पीएचई की फाउलिंग को कम करने के लिए कई तकनीकों का प्रयोग किया गया है। उनमेंसे, गर्मी हस्तांतरण सतह पर टेफ्लॉन जैसी गैर-चिपचिपी सामग्री की पतली परत चढ़ाकर उसके द्वारा फाउलिंग नियंत्रण एक हालिया और संभावित तकनीक है। वर्तमान अध्ययन में फाउलिंग शमन के लिए PTFE और  $\text{TiO}_2$  को कोटिंग सामग्री के रूप में उपयोग करके नैनोकण लेपित पीएचई का डिजाइन और विकास करने के लिए किया गया था। दो पीएचई इकाइयों, बैलेंस टैंक, पि आर डी नियंत्रित गर्म पानी जनरेटर, दूध और गर्म पानी के लिए पाइपिंग और पंपिंग सिस्टम के साथ एक स्किड माउंटेड मॉड्यूल को विकसित करके उसका और मूल्यांकन किया गया था।  $20\mu\text{m}$  मोटाई की कोटिंग के साथ 84:16 के अनुपात में PTFE और  $\text{TiO}_2$ , एसएस 316 प्लेटों की ऊष्मा वाहकता के आधार पर चुने गए थे। एक पीएचई को बिना लेपित छोड़ दिया गया था ताकि वह नियंत्रण के तौर पर इस्तेमाल हो। क्रॉस-कट टेप परीक्षण का उपयोग करके कोटिंगकी आसंजन ताकत देखी गयी। लेपित सतहों की विशेषता, SEM-EDS, XRD, जल संपर्क कोण, AFM और प्रोफीलोमीटर द्वारा की गई थी। दूध और पनीर मट्ठा के प्रसंस्करण के लिए 8 घंटे तक प्रायोगिक परीक्षण किया गया था। विकसित इकाई का मूल्यांकन क्रमशः समग्र गर्मी हस्तांतरण गुणांक, फाउलेंट्स डिपोजिशन और फाउलिंग प्रतिरोध के रूप में किया गया था, जो कि फाउलिंग के प्रत्यक्ष और अप्रत्यक्ष मापदंड थे। बिना लेपित और PTFE- $\text{TiO}_2$  लेपित एसएस 316 की सतहों का औसत खुरदरापन प्रोफीलोमीटर द्वारा नापनेपर क्रमशः  $0.74 \pm 0.09$  और  $0.2 \pm 0.02 \mu\text{m}$  पाया गया। जल के साथ बिना लेपित और PTFE- $\text{TiO}_2$  लेपित सतहों के संपर्क कोण  $66.8 \pm 6.3^\circ$  और  $112 \pm 0.8^\circ$  थे, जबकि दूध के लिए वे क्रमशः  $61 \pm 6.1^\circ$  और  $97.5 \pm 1.1^\circ$  थे। यह कोटिंग द्वारा प्लेट की सतह पर हाइड्रोफोबिसिटी के सफल प्रेरण का संकेत माना गया। एक्स-रे विवर्तन विश्लेषण से ज्ञात हुआ कि क्रिस्टलीय आकार एसएस 316 सतह पर 56.25 से 135.51 nm तक और लेपित सतह के लिए 4.19 से 173.10 nm तक था। ईडीएस विश्लेषण से पता चला कि लेपित समग्र सबस्ट्रेट (एसएस 316) की सतह पर 65.42% फ्लोरीन और 6.31% टाइटेनियम के साथ सतह के घटकों के वजन से वितरित किया गया था, जो क्रमशः PTFE और  $\text{TiO}_2$  नैनोकणों से आया था। सूखे फाउलेंट जमा के XPS ने PTFE और  $\text{TiO}_2$  की अनुपस्थिति को स्थापित किया। दूध और पनीर व्हे के प्रसंस्करण के लिए विकसित पीएचई के औष्णिक मूल्यांकन से ज्ञात हुआ कि बिना लेपित सतह के समग्र गर्मी हस्तांतरण गुणांक  $361.36$  से  $969.26 \text{ W/m}^2\text{K}$  तक था, जबकि लेपित सतहों के लिए, यह  $314.46$  से  $352.45 \text{ W/m}^2\text{K}$  तक था। स्वतंत्र टी-टेस्ट का उपयोग करके विश्लेषण किए गए फाउलेंट डिपोजिशन से पता चला है कि लेपित सतहों को दूध के साथ-साथ पनीर व्हे के लिए बिना लेपित सतहों की तुलना में काफी कम ( $p < 0.05$ ) फाउलेंट डिपोजिशन हुआ। इस प्रकार, मूल्यांकन ने PTFE- $\text{TiO}_2$  लेपित सतह के विरोधी दूषण गुणों को स्थापित किया।



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## LIST OF SYMBOL AND ABBREVIATIONS

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|                  |                                                |
|------------------|------------------------------------------------|
| AFM              | Atomic Force Microscopy                        |
| FTIR             | Fourier Transformed Infrared Spectrophotometry |
| NCA              | Notched Coating Adhesion                       |
| GDP              | Gross Domestic Power                           |
| $\beta$ -Lg      | Beta Lactoglobulin                             |
| CIP              | Cleaning-In-Place                              |
| EDS              | Energy Dispersive Spectroscopy                 |
| EP               | Electropolishing                               |
| HTST             | High Temperature Short Time                    |
| UHT              | Ultra High Temperature                         |
| PECVD            | Plasma Enhanced Chemical Vapor Deposition      |
| PVD              | Physical Vapour Deposition                     |
| HVOF             | High-Velocity Oxy-Fuel                         |
| CVD              | Chemical Vapour Deposition                     |
| PEG              | Poly Ethylene Glycol                           |
| PHE              | Plate Heat Exchanger                           |
| EPDM             | Ethylene Propylene Diene Terpolymer            |
| PS               | Perfluorooctyltriethoxysilane                  |
| PTFE             | Polytetrafluoroethylene                        |
| TiO <sub>2</sub> | Titanium Dioxide                               |
| SEM              | Scanning Electron Microscopy                   |
| SS304            | Stainless Steel 304                            |
| SS316L           | Stainless Steel 316 Low carbon                 |
| WCA              | Water Contact Angle                            |

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|       |                                                |
|-------|------------------------------------------------|
| WPC   | Whey Protein Concentrate                       |
| WPI   | Whey Protein Isolates                          |
| XPS   | X-Ray Photoelectron Spectroscopy               |
| XRD   | X-Ray Diffraction                              |
| AISI  | American Iron and Steel Institute              |
| AOAC  | Association of Official Analytical Chemists    |
| ASME  | American Society for Mechanical Engineers      |
| ASTM  | American Society for testing materials         |
| BIS   | Bureau of Indian Standards                     |
| CAD   | Computer Aided Design                          |
| FDA   | Food and Drug Administration                   |
| Fig.  | Figure                                         |
| FSSAI | Food Safety and Standards Authority of India   |
| ISO   | International Organization for Standardization |
| g     | Gram                                           |
| h     | Hour                                           |
| kg    | Kilogram                                       |
| kPa   | kilo Pascal                                    |
| cP    | Centipoise                                     |
| GPa   | Giga Pascal                                    |
| kW    | Kilowatt                                       |
| L     | Litre                                          |
| MCCB  | Miniature Current Circuit Breaker              |
| Min   | Minute                                         |
| kJ    | Kilo Joule                                     |
| mL    | Milliliter                                     |

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|               |                                  |
|---------------|----------------------------------|
| nm            | Nanometer                        |
| mm            | Millimeter                       |
| MoC           | Material of Construction         |
| NDDB          | National Dairy Development Board |
| P&I           | Piping and Instrumentation       |
| PID           | Proportional Integral Derivative |
| PVC           | Poly Vinyl Chloride              |
| PS            | Poly Styrene                     |
| Ra            | Roughness Average Value          |
| s             | Second                           |
| SNF           | Solid Not Fat                    |
| t             | Time                             |
| T             | Temperature                      |
| TIG           | Tungsten Inert Gas Welding       |
| v/v           | Volume by Volume                 |
| W             | Watt                             |
| w/w           | Weight by Weight                 |
| @             | At the rate                      |
| °C            | Degree Centigrade                |
| $\gamma$      | Surface Tension                  |
| $\mu\text{m}$ | Micrometer                       |
| $\mu$         | Mu                               |
| %             | Percent                          |
| $\Delta p$    | Pressure drop                    |
| $\rho$        | Density                          |

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# CHAPTER - 1

---

## INTRODUCTION

---



# 1.0 INTRODUCTION

---

Dairying is an important segment of Indian agriculture contributing significantly in terms of contribution towards Gross Domestic Product (GDP), food security and employment generation. As per the recent statistics, the annual milk production of India during 2017-18 was 176.4 million tonnes that represented 21.3% of the global milk production (www.nddb.coop, 2019). The Indian dairy industry is presently valued at ₹750 billion and is expected to grow at the rate of 15% annually i.e. an addition of ₹150 billion every year (www.mondaq.com, 2018). More than 20% of the Indian milk produce is handled by the organized sector through the widespread network of government, cooperative and private dairy plants (Rajendran and Mohanty, 2004). Almost every milk processing plant has Plate Heat Exchanger (PHE) as elementary equipment for the thermal treatment of milk and similar products like cream, skim milk, whey, etc. The PHE consists of vertical plates arranged in a horizontal stack with a spacing of approximately 2-5 mm between adjacent plates and sealed against the surrounding by a gasket, thus forming a flow channel between two successive plates. The product flows as thin layer through the alternate channels leaving the remaining channels for the flow of heating medium in opposite direction. Each plate supports the flow of product and heating medium on both sides and acts as heat transfer surface. The thickness of the plate usually varies from 0.2 to 0.5 mm and it is rectangular in shape with four ports near its corners and a certain pattern of corrugations on the central area confined by the gasket. Due to large contact surface and turbulence because of corrugations, the PHE has a high heat transfer coefficient, better cleanability, compact design and other features desirable for milk processing such as ease of assembling and dismantling and ease of capacity expansion. Further, the possibility of heat regeneration by appropriately dividing the flow into multiple sections greatly reduces the energy consumption in thermal processing. The PHEs are widely used in all the process industries operating in a moderate range of temperature ( $<250^{\circ}\text{C}$ ) for the thermal processing of comparatively low viscous fluids (Datta *et al.*, 2002). Therefore, plate heat exchanger is highly preferred in food industry and is indispensable in dairy industry.

However, deposition from the process fluids on the plates is a serious problem encountered with the PHE. The foulant deposition reduces effective thermal conductivity of the heat transfer surface which in turn narrows down the passage for the flow of process

fluid. The decreased thermal conductivity impedes heat transfer requiring more flow of utility and corresponding costs whereas, the narrowing of flow channels increases the pressure drop requiring high pumping power. The fouling has also been reported to increase the likelihood of biofilm formation, product contamination, frequent process run downs and higher operating costs. The plates of PHE are made of stainless steel SS 316, which is recommended and commonly used for the food contact surfaces in most of the processing equipment. Though SS 316 possesses superior mechanical properties and corrosion resistance, it is prone to fouling because of its high surface energy and hydrophilic nature that support the adhesion of product. So, frequent de-fouling and the adoption of costly and time-consuming cleaning techniques are essential to avoid consequential qualitative, technological and economic losses.

The problem of fouling is more prevalent in the case of milk processing because of its distinct composition and the presence of heat labile milk constituents such as whey proteins. Therefore, PHE used for thermal processing of milk requires regular and rigorous cleaning in place (CIP). Many times, the PHE needs to be dismantled for thorough cleaning and removal of foulant deposits from the plates, resulting in wastage of productive time and workforce. Asselt *et al.* (2005) reported that cleaning process for foulant removal in dairy processing consumed up to 15% of the production time and contributed about 80% of the production costs. Hence, the prevention or minimization of fouling in PHE has great significance in food industry particularly, dairy industry. Researchers have identified several factors that affect the fouling process of heat exchangers such as particulate deposition, protein content, mineral composition and wall heating (Bansal *et al.*, 2006). The properties of the heat transfer surface such as surface roughness, surface energy and hydrophobicity of the surface are also important factors influencing fouling (Yan *et al.*, 2017). Intensive research work has been conducted to understand the mechanism of fouling formation and to develop techniques for its prevention. Some of the techniques reported to be useful in fouling reduction include varying the processing conditions (Simmons *et al.*, 2007), alteration in design of process equipment (Samaranayake and Sastry, 2005; Stancl and Zitny, 2010), addition of chemicals in process fluid (Al-Roubaie and Burton, 1979; Joshi and Patel, 1986) and modifying the characteristics of heat transfer surface (Beuf *et al.*, 2003; Santos *et al.*, 2006a; Augustin *et al.*, 2007; Premathilake, 2008; Rosmaninho and Melo, 2006). Alterations in the process may not suit for dairy industry where each process is well

defined and legally monitored and alterations in the design have limitations in terms of energy efficiency, hygienic design protocols, while the addition of chemicals may affect product quality and safety and lead to breaching of legal norms (Müller-Steinhagen, 1998). Hence, modifying the heat transfer surface is relatively more appropriate approach to mitigate the milk fouling. Surface modification is done by applying a coating layer of inert and non-sticky materials on the heating surface. The coating application is believed to increase the surface smoothness, decrease the surface energy and make the surface more hydrophobic that prevents adhesion on it. However, scanty work on the surface modification of the plate heat exchanger used for milk processing has been reported. It was felt that successful induction of the fouling resistance in the plates of PHEs used for milk processing will be a significant accomplishment. Several materials such as polytetrafluoroethylene (PTFE), Titanium Nitride (Saravanan *et al.*, 2016), Diamond like carbon, (Takeno *et al.*, 2009), Chromium nitride and Nickel-Aluminum (Batista *et al.*, 2002) etc. have been used as coating materials for heat transfer surface modification. The PTFE possess superior properties to many other nano coating materials such as chemical stability, thermal resistance, low water absorption, potential biocompatibility, good mechanical strength and erosion resistance, making it an attractive material for anti-corrosion coatings (Chen *et al.*, 2014 and Dong *et al.*, 2014). It was envisaged that the application of coating layer of polytetrafluoroethylene (PTFE) and nano titanium dioxide (TiO<sub>2</sub>) composite over the traditionally used SS 316 plates of PHE will reduce its surface roughness and increase the hydrophobicity. Such an intervention is expected to retard the fouling deposition and increase the thermal performance of the PHE will improve as compared to that of traditional plates. Hence, the present study was undertaken to design and develop a nanoparticle coated PHE for fouling mitigation by using PTFE and TiO<sub>2</sub> as nanocoating materials with following objectives:

- Optimization of composition and coating thickness of select nanoparticles for development of anti-fouling plate heat exchanger.
- Design and fabrication of nanoparticle coated plate heat exchanger module.
- Evaluation of the developed nanoparticle coated plate heat exchanger module for anti-fouling and heat exchange performance.



# CHAPTER - 2

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## REVIEW OF LITERATURE

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## 2. REVIEW OF LITERATURE

---

This chapter details about the literature related to the objectives of the present study and about the different methods planned to be followed during the course of this work. For convenience, the literature is divided under the following heads.

- ❖ Plate heat exchanger
- ❖ Fouling in PHE
- ❖ Mechanism of fouling
- ❖ Cleaning of PHE
- ❖ Approaches to prevent fouling
- ❖ Modification of processing surface
- ❖ Surface coating with nanoparticle materials
- ❖ Coating methods
- ❖ Assessment of the surface coating

### 2.1 Plate Heat Exchanger

Plate Heat Exchangers (PHE) have become integral part of food processing, especially dairy processing, because of its excellent characteristics such as high heat transfer coefficients, versatility to handle different types of liquid products, less space requirement, easy to assemble and dismantle, easily variable capacity and possibility of Cleaning-In-Place (CIP). The flow configurations of the heating/cooling medium and product can be set to parallel flow, counter flow, cross flow and mixed flow as per the requirement of a process. The common flow pattern for milk processing is counter flow that gives comparatively uniform temperature difference between the product and medium throughout the length of PHE and product's outlet temperature close to the inlet temperature of medium.

The hot and cold fluids flow through the narrow gap of 3-6 mm between two adjacent plates in such a manner that each plate is exposed to hot on one side and cold fluids on other side (Bejan and Kraus, 2003). As it is not possible to accommodate complete flow in single gap, the flow is divided into multiple channels at a time, depending on the ratio of hot and cold fluids. This is described by the flow pattern of given PHE (Kessler, 1981; Das, 2005) as follows:

$$\text{Flow Pattern} = \frac{\text{No. of passes of milk} \times \text{No. of channels filled by milk per pass}}{\text{No. of passes of medium} \times \text{No. of channels filled by medium per pass}} \quad (2.1)$$

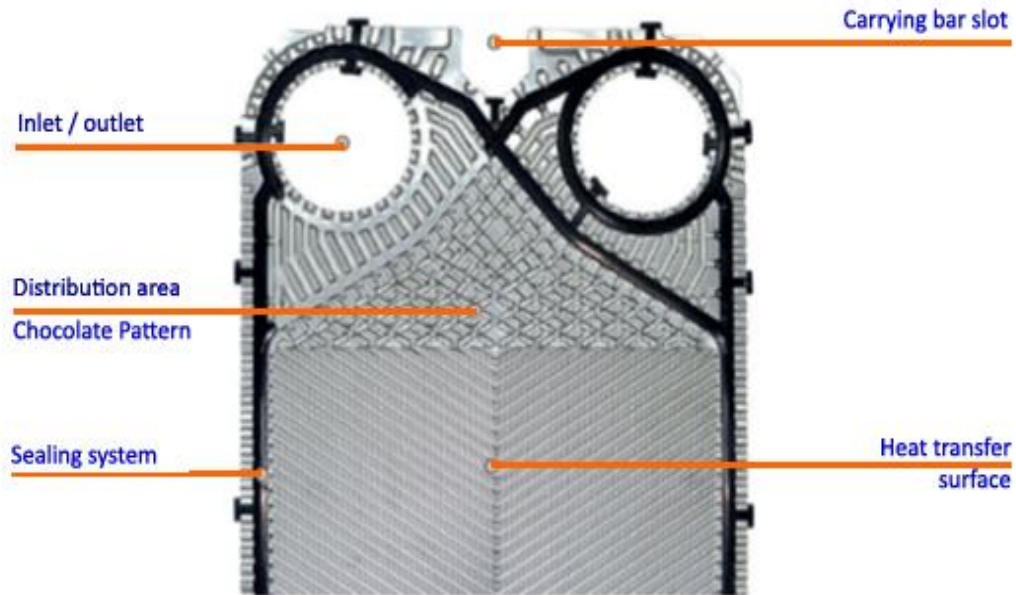


Fig. 2.1 Pictorial representation of a clip-on type plate of PHE

The stacking of plates ensures direct contact of major portion of fluids with its surface while maintaining sufficient contact points to prevent the plates from collapsing. Nevertheless, most of the PHE gaskets can't sustain processing pressure higher than 2-3 MPa (Lewis, 2006). Hence, alternative designs of PHE have been developed. Ola (2011) classified PHEs into six types as gasketed, welded, spiral, brazed, fusion-bonded and lamella PHEs. Choice among these types depend both on the scale and the nature of the process. Balasubramanian and Puri (2009) stated that gasket type of PHE would be preferable as it allowed dismantling and cleaning when the process caused fouling.

The heat transfer is enhanced by higher thermal conductivity of the plate material and lower thickness; however, the thickness is limited by requirement of the strength of the plate. The plates of the PHE meant for food and milk processing are invariably made of stainless steel of 304 or 316L grade as it is highly resistant to corrosion. The corrosion resistance of stainless steel comes from passivation i.e. formation of a barrier layer of chromium rich oxide-hydroxide on SS surface when it gets exposed to air (Feng *et al.*, 2012). This layer prevents diffusion of ion between the SS surface and air. The SS 316L is the most preferred grade of stainless steel

for fabrication of food processing equipment, PHE, CIP tanks, etc. However, due to its high surface energy and hydrophilic nature, the SS 316L is prone to fouling (Barish *et al.*, 2013), which has been a problem for food processing industry. Development of effective defouling techniques or antifouling plates for PHE in milk processing was recommended as one of the research needs in the area of milk pasteurization using PHE (Dhotre, 2014).

## **2.2 Fouling in PHE**

Fouling is an unwanted deposition of constituents from the product on the surface of equipment that hampers heat transfer, product flow and may lead to contamination problems (Sandu and Lund, 1983). In heat exchangers, it is exacerbated due to wall heating and the resultant precipitation of minerals. The fouling deposits harbour microorganisms and protect them from destruction during thermal processing, which on subsequent growth threaten the safety and quality of the food (Belmar-Beiny *et al.*, 1994).

Toyoda *et al.* (1994) found that fouling blocked the passage and reduced the heat transfer resulted into operational losses. Frequent shutdowns for cleaning the heat exchanger surfaces further increased operating costs and the corresponding use of chemical detergents and sanitizers, which also increased the environmental load and impact (de Jong, 1997). It was also found that fouling supported microbial adhesion to heat transfer surface and their growth. This made the CIP essential after every 5 to 10 h of processing depending on the severity of fouling (Murray and Deshares, 2000).

Augustin *et al.* (2007) found that the plant capacity was adversely affected over a period of processing time by decreased heat transfer and increased pressure drop occurred due to fouling. They suggested to follow intensive cleaning at regular intervals of time for complying with existing hygiene and quality norms of the dairy industry. The fouling of stainless steel surfaces resulted into reduced operating efficiency, shortened runtime and favoured the biofilm formation (Agle, 2007)

Murugesan and Balasubramanian (2013) reported that process engineering related implications of fouling included retarded heat transfer, reduced capacity due to narrowing of flow passage, increased pressure-drop in flow passage and increased risk of product contamination.

## 2.3 Mechanism of Fouling

One of the preliminary studies on fouling conducted by Burton (1968) revealed that scaling occurred both on the product as well as utility sides of the heat exchanger plate. But the fouling (scaling) on the utility side was lesser and composed of majorly minerals. The composition of product side fouling varied with the composition and nature of the parent product. Milk fouling deposits composed mainly of proteins and minerals.

Based on composition and structure as depicted in Table 2.1, the milk fouling can be of Type A and Type B (Burton, 1968). Tissier *et al.* (1984) reported that Type B fouling occurred during milk processing in which calcium and phosphate were the major contributors. The study conducted by Hiddink *et al.* (1986) on the fouling behaviour of whipped cream with 36% fat during pasteurization revealed that whey proteins mainly  $\beta$ -lg, and calcium played a key role in the fouling deposition mechanism, whereas fat had no significant effect. Changani *et al.* (1997) studied the processing conditions and observed that milk processing at 75–110°C formed Type A deposits whereas processing above 110°C formed Type B deposits.

Visser and Jeurnink (1997) found that whey proteins and immunoglobulins formed major portion of the protein component in Type A deposits, whereas  $\beta$ -casein and  $\alpha$ s1-casein formed major portion of the protein component in Type B deposits. They also observed that fat and lactose had no effect on the fouling process.

**Table 2.1** Classification of milk fouling deposits (Burton, 1968)

| Component            | Type A                           | Type B                          |
|----------------------|----------------------------------|---------------------------------|
| Protein (%)          | 50-70                            | 15-20                           |
| Minerals (%)         | 30-40                            | 70-80                           |
| Fat (%)              | 4-8                              | 4-8                             |
| Structure of deposit | Soft, voluminous, white coloured | Brittle, compact, grey coloured |

Morison and Tie (2002) found that fouling behaviour of the mineral solution added with whey proteins was controlled primarily by the surface reactions. However, the mass transfer of fouling species played a vital role in addition to the surface reactions.

Muller-Steinhagen *et al.* (2007) reported that deposition of denatured and aggregated proteins with minerals followed a typical mechanism involving bulk fluid and surface

interactions. The fouling by milk proteins and minerals during the thermal processing of milk is considered to be a major problem in dairy industry.

### **2.3.1 Microbial Fouling**

The foulant deposition on the process surfaces also influences bacterial adhesion and creates favourable conditions for bacterial proliferation resulting into biofilm formation, also referred as biofouling. The biofouling occurs through the deposition of microorganisms on a processing surface and through the deposition / attachment / entrapment of microorganisms by the deposit layer formed on the processing surface (Bott, 1993).

Flint and Hartley (1996) and Flint *et al.* (1999) studied biofouling and its impact on milk processing plants. The utilization of multi nutrients by the microorganisms from the milk and milk products helped bacterial multiplication on the fouling deposits. The presence of microorganisms in the process stream and/or in the deposit layer not only degraded the quality of the final product but also aided in the fouling formation (Yoo *et al.*, 2006).

Antifouling materials can be fabricated by using physio-chemical surface modification techniques, usually modifying both surface chemistry and topography. Lowering the critical surface energy through self-assembled monolayers or through steric repulsion at the surface of the material was found effective against biofouling. Many research findings confirmed the relationship between the critical material surface energy and fouling adhesion, which agreed with Baier curve (Brady and Singer, 2000; Baier, 2006; Webster and Chisholm, 2010).

## **2.4 Factors Influencing Milk Fouling**

Fouling deposition is affected by three groups of factors: Intrinsic factors, processing parameters and processing equipment design.

### **2.4.1 Intrinsic factors**

The intrinsic factors such as milk composition, pH, dissolved gases and the source of milk have been found to influence fouling in number of studies mentioned below.

Milks with different compositions on account of the difference of species, breed, feed, lactation period, climate or seasons was found to significantly influence the fouling deposition process in many studies (Burton, 1968; Grandison, 1988; Changani *et al.*, 1997).

The pH of the milk is an important indicator of the stability of milk. Alteration from the normal pH of milk decreases its stability and increases the fouling tendencies. Foster *et al.* (1989) and Xiong *et al.* (1993) reported that decrease in pH influenced the heat stability of milk due to denaturation of the proteins and increased ionic calcium concentration. Lewis and Heppell (2000) did not observe any evident relationship between pH and the mass of fouling deposit for pH above 6.65.

Jeurnink and de Kruif (1995) found that any change (i.e. increase or decrease) in the concentration of calcium content in the milk adversely affected the heat stability of milk and led to greater fouling as compared to that in case of milk with normal calcium content. However, for Whey Protein Concentrates (WPC) solution the fouling deposition reduced with the addition of calcium and phosphorus (Christian *et al.*, 2002).

The concentration of dissolved gasses in milk was found to influence the fouling. Fryer *et al.* (1995) observed that fouling deposition increased with the increase in dissolved air concentration. This was attributed to the higher turbulence caused due to the presence of air bubbles on the heat transfer surface. Bylund (1995) reported that freshly drawn milk contained 4.5 to 6% dissolved gases (0.1% O<sub>2</sub>, 1% N<sub>2</sub> and 3.5 – 4.9% CO<sub>2</sub> by volume) part of which escaped to the atmosphere with time due to concentration and solubility differences. de Jong (1997) found that rise in temperature of milk during thermal processing reduced the solubility of gases that resulted in air bubbles formation in the milk. Generation of air bubbles induced nucleation at processing surfaces and it favoured the deposit formation.

de Jong (1997) reported that aged milk increased the fouling deposition as compared to relatively fresh milk. It was attributed to the presence of proteolytic enzymes produced by psychotropic bacteria. Contrarily, Lewis and Heppell (2000) observed reduction in the mass of fouling deposit for milk aged for 15–30 h due to unknown reason. The redistribution of minerals and proteins with aging as reported by Burton (1968) was stated as the reason for this finding.

Fouling behaviour of reconstituted milk was different from fresh milk. Changani *et al.* (1997) reported significantly less fouling deposit from reconstituted milk and claimed that such milk had about one-quarter of the  $\beta$ -lg in denatured form and 9% lower calcium concentration than fresh milk. Contrary to this, Srichantra *et al.* (2006) reported rapid fouling deposition in case of processing reconstituted milk. They reported that severe processing conditions used during concentration and drying of milk as the possible reason for enhanced fouling deposition.

### 2.4.2 Processing parameters

In thermal processing, the temperature is the most important processing parameter and it affects the heat stability of the milk at various stages of processing along with the time of exposure. The unstable constituents tend to adhere to the surface more easily. Foster *et al.* (1989) observed that preheating of milk lowered the denaturation and aggregation of proteins and suppressed fouling. Belmar-Beiny and Fryer (1993) and Corredig and Dalglish (1996) studied the fouling behaviour of whey and found that monomers and dimers of native  $\beta$ -lg in milk adhered to the processing surface at room temperature in a monolayer and contributed significantly in fouling deposition. It was also suggested that denatured and aggregated  $\beta$ -lg were major contributors in fouling deposits and their content was strongly affected by processing temperature. Lewis and Heppell (2000) noted that preheating of milk caused the precipitation of calcium ions on casein micelles and reduced the availability of calcium ions for aggregation. In contrast, Srichantra *et al.* (2006) observed that preheating of milk for UHT processing accelerated the fouling. Simmons *et al.* (2007) studied the whey proteins aggregation in 1.5% (w/w) WPC solution and reported that the aggregates formed at 80–90°C were comparatively larger, denser and more strongly bonded through covalent disulphide bonds than those formed at 70–75°C. Many researchers observed that fouling deposition was affected by bulk fluid temperature, surface temperature and the difference between them (Rosmaninho, *et al.* 2007).

Flow velocity was another major factor affecting fouling (Visser and Jeurink, 1997) as the flow velocity decided the degree of turbulence. The fouling was observed to be lesser at higher degree of turbulence. Changan *et al.* (1997) suggested that PHE had complex flow geometries with a number of low velocity regions at the contact points between the adjacent plates, hence the effect of velocity on fouling in PHE would be different. Guerin *et al.* (2007) investigated the effect of flow velocity on fouling from whey protein solutions in PHE and observed that increased fouling deposition with increase in the flow velocity until a critical Reynolds number ( $N_{Re}$ ), which was expected to lie between 3200 and 5000. Above critical  $N_{Re}$ , the increased turbulence gave a lower amount of fouling mass, which was attributed to possible re-entrainment of the deposited fouling species because of higher local shear stress induced by the higher flow velocity. The study also found that the flow velocity affected the structure of the deposit, with a granular deposit at  $N_{Re}$  2000, a denser deposit at  $N_{Re}$  3200 and a smooth and compact deposit at  $N_{Re}$  5000.

Bradley and Fryer (1992), Bode *et al.* (2007) and Scholer *et al.* (2009) studied the effect of pulsating flow on fouling deposition and found reduced fouling when the boundary layer was sufficiently hot to denature and aggregate proteins. Moreover, for the removal of fouling deposits from whey protein isolates (WPI) solution showed that the best cleaning performance was achieved by a combination of flow velocity and pulsating flow.

#### **2.4.3 Design of equipment**

In food processing equipment stainless steel 316 (SS316) is used as one of the most common food contact materials for the manufacture of food, including high temperature short time (HTST) processing by heat exchangers. Unfortunately SS316 is susceptible for fouling due to its more surface energy and higher hydrophilic nature (de Jong, 1997).

Among different types of heat exchangers used in the dairy industry, PHEs foul rapidly as they have narrow flow paths and regions of low mixing (Delplace *et al.*, 1997).

Master *et al.* (2003) recommended that the helix changer and heat exchangers equipped with turbulence promoters did not foul easily and could be the best choice for fouling prevention. Klaren *et al.* (2007) compared the fouling tendencies in shell and tube heat exchanger and PHE and found that PHE fouled more easily.

The properties of the surface in contact with milk are found to influence fouling as fouling deposition process is a combination of bulk and surface phenomenon (Wahlgren and Arnebrant, 1990, 1991). Krisdhasima *et al.* (1992) reported that alteration of the surface properties influenced the fouling deposition. They modified the surface properties by application of coating, ion implantation, sol–gel application or electroplating techniques and studied the performance of modified surfaces for the fouling and cleaning behaviour with variety of fluids. Jeurnink *et al.* (1996) found that fouling deposition was affected by passivation (formation of the chromium oxide layer) on the heat transfer surfaces of SS, microstructure and surface finish, charges on the surface, surface energy, wettability and residual deposits on the surface from previous processing. Augustin *et al.* (2007) observed that surface energy had significant impact on fouling deposition and removal, whereas the effect of surface roughness from 0.08–0.6  $\mu\text{m}$  was non-significant. In contrast, Herz *et al.* (2008) studied the effect of surface roughness (in the range of 0.18–1.55  $\mu\text{m}$ ) on heat transfer to calcium sulphate aqueous solutions and reported that the rougher surfaces fouled rapidly as they provided more nucleation sites.

## 2.5 Cleaning of PHE

The cleaning of closed systems such as PHE was earlier a cumbersome operation as it required dismantling equipment followed by manual cleaning and reassembling, but the development of CIP in 1950's made cleaning possible without dismantling and drastically eliminated manual cleaning practices (Timperley, 1989).

Bird and Espig (1994) observed that CIP of PHE used in milk processing could be done in 35 minutes using the following steps.

- (1) Pre-rinsing with water to remove loose deposits for about 5 min.
- (2) Alkali-cleaning (detergent wash) with usually 1% (w/w) sodium hydroxide (NaOH) is done to remove the proteinaceous deposits and also acts as bactericide for about 15 min.
- (3) Water rinse to flush out alkali residues for about 3 min.
- (4) Acid rinse with nitric acid (HNO<sub>3</sub>) or phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) to remove incrustated salts for about 5 min.
- (5) Final rinse with water to cleanse the system for about 7 min.

Bird and Bartlett (1995) claimed that CIP was beneficial over manual cleaning as it consumed lesser material (water, detergents and sanitizer), energy (power, labour) and time compared to manual cleaning. Effectiveness of CIP was affected by the type, velocity, strength and temperature of cleaning solutions, and the duration of contact between cleaning solution and deposits. Gillham *et al.* (1999) suggested that cleaning of process equipment was necessary not only for hygiene, food quality and food safety but also for restoring the heat transfer and flow supporting characteristics. An additional step of disinfection, following CIP was suggested. Holah (2003) reported that ozone (O<sub>3</sub>) was widely preferred over chlorine (Cl<sub>2</sub>) as it was more powerful and left no residues. The removal rate of deposits in CIP was affected by temperature and concentration of the solution, contact time, pressure and flow hydrodynamics (Lorenzen, 2005). Lloyd (2008) studied these factors and recommended 55 to 70°C, concentration of 1.0% NaOH, pressure not less than 4.1 bar for tanks and a turbulence with  $N_{Re} > 4000$  to be useful for dairy plants.

Caroline (*et al.*, 2010) reported that CIP could remove organic deposits containing proteins, carbohydrates, fats and minerals that formed the nutritional base for bacterial growth on the equipment surface. Two stage CIP using sodium hydroxide and nitric or phosphoric acid

with water circulation as intermediate step was recommended. Using some special detergents formulations, the CIP could be carried out as a single-stage process.

Time required for CIP contributed in non-production period ranging from 4 to 6 h per day for milk evaporators (Alvarez *et al.*, 2010) and 30–40 min after every 8 h of processing for milk pasteurizers. The CIP is usually followed by disinfection using  $\text{Cl}_2$  or  $\text{O}_3$  to destroy micro-organisms.

## **2.6 Approaches to Prevent Fouling**

The prevention or mitigation of fouling in dairy industry has become very important due to its severe technological, qualitative and ultimately economic implications. In spite of advancements in cleaning technologies and development of newer systems, the fouling-cleaning still carries huge cost. As per the finding of Bansal and Chen (2006) the fouling and resultant cleaning operations in dairy industry account for about 80% of total production cost. Research attempts have been made to prevent fouling deposition or to improve fouling removal i.e. cleanability of fouled surface. These approaches can be categorized as: modification of processing conditions, modification of equipment design, addition of fouling inhibiting agents, modification of processing surface and alteration of operating parameters of these approaches. Among these, modification of surface by applying coating is considered as most practicable and effective in milk processing equipment (Patel, 2013).

## **2.7 Modification of Processing Surface**

The fouling process is a bulk as well as surface phenomenon where deposition occurs layer by layer (Wahlgren and Arnebrant, 1991). Haynes and Norde (1994) and Visser and Jeurink (1997) reported that initially product constituents adhered to the surface by covalent bonds, hydrogen bonds and van der Waals forces of attraction individually or together, which was followed by formation of subsequent layers. Ren *et al.* (2001) found that the rate of fouling of heat exchanger and processing equipment was influenced by the nature and properties of the surface and it could be reduced by surface modification that minimized the surface free energy. The surface properties such as surface roughness, surface charge, surface energy and the presence of oxide or passive layers predominantly affected the fouling. Experiments conducted to observe fouling during the pool boiling of  $\text{CaSO}_4$  solution on modified surface revealed significant reduction in fouling. Many studies discussed below, attempted to modify surface characteristics for fouling prevention. The modified surfaces on account of their low surface

energy exhibited lesser fouling compared to non-modified surfaces and could be rapidly and easily cleaned.

Muller-Steinhagen and Zhao (1997) developed a stainless steel surface with low surface free energy by using ion implantation technique. Muller-Steinhagen (1998) reported the modification of surface as a better approach for fouling mitigation than other options i.e. altering the process parameters and adding fouling inhibitors might affect sensory qualities of product and lead to product contamination, respectively.

Apart from coating application, the surface modification process was done by creating super hydrophobic (SH) surfaces. The SH surfaces are the solid surfaces that on contact with water make a contact angle of greater than  $150^\circ$  (Miwa *et al.*, 2000). Feng *et al.* (2002) suggested two conventional ways to produce SH surface: creating a rough structure on a hydrophobic surface and modifying rough surfaces with low surface free energy materials.

Santos (2004) suggested modification of surface properties by applying coatings through chemical vapour deposition (CVD) or sputtering, ion implantation, sol-gel or electroplating techniques. A number of techniques are available for surface modification. Zettler *et al.* (2005) classified these techniques into mechanical and chemical methods. The mechanical methods such as sand blasting, machining and pulsed plasma combined with photolithographic techniques were used to manipulate the surface roughness as a means of surface modification (Pier-Francesco *et al.*, 2006; Muller *et al.*, 2006). The chemical methods such as coating with antifouling materials such as polytetrafluoroethylene (PTFE) or silica were used to produce non-sticky, non-frictional surfaces. Such coated surfaces showed significant influence on milk fouling prevention although its wear resistance and adhesion properties were found to be lower than stainless steel (Wu *et al.*, 2006).

Saikhwan *et al.* (2006) studied the effect of surface modification on the removal of deposits of tomato paste and found that the deposits were weakly adhered to the modified surfaces and the surface energy ranged from 20–30 mN/m.

Balasubramanian and Puri (2009) studied the effect of coating the SS 316 plate of PHE used for tomato juice processing on fouling behaviour. It was found that the coated plate was fouled significantly lesser than the uncoated plate and showed improved energy efficiency. On the contrary, Kananeh *et al.* (2009) found that there was no significant difference in the fouling of PTFE coated SS surface and uncoated SS surface during thermal treatment of carrot juice. The foulant deposits of carrot juice were found to be more strongly bonded to surface than

whey proteins deposits. Scheen *et al.* (2011) observed that SH surfaces having 150° or larger contact angle often promoted the rolling off of water drops. Its surface had bump and hair like characteristic structures in the nanoscale and offered same effect as that of natural water-repellent lotus leaf.

Bhushan *et al.* (2012) reported that for creating SH surface, firstly, the surface should be basically hydrophobic and should have low surface energy and secondly, it should be rough.

Celia *et al.* (2013) stated that the hydrophobicity of any surface could be improved just by altering its surface roughness. Hao *et al.* (2013) compared the characteristic with the lotus effect wherein the hierarchical nanospikes on a lotus leaf impart roughness and underlying wax reduced the overall surface energy. Because of this hierarchical structure with low surface energy on lotus leaves water forms spherical beads and subsequently rolls off quickly with less resistance and sweep away dust particles leaving a clean and clear surface behind. This self-cleaning phenomenon of lotus leaves is popularly known as the 'Lotus effect'.

On SH surface, the water acted as a dynamic element for the flowing system and swept away the solid material by cleaning the underlying surface (Yoon *et al.*, 2014). The phenomenon of rapid and natural sweeping of particles from a surface by water was referred as self-cleaning.

## **2.8 Surface Coating**

Nanotechnology is a booming stream in all fields of scientific applications. The concepts of the nanoparticles, nano plates and nanofibers have evolved from nano technological applications. As per the definition given by the International Organization for Standardization (ISO/TS 80004-1, 2015) any nano-object having all its external dimensions in the range of 1 to 100 nm and where the lengths of longest and shortest axes do not differ significantly can be called as nanoparticle (Calderon-Jimenez *et al.*, 2017). The scientific exploration on nanoparticles is described below.

The nanoparticles possess considerably different properties due to greater surface area to volume ratio. A large fraction of its atoms is exposed on the particle surface. As surface atoms don't have many adjacent atoms, they are chemically more active than those in the bulk atoms (Coombes, 1972).

Ercolessi *et al.* (1991) reported that many materials with decreased particle size (in nano range) showed decreased melting temperatures. The decreased size of nanoparticles increased

the proportion of surface energy in the overall energy, which resulted in depression of the melting peak temperature. Goldstein *et al.* (1992) confirmed that surface characteristics of nanoparticles were decisive for their fundamental properties.

Muller-Steinhagen and Zhao (1997) coated heat-exchanger surfaces with teflon to reduce the adhesive force between the surfaces and foulants. Several experiments revealed that operation time was significantly prolonged until severe fouling was seen.

Takata (1999) observed enhanced rate of heat transfer during boiling, film evaporation and immersion cooling by applying the superhydrophilicity. The results indicated that due to the breakdown of film regime at higher temperature and shifting of minimum heat flux point, TiO<sub>2</sub>-coated specimen cooled faster than the noncoated one. In the same study, it was revealed that the TiO<sub>2</sub>-coated specimen showed 40 times higher heat-transfer coefficient for falling film evaporation as compared to noncoated surface because a thin stable film could be realized even in a low flow rate region.

Sawai *et al.* (1995) concluded that ZnO has an antibacterial activity against some strains of the bacteria. Many researchers from recent studies revealed that ZnO showed higher degree of antibacterial effect particularly against *Staphylococcus aureus* in comparison to the other metal oxides (Jones *et al.*, 2008). Tam *et al.* (2008) reported that ZnO showed antibacterial action against the *Bacillus atrophaeus* and *Escherichia coli*. The authors reported that ZnO nanoparticles showed higher antibacterial activity in comparison to the ZnO bulk particles.

In many investigations, metal surfaces were modified by manipulating roughness and the surface energy was reduced by chemical treatment. It was concluded that PTFE was an excellent option for incorporating nanoscale roughness onto the heat-exchanger surface and for reducing surface energy required to get SH surfaces (Sabbah *et al.*, 2016; Yang *et al.*, 2018; Luo *et al.*, 2018). The metallic particles emulsified with PTFE and PTFE coatings were treated by plasma, laser ablation techniques, etc.

### **2.8.1 PTFE as coating material**

PTFE is a polymer containing carbon and fluorine atoms and it represents the extreme of known polymers (Plunkett, 1941). PTFE is an established thermally stable, chemically inert, strongly dielectric with very less dielectric loss factor, insoluble in common solvents, non-adhesive, anti-frictional polymer with high melting temperature, molecular weight and melt viscosity through various studies over the years as discussed below.

Hanford and Joyce (1946) found that melt viscosity of PTFE ranged from  $10^{10}$  to  $2 \times 10^{11}$  Poise at  $380^\circ\text{C}$ . The long-chained structure of the PTFE was given the reason for its so high viscosity even at higher temperature. The same researchers reported that the dielectric loss factor of PTFE was less than  $10^{-4}$  and it remained almost constant over the frequency range of  $60 - 10^6$  Hz and the temperature range of  $25$  to  $310^\circ\text{C}$ . Such low dielectric loss factor is one of the lowest values known for solid substances. The low dielectric constant ( $\sim 2$ ), low dielectric loss factor and very high resistivity ( $>10^{18} \Omega\text{m}$ ) make PTFE an excellent coating material in food processing equipment. However, processing PTFE into coat could be challenging because of high melt viscosity and lack of Newtonian behaviour.

Lontz and Happoldt (1952) studied the flow behaviour of PTFE and found that, unlike other thermoplastics that show Newtonian flow after yield point, the PTFE exhibited very slow plastic flow in semi-solid gel state, even above  $370^\circ\text{C}$ . It could retain complete tensile strength at  $230^\circ\text{C}$  for one month and up to 80% of tensile strength at  $300^\circ\text{C}$  when compared to room temperature, which indicated its thermo stability. It was insoluble in polar as well as non-polar solvents, except some perfluorokerosenes and perfluorinated oils that could dissolve 1-2% (w/w) of PTFE at  $290 - 310^\circ\text{C}$ .

Suwa *et al.* (1975) reported that the melting point of melt-processed PTFE was about  $327^\circ\text{C}$  where as that of virgin polymer was up to  $345^\circ\text{C}$ .

Jog (1993) and Jog *et al.* (1994) suggested powder processing techniques such as compression molding, preforming, sintering, ram extrusion and paste extrusion for fabrication of PTFE. Blending of PTFE powder with 18 to 20% (w/w) of a lubricant facilitated the extrusion below its melting temperature.

Shimizu (1997) produced PTFE fibres by formulating dispersions and spinning it through a spinneret in the fluidized bed. Uehara *et al.* (1997) showed that some nascent PTFE powders could be made ultra-drawable by utilizing solid-state extrusion and two-stage drawing.

Morooka *et al.* (2011) observed that modifying two-stage draw technique by applying so-called PIN draw above melting temperature, it was possible to achieve a super drawing of compacted films of nascent PTFE powder to draw ratios up to 500 and the tensile modulus of  $120 \text{ GPa}$ . This technique seemed to be promising to develop high performance PTFE fibres.

Aqueous dispersions PTFE particles were found suitable for film forming, dip coating, impregnation applications, film casting, coating valves, conveyer belts, tubes, etc. (Chen *et al.*, 2014; Dong *et al.*, 2014).

## 2.8.2 Titanium Dioxide (TiO<sub>2</sub>) as coating material

The TiO<sub>2</sub> is basically a non-flammable, non-hazardous, thermostable and poorly soluble, semiconducting white solid organic substance. It is used as photocatalyst for water in the self-cleaning surfaces and as bactericidal agent in environment purification (Anthony, 1998). TiO<sub>2</sub> is naturally found in three forms known as anatase, brookite and rutile (Thayer, 1998) and has other applications such as in paints, plastics, paper and cosmetic products as whitening agent and as gas sensor (Selhofer and Müller, 1999).

Wang *et al.* (1999) observed that dried TiO<sub>2</sub> surfaces were oleophilic and hydrophobic therefore were useful as antifogging and self-cleaning substances. After UV irradiation, TiO<sub>2</sub> surfaces became amphiphilic and water droplet spread out on it. The change could be reversed by keeping TiO<sub>2</sub> in dark.

Zhang and Banfield (2000) found that anatase form of TiO<sub>2</sub> possessed maximum stability below 11 nm particle size, whereas the brookite and rutile forms had maximum stability between 11-35 nm and above 35 nm particle sizes, respectively. General properties of TiO<sub>2</sub> are shown in Table 2.2.

Wang *et al.* (2004) reported that TiO<sub>2</sub> was used as nanoparticles in suspension for high catalytic surface area and activity due to its distinguishing properties in photocatalytic applications and for environmental remediation.

Zhu *et al.* (2004) applied TiO<sub>2</sub> as filler in the preparation of polyvinyl chloride, polystyrene (PS), acrylonitrile butadiene styrene and other polymer's composites to improve their physical and mechanical properties.

**Table 2.2.** General properties of titanium dioxide (DuPont, 2019)

| Titanium Dioxide            |                        |
|-----------------------------|------------------------|
| Chemical symbol             | TiO <sub>2</sub>       |
| Chemical structure          | O=Ti=O                 |
| <b>Chemical Composition</b> |                        |
| Titanium                    | 59.93%                 |
| Oxygen                      | 40.55%                 |
| <b>Physical Properties</b>  |                        |
| Density                     | 4.23 g/cm <sup>3</sup> |
| Molar mass                  | 79.9378 g/mol          |

### **Thermal Properties**

|               |          |
|---------------|----------|
| Melting point | 1,843° C |
| Boiling point | 2,972° C |

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Hou and Wang (2009) used solution casting method for preparation of SH PS/TiO<sub>2</sub> nanocomposite. The nanocomposite coatings showed SH behavior when it was dried between 100 and 180°C. On exposure to UV for 1 h, the nanocomposite coatings turned strongly superhydrophilic and regained their original superhydrophobicity on heating at 180°C. Research outcome suggested that composite TiO<sub>2</sub> films under UV exposure became superhydrophilic (Kamegawa *et al.*, 2012).

## **2.9 Coating Methods**

There are many techniques developed for application of coatings on a surface. All of them have common step of surface preparation that involves decontamination of the substrate surface and enhancement of its adhesiveness to support coating. The subsequent steps are the differentiating for each technique. Coating applications in food processing industry majorly include applying hydrophobic coatings on the heat transfer surfaces to prevent contamination and to empower self-cleaning. Some of the coating methods used in food industry include chemical vapor deposition (CVD) (Chen *et al.*, 1999), carbon nanotubes and walls, modulated radio frequency glow discharge (Favia *et al.*, 2003), microwave Plasma Enhanced Chemical Vapor Deposition (PECVD) and self-organization of fluorinated polymers (Yabu *et al.*, 2005). The selection of proper technique is made based on the nature of the substrate surface and coating material.

When the substrate surface is a metal with irregular geometry such as plate of PHE and the coating material is a liquid or emulsion of liquids, the spray coating is preferred (Kuroda *et al.*, 2008). Six different types of spray coating techniques were observed in the literature reviewed. These are thermal spraying, high velocity oxygen fuel spraying, plasma spraying, vacuum plasma spraying, cold spraying and warm spraying.

Leroux *et al.* (2008) described thermal spraying as a process in which the particles of coating materials (1–50 µm) were molten and sprayed on the preconditioned substrate surface (usually metal, ceramic or polymer). Thermal spraying could produce a coat as thin as 10–15 µm at higher rate compared to the physical vapour deposition (PVD) and CVD techniques.

Thermal spraying was modified to high-velocity oxy-fuel (HVOF) spraying technique, in which powdered coating material was injected into high velocity hot stream of gases produced due to combustion in separate chamber. Powder particles melt due to stream temperature and impact due to high velocity made them deposit over the targeted surface (Kuroda *et al.*, 2008).

In plasma spraying the coating material was brought into contact with a plasma jet at 10000 K which melted the material and sprayed over the substrate surface. The reaction between plasma state coating material and surface influenced the process. Tummala *et al.* (2012) used plasma spraying to prepare nanostructured  $\text{Co}_3\text{O}_4$  electrodes and replaced multistep procedure involving sol-gel and hydrothermal techniques. Analysis of the film coatings with X-ray diffractometer and differential scanning calorimetry-thermogravimetry (DSC-TGA) revealed better results than conventional techniques.

Vacuum plasma spraying was invented to protect heat sensitive coating materials such as rubber from thermal damage. It could operate at temperature as low as 40–120°C due to presence of vacuum. Hu *et al.* (2012) used the vacuum plasma spray coating along with heat treatment to apply the SiC coating on Carbon/Carbon composites as substrate.

In cold spraying coating, particles were accelerated by a carrier gas coming through a nozzle to high speed and forced on the substrate to be coated. Upon impact, the coating particles deformed plastically and bonded mechanically to the surface as a coat. Thus, cold spraying applied the coating materials in solid state at a temperature below their melting point. Singh *et al.* (2018) reviewed the principles, application and potential of cold spraying coating technique.

Kuroda *et al.* (2008) described warm spraying as a modified HVOF method, wherein the temperature of combustion gas was lowered by mixing it with nitrogen followed by remaining the process of cold spraying. The coating efficiency was better than cold spraying and the disadvantages of the HVOF were eliminated. The method was recommended for coating materials such as titanium, plastics and metallic glasses as these materials were prone to oxidation.

Apart from these spray coating techniques, other methods have been reported as follows.

Electrochemical plating method was used for coating applications in the food industry. It consisted of using a highly reactive material such as magnesium alloys that forms the oxides layer on surface when exposed to air. Hajdu *et al.* (1990), Innes (1974) and Sharma *et al.*

(1997) reported that it was difficult to find appropriate chemical method to prevent the oxide formation prior to the plating process. Moreover, non-uniform coating application because of uneven distribution of current density in the plating bath was also a problem in this method.

Another method, electroless chemical plating was proposed as alternative to the electroplating to overcome its drawbacks and to allow coating of complex morphology. In electroless plating process, co-deposition for second-phase particles such as carbides, alumina, or diamonds to improve the properties such as hardness, wear resistance or abrasion was also possible (Wang *et al.*, 1999).

Anodizing process consisted of the formation of thick oxide layer on the surface of substrate (metals or metal alloys). Mittal (1995) and Kasten *et al.* (2001) highlighted five stages in the process of anodizing coating as: (i) mechanical treatment, (ii) degreasing, cleaning and pickling (iii) electropolishing, (iv) anodizing using AC or DC current and (v) dyeing or post-treatment and sealing. The anodizing process improved corrosion resistance and paint adhesion of the metal surfaces.

The composite coating technology has been developed for coatings whose specification standards were higher than the conventional coating technologies and that were unable to function in extreme environmental condition such as temperature, corrosion, abrasion, fatigue, friction and erosion (Allcock *et al.*, 2003).

Brock *et al.* (2005) studied new coating technique using hybrid polymers that were found to play functional role. Mixture of organic polymers and silicates helped in improving the overall coating qualities. Combining stability and scratch resistance of inorganic networks with the elasticity of organic polymers could achieve the desirable objectives. Based on the salts being used such as molybdate, silicates, stannite and zirconate chrome-free conversion was developed. These have capability to form strong covalent bond for coating adhesion and also functions as a barrier coating, limiting the transport of water to the surface of the material (Hamdy, 2009; Hamdy and Farahat, 2010).

Anon (2010) described roll-to-roll coating process in which the flat substrate was passed between the two or more rollers. One of the rollers applied the coatings on the substrate while remaining shaped the coated substrate. The coated surface was shaped to the final form after curing and it had no specific influence on properties of the coating.

## **2.10 Assessment of Surface Coating**

### **2.10.1 X-Ray Photoelectron Spectroscopy (XPS)**

The X-Ray Photoelectron Spectroscopy (XPS) is used to determine the atomic composition at a solid surface by exposing it to X-rays and comparing the binding energies of the photoelectrons emitted due to X-ray exposure with known values to identify the elements and its oxidation state. XPS became a key surface characterization method that integrated surface sensitivity with the capability to quantify both elemental and chemical information and it was used to determine the material surface compositions (Beamson and Briggs, 1992).

Sabbatini and Zambonin (1993) used XPS analysis to quantify the atomic composition and stoichiometric ratios and found that it could give detailed information about the composition and chemical state of the surface up to a depth of 5–10 nm from surface. Chemical state of the emitting atom could lightly change the shape of each peak and the binding energy. The XPS proved that chemical bonding information could be analyzed and it could detect all elements except hydrogen or helium.

Ratner and Castner (1997) determined the kinetic energy of emitted photoelectrons with a hemispherical sector analyzer to calculate corresponding electron binding energy. Characteristic peaks in the spectra indicated the presence of species while the chemical shifts and curve fitting gave the state of surface species. XPS could be used to correlate elemental and functional groups present on the surface and their binding energy in many studies. However, Vickerman and Briggs (2001) cautioned for care while using XPS as its depth was limited to top few nanometers of the surface.

Further, the XPS estimated the degrees of reaction through ratios of measured atomic concentrations to the theoretical values needed for the complete conversion (Kingshott *et al.*, 2003; Crombez *et al.*, 2005).

Balasubramanian and Puri (2009) used XPS to analyze the foulant deposited on the Ni-P-PTFE coated plate of PHE used for processing skim milk with a view to investigate the leaching of coating materials.

### **2.10.2 Atomic Force Microscopy (AFM)**

Atomic force microscopy (AFM) is a group of microscopic techniques useful in examining the morphology of given surface at atomic scale.

The phenomenon of bacterial adhesion effect on heat exchanger surface was found by surface topography. The higher microbial adhesion forces and cell retention was seen in scanning with an AFM tip on abraded surfaces (unidirectional topography) as compared with either polished or unpolished (grain structure) surfaces (Boyd *et al*, 2002).

Vickerman (2003) reported that AFM could detect topographical changes occurred in the surface after treatment with atomic resolution in vertical plane and 0.01 nm resolution in horizontal plane.

Santos *et al.* (2004) revealed that images obtained using AFM under 2R SiF<sub>3</sub><sup>+</sup>, SiO<sub>x</sub>-plasma-CVD and DLC sputtered surfaces showed more heterogeneous topography with some cracks present along the surface and particles diameter was larger than 100 nm. The profiles for the silica coated surface indicated a better smoother surface than the untreated surface. The AFM for 2B SiO<sub>x</sub>-plasma CVD and DLC sputtered surfaces were different compared to the featured particle diameter greater than 500 nm and unmodified surface.

The AFM was used to analyze the morphology and roughness of a nano-thick fouling layer obtained after 1 min of fouling (Jimenez *et al.*, 2013) and the average roughness ( $R_a$ ), quadratic roughness or RMS ( $R_q$ ) and 3D pictures could be obtained.

Barish and Goddard, (2013) performed AFM analysis to determine the roughness as quantified by arithmetic average of absolute values ( $R_a$ ) of the vertical differences ( $\mu\text{m}$ ) during each phase of the SS 316 surface modification process. From AFM image analysis, it was concluded that roughness values increased with increasing PTFE content, although even at the highest level ( $\sim 10.5$  wt %) roughness values were at or below that of native SS316.

Durairaj *et al.* (2015) performed AFM studies on coated SS 316 surface to examine the surface roughness and maximum peak of the coating. The 2D and 3D images obtained from AFM analysis revealed that elevated part of the surface seen as white part in the images whereas the submerged parts with dark. In the maximum peak region where the elevated part of the coated material showed the slight increment due to the coating.

### **2.10.3 Scanning Electron Microscopy (SEM)**

Scanning electron microscopy (SEM) is a technique of examining the topography of a surface below atomic level by using the principle of electron scattering. Sometimes, the sample surface is coated to make it conductive before subjecting to SEM. The SEM can generate images of few nanometers spatial resolution and has a deeper field (100 times that of an optical

microscope) that enables to understand the reaction between surface treatment and substrate. It is widely used for surface analysis and surface topography measurement (Sheng *et al.*, 1995; Bag *et al.*, 1999; Desai *et al.*, 2003; Kongdee *et al.*, 2005).

Santos *et al.* (2004) analysed SEM images for studying the morphology of modified stainless steel 2B surfaces and reported that Ni–P–PTFE coating significantly changed the morphology of the steel surface.

Kongdee *et al.* (2005) experimented to confirm the fixation of silk sericin on a cellulose fibre using SEM and Fourier transformed infrared spectrophotometry – attenuated total reflectance (FTIR-ATR) and found that SEM was less surface sensitive and also required the non-conducting polymers be sputter-coated prior to analysis.

Wang *et al.* (2009) performed SEM morphology for the uncoated, polished and TiO<sub>2</sub> coated surface with different film thickness to investigate the CaCO<sub>3</sub> deposits. From SEM images it was found that large amount of CaCO<sub>3</sub> scale was formed on untreated and polished surfaces. On the contrary, there was very little deposit on coated surfaces with a loose structure partly due to the weak adhesion force between deposit and coated surface.

Barish and Goddard (2013) captured SEM micrographs of SS 316 and EN-PTFE-SS 316 surfaces to qualitatively check the uniformity of the nanoparticle dispersion and to confirm the reported size of the fluorinated nanoparticles. The SEM micrographs indicated micro-cracks were on SS 316 surface, while the EN-PTFE-SS316 presented a surface with uniformly dispersed nanoparticles and no evident surface cracks. AFM and hysteresis analysis further supported these results. Uniform dispersion of PTFE deposits across the surface was confirmed.

Kim *et al.* (2015) concluded from SEM analysis that the surface morphology of the nanocomposite films could be altered from compact state to porous structure by increasing TiO<sub>2</sub>. Despite relatively compact morphology, air pockets existed and they promoted the superhydrophobicity, which in turn retained the Cassie-Baxter state.

The morphological structure of the bare and coated substrate such as uncoated 316L and PTFE coated substrate after electrochemical corrosion test were compared using SEM (Maqsood *et al.*, 2017). They revealed that no cracks were seen in images or discontinuities were observed by SEM analysis on the coating before and after electrochemical corrosion test but very small pores were detected on the sample.

#### 2.10.4 Contact angle measurement

The method of contact angle measurements is considered as the simplest among all the methods viz., direct force measurements, capillary penetration, particle sedimentation, film flotation, etc., which are available for determination of the affinity between a liquid and a solid interface. In case of water and a solid, contact angle (CA) indicates hydrophobicity of the solid surface. In CA measurement, a liquid drop is released on a solid surface and the angle made by the drop surface with the solid surface at their contact point is measured. Young (1805) proposed following equation to determine the surface tension from CA. The Young's equation defined the CA by mechanical equilibrium between solid-vapor, ( $\gamma_{sv}$ ), solid-liquid, ( $\gamma_{sl}$ ) and liquid-vapor, ( $\gamma_{lv}$ ) interfacial tensions.

$$\gamma_{lv} \cos\theta_Y = \gamma_{sv} - \gamma_{sl} \quad (2.2)$$

where,  $\theta_Y$  is the Young's contact angle, i.e. the value that can be used in Young's equation.

Neumann (1974) found that contact angles made by advancing liquid ( $\theta_a$ ) and receding liquid ( $\theta_r$ ) were not identical and almost all solid surfaces exhibited contact angle hysteresis (H) given by,

$$H = \theta_a - \theta_r \quad (2.3)$$

Adamson and Gast (1997) suggested that Wilhelmy plate technique measurement clearly showed advancing and receding contact angles, chemical heterogeneity and roughness of the surfaces that contributed to the contact angle hysteresis.

Zettler *et al.* (2005) found that the CA on rough surfaces were larger than that on the chemically identical smooth surfaces and suggested that interpretation of such angles in terms of ( $NA = n \cdot \sin \theta$ , where NA-numerical aperture, n-refractive index) might lead to erroneous results as the CA would reflect only surface topography and not the surface energy.

Santos (2004) concluded that presence of concentrated impurities on the surface, crystal imperfections and different properties of crystal surface caused the heterogeneity. Higher values of hysteresis were found for the 2R DLC sputtered and Ni-P-PTFE samples that were related to more heterogeneous topography and the increased roughness on the Ni-P-PTFE, respectively.

Following equation was developed by Dupre (Subide, 2011) to compute the work of adhesion (WA) between a solid (s) and a liquid (l) as a measure of surface energy.

$$WA = \gamma_s + \gamma_l - \gamma_{sl} \quad (2.4)$$

The WA was the reversible work done in separation of unit area of a solid-liquid interface and is half of the work of cohesion when surface molecules are arranged as if they were in the bulk.

$$WA = \gamma_s(\cos \theta + 1) \quad (2.5)$$

The Eq. (2.3) evaluated the WA from the accessible quantities  $\gamma_l$  and  $\theta$ . The interpretation of all contact angles was started with Equation (2.3) to get WA and was followed by the surface energy of the solid  $\gamma_s$  by using other models.

The influence of surface roughness was also seen in the contact angle measurements, specifically the hysteresis values. Barish and Goddard (2013) measured dynamic contact angle of advancing angle ( $\theta_a$ ), receding angle ( $\theta_r$ ), hysteresis and surface energy for native stainless steel 316L and EN-PTFE surface modified stainless steel and concluded that SS 316 had higher hysteresis value and exhibited lower hydrophobicity. The non-uniformity in the surface due to cracks and scratching that occurred during manufacturing or transport was stated as the reason behind the findings. Such surface cracks are also a likely source of the large standard deviations observed during the contact angle analysis of SS 316.

### **2.10.5 Roughness measurement**

Measurement of surface roughness, often briefed as roughness, is very important in the analysis of frictional resistance, pressure drops, heat transfer, etc. The roughness is determined from the deviations of the real surface at random points from its ideal datum form. The large deviations indicate more roughness. As real surface geometry is complicated, the surface roughness is evaluated using different parameters.

Gadelmawla *et al.* (2002) studied 59 parameters used for surface measurement and grouped them into amplitude, spacing and hybrid parameters. The average roughness ( $R_a$ ), quadratic roughness ( $R_q$ ), ten-point roughness ( $R_z$ ) were some of the common parameters.

Hsieh *et al.* (2005) studied the effect of roughness on water and oil repellency of surfaces coated with  $TiO_2$  nanoparticles and observed a nonlinear positive correlation between roughness and contact angle. The  $R_a$  of various coated SS surfaces was measured using profilometer that measured minute variations in stylus displacement as a function of position.

The profilometer measured vertical variations in the range of 10 nm to 1 mm. The analog signal generated by the vertical position of stylus was digitalized, stored, analyzed and displayed. Radius of the diamond stylus ranged from 20 nm to 50  $\mu\text{m}$ . The horizontal resolution was controlled through scanning speed and sampling rate.

Adams *et al.* (2012) claimed that the  $R_a$  was the most common method to quantify express surface roughness among all the available methods.

#### **2.10.6 X-Ray Diffractometry (XRD)**

The x-ray diffractometry (XRD) is a versatile, non-destructive technique for checking the molecular and atomic structure of a crystal or a crystalline material. In XRD, the X-rays are made to incident on the sample surface which hit and excite the surface atoms. The excited electron to be stable again emit the energy at the same wavelength. Depending upon the arrangement of atoms on the surface (crystal), the emitted X-rays form constructive or destructive interference, which is an indication of the molecular arrangement in the crystal. d'Amorim *et al.* (2013) performed XRD analysis on the morphological characteristics of PTFE and reported that the angle of diffraction ( $2\theta$ ) for Teflon as  $18^\circ$ . Kim *et al.* (2015) prepared self-cleaning SH PTFE-TiO<sub>2</sub> nanocomposite films by using supersonic spray coating of PTFE-TiO<sub>2</sub> on the glass and stainless steel mesh as substrate surfaces. The XRD analysis of the films revealed that  $2\theta$  for PTFE and TiO<sub>2</sub> were  $17.96^\circ$  and  $25.32^\circ$ , respectively.

#### **2.10.7 Adhesion test**

The mechanical stress induced during various processes deforms the coated materials leading to coating failure. Various aspects of coatings and coated materials such as adhesive bonding and surface contact damage are investigated in such surface coating related studies.

Chang *et al.* (1997) developed a notched coating adhesion (NCA) test to estimate the adhesive performance and durability of coating by using special specimen that accelerated humidity conditioning. The specimen were subjected to uniaxial tensile strain and the strain at which the coating de-bonded was used to calculate the critical strain energy release rate. The NCA test method was used to measure the interfacial fracture toughness of certain coatings.

Gay (2000) studied the adhesion between solid and a stretched elastic material and found that the adhesion was not affected at molecular scale but at macroscopic scale and was changed due to elastic response of the material.

Later, Dillard *et al.* (1999) conducted finite element analysis to determine the critical strain energy release rates for the NCA specimen. Even though plastic deformation was developed when the NCA specimen were placed in tension, the NCA test could not predict the adhesion failure of coatings on deformed substrates in practical situation of complex metal forming.

Vayeda and Wang (2007) studied the adhesion of two coatings of polyvinylidene fluoride (PVDF), one of which was added with polyester as primer and another with polyurethane as primer, on sheet metal by using the cross cut tape test under plastic deformation of the substrate and concluded that the test was suitable for evaluation of adhesion of both the coatings on selected substrate under plastic deformation.

Horkavcová *et al.* (2008) evaluated the cross cut tape test by checking the adhesion strength of a bioactive coating layer on the ground and sand blasted surface of titanium alloy (Ti6Al4V), taken as substrate, after treatment with alkali and pre-calcification for 2 h. The results indicated that the test was suitable.

Xu *et al.* (2010) used cross cut tape test for examining the adhesion strength between dual silica coating on glass as substrate. They employed a 1 mm square grid on the coating by using a steel blade. The result showed that the coating was intact without any sign of shedding of grid area, thus, confirming to the strong (5B grade) adhesion.



# CHAPTER -3

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## MATERIALS AND METHODS

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### 3. MATERIALS AND METHODS

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This chapter deals with the experimental techniques employed to fulfill the objectives envisaged for this study. It includes design of Plate Heat Exchanger (PHE), fabrication and assembly of various components of the PHE module on the skid structure, surface coated process, characterization of coated surface, experimentation to study fouling of PHE with coated surface against that without coated surface using milk and paneer whey as processing fluids and evaluation of the performance of the developed module.

#### 3.1 Materials

Austenite stainless steel of grade 304 or 316 was used for fabricating different components of skid mounted plate heat exchanger module since it is best suited for dairy equipment (Budinski and Budinski, 2002).

The polytetrafluoroethylene (PTFE) emulsion used as one of the surface coating materials was supplied by Whitford India Pvt. Ltd., Bengaluru, on gratis basis. The emulsion had a crystallinity of 90-95% and melting point of 327°C. Another coating material, the titanium oxide (TiO<sub>2</sub>) in anatase form, was procured from Sigma-Aldrich, USA. The TiO<sub>2</sub> had the density of 0.04-0.06 g/mL, with particle size of less than 25 nm, purity of 99.7% and surface area of 45-55 m<sup>2</sup>/g.

Fresh raw milk and paneer whey were collected from the Livestock Research Centre (LRC) and Dairy Plant of SRS, ICAR-NDRI, Bengaluru, respectively.

#### 3.2 Design of PHE Module

For the design of PHE, the minimum heat transfer area that could provide sufficient heat exchange to meet the given heat duty of the intended process was estimated as most important design parameter. The PHE module for processing of 25 L/h of milk from the initial temperature of ~ 30°C to pasteurization temperature was designed and assembled.

The temperature of hot water as heating medium was 90°C. The ratio of flow rates of milk to hot water was 1:3. As per the general design protocol for milk pasteurizer, an approximation of the heat balance between the milk and heating medium was made and is given below.

$$\text{Heat absorbed by milk} = Q_m = m_m C_{pm} (T_{mi} - T_{mo}) \quad (3.1)$$

$$\text{Heat rejected by hot water} = Q_w = m_w C_{pw} (T_{wi} - T_{wo}) \quad (3.2)$$

$$\text{Heat rejected by hot water} = \text{Heat absorbed by milk} \quad (3.3)$$

$$Q_r = m_w C_{pw} \Delta T_w = m_m C_{pm} \Delta T_m \quad (3.4)$$

where, 'Q' is the amount of heat, 'm' is the mass, 'T' is the temperature, 'm' is the mass flow rate, 'C<sub>p</sub>' is the specific heat and the subscripts 'm', 'w', 'i' and 'o' stand for milk, hot water, inlet and outlet, respectively. The  $\Delta T_w$  and  $\Delta T_m$  indicate the temperature differentials of entering and leaving conditions of hot water and milk, respectively.

The heating of milk to the desirable temperature could not be achieved until the heat requirement obtained by Eq. (3.1) is met by the heat transfer given by Eq. (3.5). By equating Eqs. (3.1) and (3.5), the value of required heat transfer area can be obtained.

$$Q_r = U \times A \times \text{LMTD} \quad (3.5)$$

$$A = \frac{Q_r}{U \times \text{LMTD}} \quad (3.6)$$

where, 'U' is the overall heat transfer coefficient, 'A' is the heat transfer area and LMTD is the log mean temperature difference between the fluids exchanging heat. The LMTD was calculated for counter flow arrangement by taking into consideration the inlet and outlet temperatures for milk and hot water in a PHE.

$$\text{LMTD} = \frac{(T_{wi} - T_{mo}) - (T_{wo} - T_{mi})}{\ln \left[ \frac{(T_{wi} - T_{mo})}{(T_{wo} - T_{mi})} \right]} \quad (3.7)$$

The overall heat transfer coefficient (U) was computed from Eq. (3.8).

$$\frac{1}{U} = \frac{1}{h_w} + \frac{\delta x}{k_s} + \frac{1}{h_m} \quad (3.8)$$

where, ' $h_m$ ' and ' $h_w$ ' are the convective heat transfer coefficients on milk and hot water sides, respectively, ' $k_s$ ' is the thermal conductivity of SS 316 of the plate material (coated and non-coated) and ' $\delta x$ ' is the thickness of the plate. The convective heat transfer coefficients ( $h_m$  and  $h_w$ ) were calculated by using the appropriate empirical relationships for the Nusselt number ( $N_{Nu}$ ), available for prevalent flow conditions as characterized by the Reynolds number ( $N_{Re}$ ). For turbulent flow regime, following correlation was used.

$$N_{Nu} = 0.44 \left( \frac{\beta}{30} \right)^{0.38} (N_{Re})^{0.5} (N_{Pr})^{0.33} \left( \frac{\mu_b}{\mu_w} \right)^{0.14} \quad (3.9)$$

$$h = 0.44 \left( \frac{\beta}{30} \right)^{0.38} (N_{Re})^{0.5} (N_{Pr})^{0.33} \left( \frac{\mu_b}{\mu_w} \right)^{0.14} \left( \frac{k}{d_c} \right) \quad (3.10)$$

$$N_{Nu} = \frac{h d_c}{k} \quad (3.11)$$

$$N_{Re} = \frac{\rho v d_c}{\mu} \quad (3.12)$$

$$N_{Pr} = \frac{C_p \mu}{k} \quad (3.13)$$

where, ' $\rho$ ' is the density of milk, ' $v$ ' is the average velocity of milk in flow channel, ' $d_c$ ' is the characteristic dimension of the flow channel (here hydraulic diameter), ' $\mu_b$ ' and ' $\mu_w$ ' are the dynamic viscosities at bulk fluid temperature and surface temperature of wall, respectively, ' $C_p$ ' is the specific heat of milk and ' $k$ ' is the thermal conductivity of milk. Same equation was used to calculate the ' $h$ ' value for hot water side by replacing the values of milk properties with the corresponding values for the properties of hot water at respective temperatures.

The hydraulic diameter of the flow channel in PHE was found out using Eq. (3.14).

$$D_h = \frac{4 \times \text{Channel flow area}}{\text{Wetted perimeter}} = \frac{4 \times W \times b}{2(W + b)} \approx 2b \quad (3.14)$$

where, ' $W$ ' is the width of the plate of PHE, ' $b$ ' is the spacing between the plates and  $W \gg b$ .

The velocity of the media depends on the flow pattern and the cross-sectional area of the flow channel ( $A_f$ ), which is given by

$$A_f = N \times W \times b \quad (3.15)$$

where, 'N' is the number of flow channels per pass, 'W' is the width of a plate and 'b' is the spacing between the plates.

The resultant velocity ( $v$ ) of each fluid flowing through the channel was estimated using the continuity equation for an incompressible steady state flow.

$$v = \frac{Q}{A_f} \quad (3.16)$$

### **3.2.1 Piping and instrumentation diagram (P&ID) of PHE module**

The piping and instrumentation diagram (P&ID) was prepared using Auto CAD software to get clarity of the required number of components, their sizing and inter-connections in the developed PHE module. The P&ID (Fig.3.1) representing the feed tank, PHE, hot water generator, feed pump, hot water pump, valves, process piping and drainage piping connected together to work as an integral and functional system is shown in Fig. 3.2. A 3D model of the PHE module indicating all above-mentioned components was prepared using Pro/Engineer software as shown in Fig. 3.3. The P&ID and 3D model served as road maps for the design, development and assembly of individual components to form a module and placement of measuring instruments and process controls.

### **3.2.2 Fabrication and assembly of various components**

The fabrication of PHE module was carried out as per 3A hygiene standards (Schmidt and Daniel, 2004). The components of PHE modules were fabricated, fitted on the skid structure and interconnections between the components were established by using SS pipelines. The steps involved in the fabrication process and assembly of components are shown in Fig. 3.4 and the detailed description is outlined below.

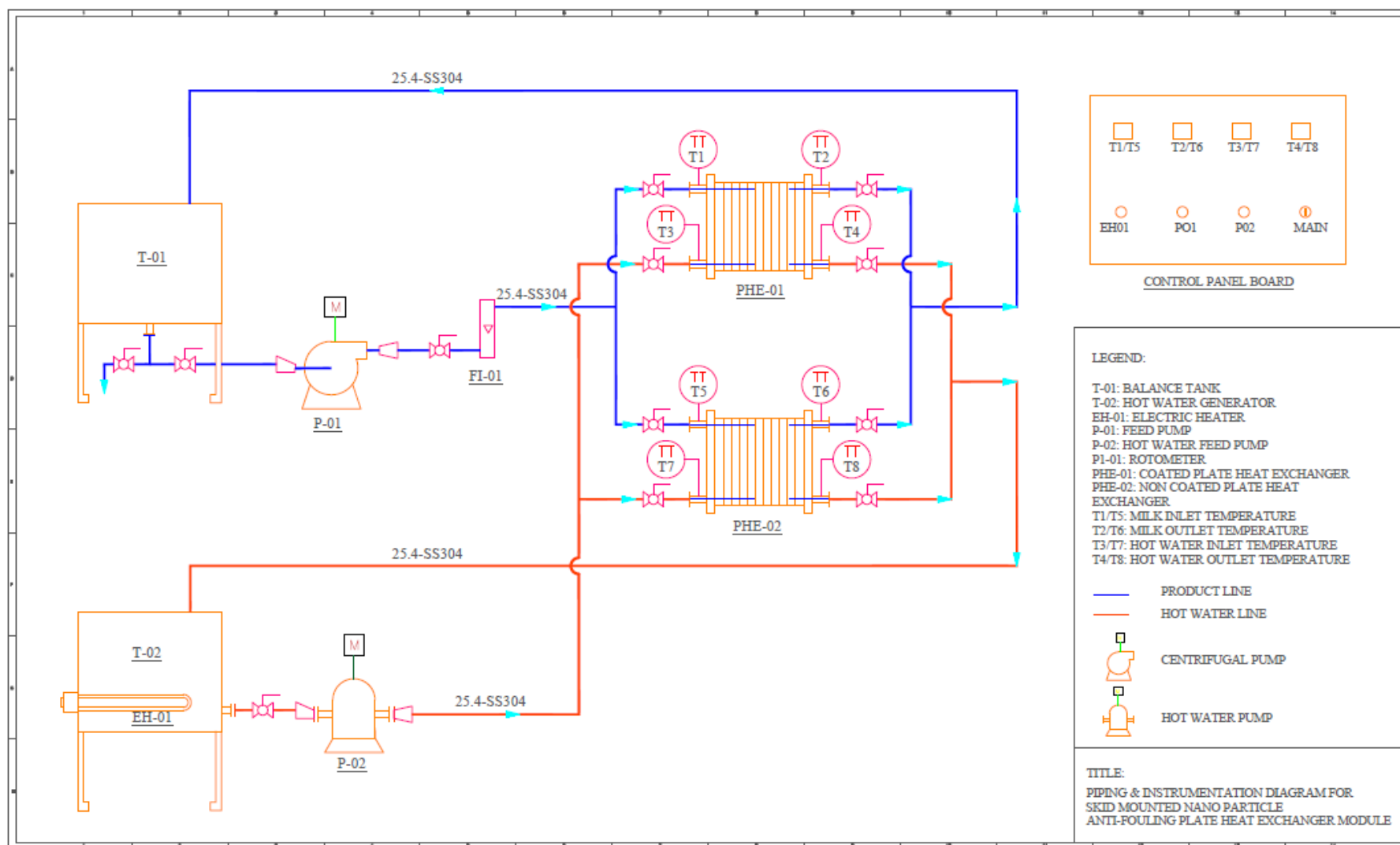


Fig. 3.1 Piping and Instrumentation Diagram of PHE module

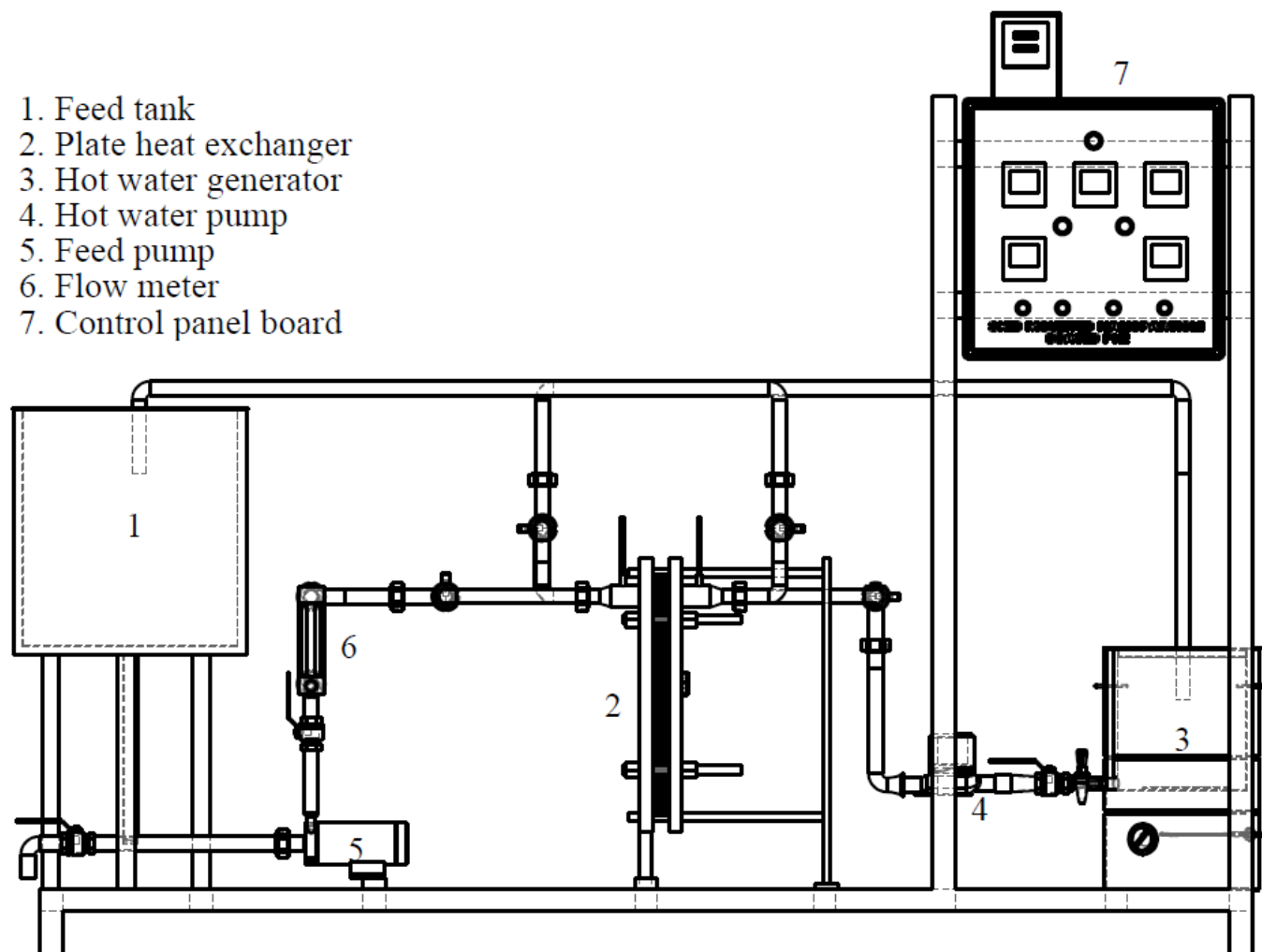


**Fig. 3.2 2D View of Skid Mounted PHE Module**

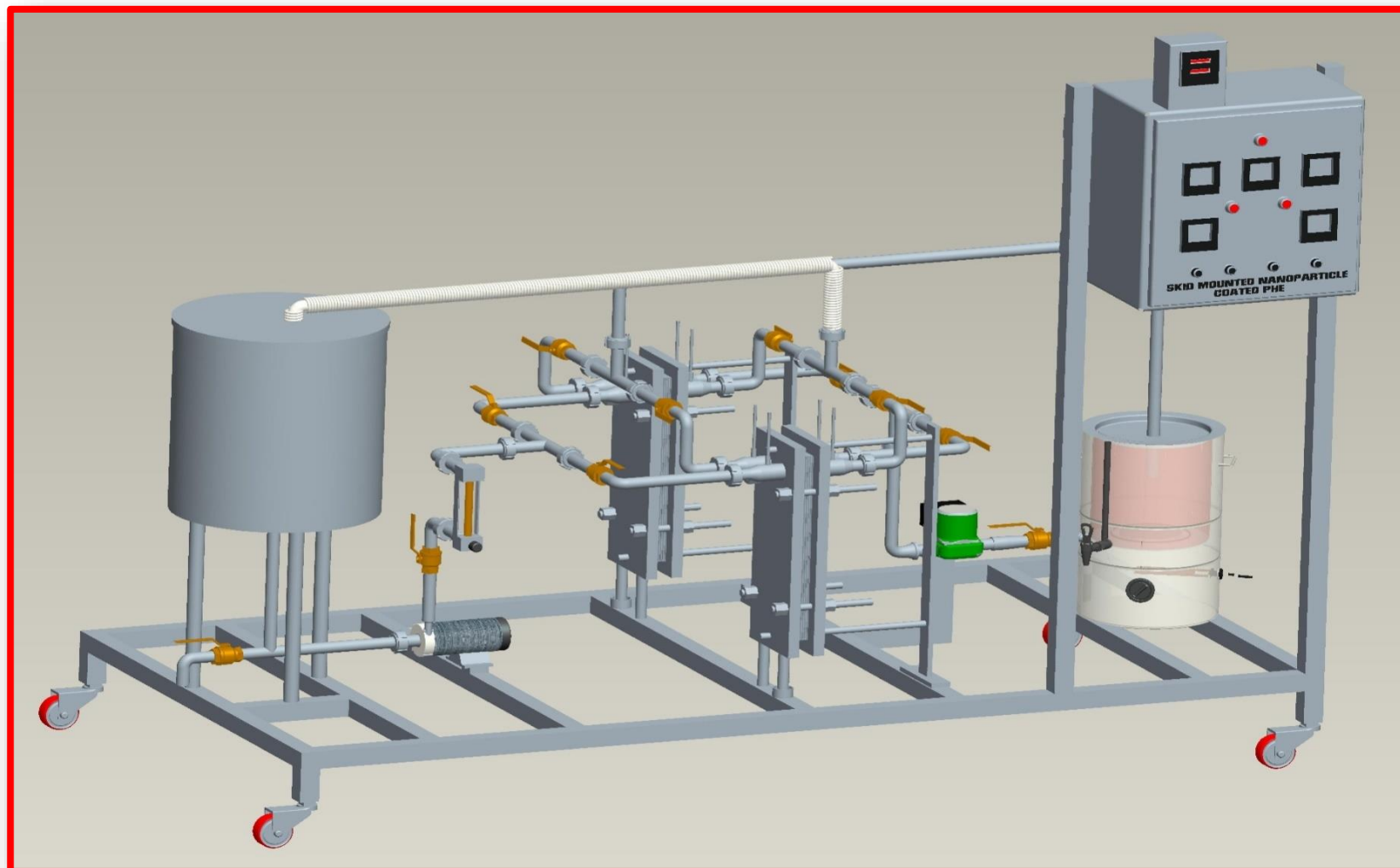


**Fig. 3.3. Piping and instrumentation diagram (P&ID) of the experimental setup in 3D View setup**

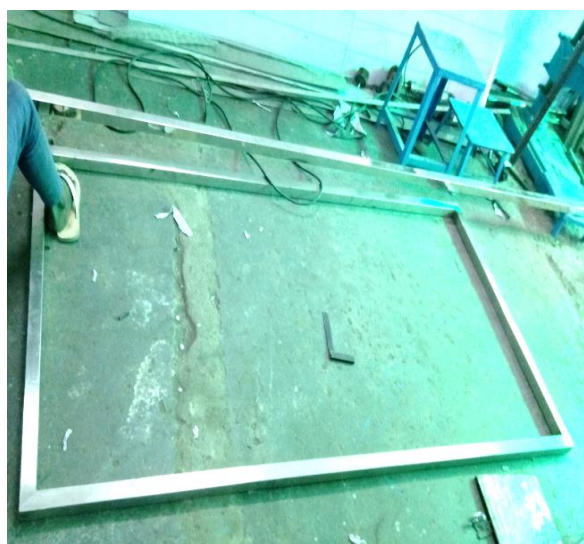
Two identical PHEs (one fitted with uncoated SS 316 plates and another with PTFE-TiO<sub>2</sub> coated plates) along with the hot water generator, feed tank, milk and water pumps and the control panel box were fitted on the skid. All the processing components were connected through 25.5 mm SS piping installed with valves at appropriate locations so that one PHE could be operated at a time keeping another in idle condition. Eight RTD type (Pt100) temperature sensors were fitted on the module. One each at the inlet and outlet of milk and water on both the PHEs. The power supply to the hot water generator was controlled through PID controller.



**Cutting operation of square pipe**



**Welding operation**



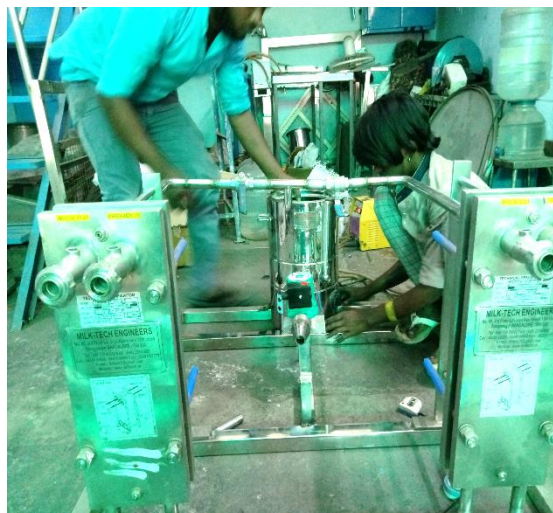
**Frame**



**PHEs**



**Hot water pump**



**Hot water generator**



**Auxillary assembly**



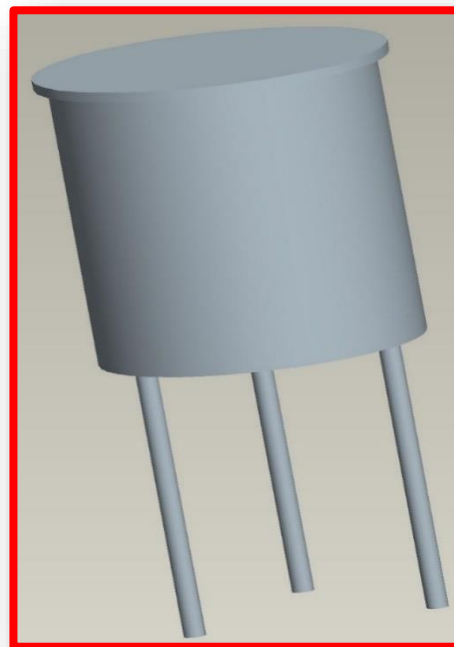
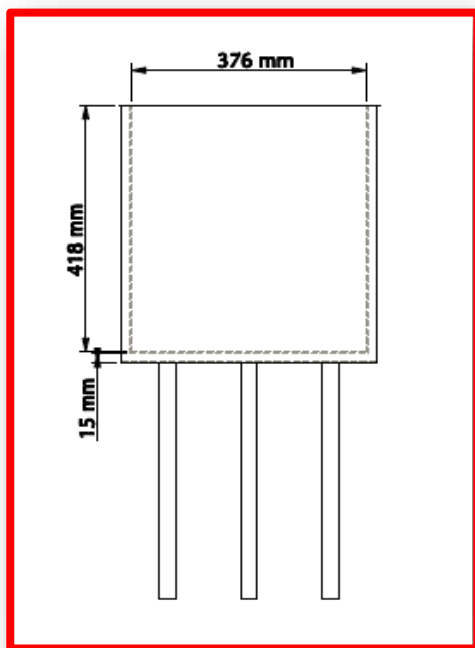
**PHE module testing**

**Fig. 3.4. Fabrication Stages of PHE Module**

### **3.2.2.1 Feed tank**

Austenite SS 316 sheet of 2 mm thickness was selected for the fabrication of feed tank and was bent using a sheet bender and rolled to form a cylinder of 376 mm diameter. The dimensions of the feed tank (376 mm internal diameter and 418 mm height) were marked on the sheet and was cut using laser cutter. The cut sheet was rolled to cylindrical shape and

the two edges were aligned. The edge was joined immediately by spot welding followed by the complete joint with The Tungsten Inert gas TIG welding. The TIG welding technique was employed to weld all the joints in stainless steel parts so that the inert argon gas over the tungsten electrode at the welding point prevents oxidation of the joints. Distortion during the process of welding was controlled by staggering the welds by applying braces near the weld point. Proper weld was ascertained with weld joint having a copper brown colour. All the welds were smoothened and polished so as to meet the sanitary standards. All welded joints were finished using angle grinder fitted with a 60-120 grit wheel (Make: Bosch, Model: GWS 9-115 P). The ground surface was progressively polished from 120 to 180 grit sanitary finish using flexible shaft grinder with buffing and polishing wheels. Thermal insulation was provided to prevent heat losses from the hot surface of feed tank to atmosphere. The feed tank was insulated with 50 mm thick preformed ceramic wool insulation and cladded with SS 304 of one mm thickness. An outlet of 25 mm diameter was given near the bottom of tank as milk outlet and an inlet of the same size was introduced at the top as shown in Fig 3.5. The feed tank was mounted on the skid with three-leg support. It could hold up to 43 L of milk and it ensured constant supply of milk to the PHE.



(a) (b)  
**Fig. 3.5. Feed Tank (a) 2D and (b) 3D Views**

### 3.2.2.2 Plate heat exchanger

As per the estimated area of the heat transfer using the Eq. 3.6 explained in the section 3.2, the plates of nearest size (430×130 mm) available in the market were procured along with clip-on type EPDM gaskets (Fig. 3.6). and SS frames to assemble the plates into two identical PHEs. The plates used in PHE modules were manufactured from austenitic stainless steel of grade 316 with 2B mill finish, commonly used in dairy industries. Two units of clip-on-type PHE, one as control (without coating) and other with PTFE-TiO<sub>2</sub> coated surface were fixed on the developed module. Each of the PHE was fitted with 5 plates in order to have counter current arrangement of hot water and milk with 2×1:2×1 flow configuration (Fig. 3.7).

Provisions were made to expand the capacity of the PHE by providing more number of plates. The pack of plates was assembled between the frame and the end plates and compressed by four number of tightening bolts to get 2 - 4 mm spacing between the plates. The gasket on each plate sealed the plate against exterior and directed the fluids into alternate channels. The specifications of the PHE are tabulated in Table 3.1.

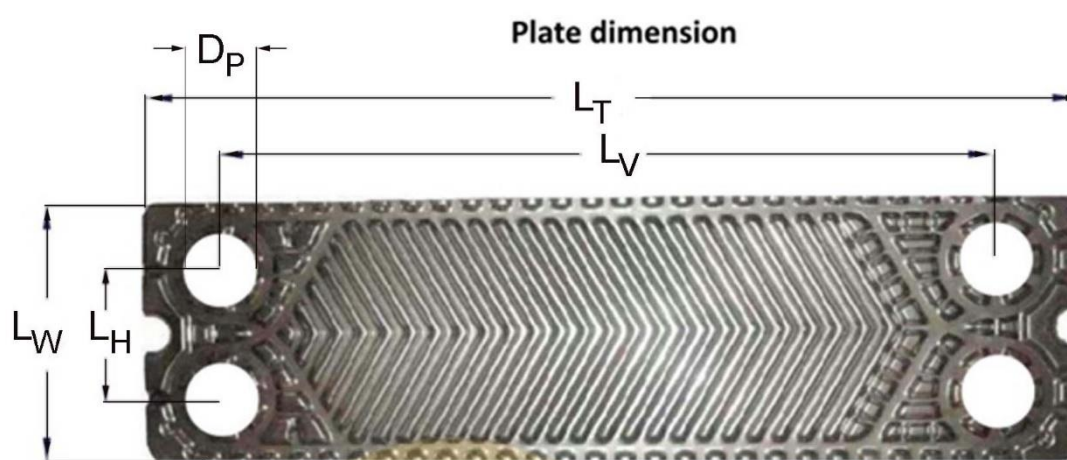


**Fig. 3.6. Photograph of Clip-on-type PHE Plate**

**Table 3.1 Technical specifications of PHE**

| Particulars                           | Specifications |
|---------------------------------------|----------------|
| Material of construction (Plates)     | SS 316         |
| Material of construction (End plates) | SS 304         |
| Plate height ( $L_T$ )                | 430 mm         |

|                                                 |                      |
|-------------------------------------------------|----------------------|
| Plate width ( $L_w$ )                           | 120 mm               |
| Plate thickness                                 | 0.5 mm               |
| Port diameter ( $D_p$ )                         | 29 mm                |
| Vertical distance between the ports ( $L_v$ )   | 360 mm               |
| Horizontal distance between the ports ( $L_H$ ) | 60 mm                |
| Chevron angle ( $\beta$ )                       | 30°                  |
| Heat transfer area per plate                    | 0.1 m <sup>2</sup>   |
| Total number of plates (N)                      | 5                    |
| Number of effective plates                      | 3                    |
| Number of passes                                | Two pass / Two pass  |
| Effective channel width                         | 10 mm                |
| Thermal conductivity of the plate material      | 16.5 W/mK            |
| Gasket material                                 | Nitrile Rubber (NBR) |
| Design pressure                                 | 6 bar                |
| Design temperature                              | 110°C                |
| Relative direction of flow                      | Counter flow         |

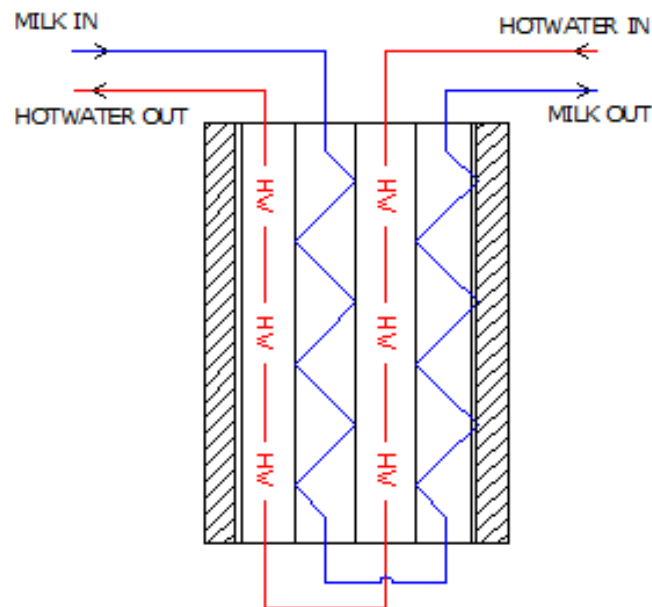


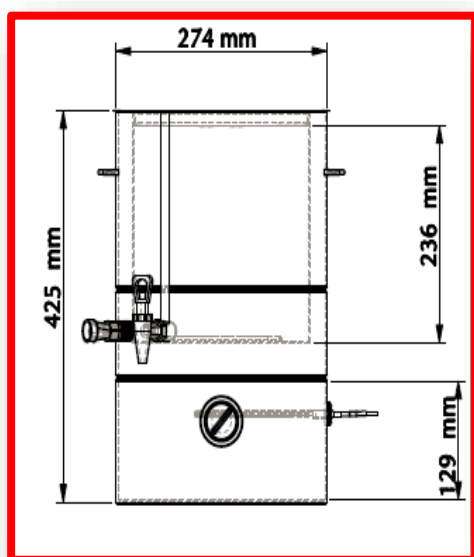
**Fig. 3.7. Diagram showing Flow Arrangement in PHE**

### 3.2.2.3 Hot water generator

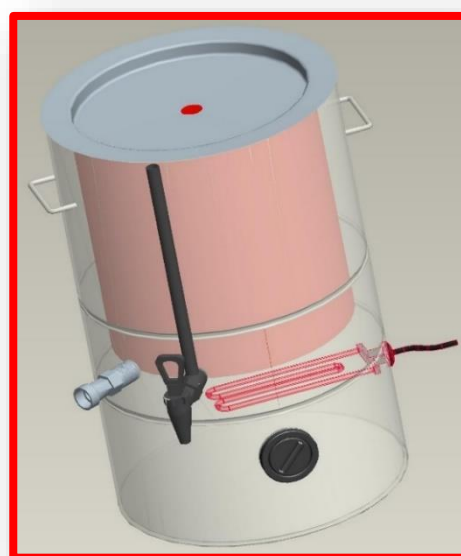
An electrically operated hot water generator fabricated from SS 304 was used to ensure the continuous supply of hot water as heating medium to both the PHEs. The hot water generator had heavy duty coil in the jacket to be filled with water prior to use and other fittings such as level indicator, thermostat, lid with an inlet port and water outlet nozzle as shown in Fig. 3.8. The specifications are given in Table 3.2.

**Table 3.2 Technical specifications of hot water generator**

| Particulars              | Specifications                  |
|--------------------------|---------------------------------|
| Make                     | Amirtha, Chennai                |
| Capacity                 | $10 \times 10^{-3} \text{ m}^3$ |
| Diameter                 | 274 mm                          |
| Total height             | 425 mm                          |
| Height of water vessel   | 236 mm                          |
| Height of heater housing | 129 mm                          |
| Heating coil capacity    | 230V A/C, 2000 W, 8 A           |
| Initial startup time     | 40 min                          |



(a)



(b)

**Fig. 3.8. Design of Hot Water Generator (a) 2D and (b) 3D Views**

#### 3.2.2.4 Hot water pump

A low head monobloc centrifugal pump with following specifications (Table 3.3) was employed for the circulation of hot water throughout the system.

**Table 3.3 Technical specifications of hot water pump**

| Particulars               | Specifications     |
|---------------------------|--------------------|
| Make                      | Wilo               |
| Model                     | RS25/8             |
| Capacity                  | 200 L/h            |
| Operating temperature.    | -10 to 95°C        |
| Operating pressure        | 6 bar              |
| Shaft                     | 1.4028, × 30Cr13   |
| Pump housing              | 5.1300, EN-GJL-200 |
| Impeller                  | PP-GF40            |
| Bearing                   | Total Carbon       |
| <b>Motor data</b>         |                    |
| Mains connection          | 1~230 V, 50 Hz     |
| Power consumption         | 151 W              |
| Max. speed ( $n_{\max}$ ) | 2760 rpm           |

#### 3.2.2.5 Feed pump

A hermetic magnetic drive pump was used as the feed pump to circulate the milk from feed tank throughout the PHE module and back to the feed tank. The specifications of feed pump are listed in Table 3.4.

**Table 3.4. Technical specifications of feed pump**

| <b>Particulars</b>                | <b>Specifications</b>         |
|-----------------------------------|-------------------------------|
| Model                             | MP-20 RM                      |
| Maximum capacity                  | 27 L/min                      |
| Standard capacity                 | 3.1 L/min                     |
| Maximum head                      | 17 m                          |
| Standard head                     | 2 m                           |
| Motor                             | 10 W 220 V/ 50 HZ             |
| Connection                        | 3/4" thread                   |
| Max permissible fluid temperature | 80°C                          |
| Working principle                 | Centrifugal, magnetic coupled |
| Casting parts material            | SS 304                        |

#### **3.2.2.6 Flowmeter**

A variable area flowmeter (Make: ATS, India) of capacity ranging from 0 to 100 L/h was used to measure the flow rate of milk.

#### **3.2.2.7 Temperature sensors and display**

Resistance Temperature Detector (Pt-100) sensors (Radix ElecroSystems Private Limited, Maharashtra, India) having SS 316L sheathed probe of 25 mm sensor length and a 5 m long cable were fixed in-line to sense the inlet and outlet temperatures of the product and hot water streams. An eight channel temperature indicator (Model: TC244, Make: Selec, Mumbai) was used to display the temperatures read by temperature sensors located at the inlets and outlets of water and product ports.

#### **3.2.2.8 Control panel board**

The control panel board housed a time indicator, a 4-channel digital temperature indicator, toggle switches and ON/OFF switches to monitor and control the process during the experimental trials. It was fabricated using 2 mm thick mild steel as per CE and IE

standard using mechanical press, laser cutting and welding processes. The hot water generator was operated from the panel using Proportional Integrated Derivative (PID) control. The specifications are given in Table 3.5.

**Table 3.5 Specifications of control panel board**

| Particulars             | Specifications          |
|-------------------------|-------------------------|
| Size of the panel board | 0.460 × 0.250 × 0.630 m |
| Temperature indicators  | 4 Nos.                  |
| Time indicator          | 1 No.                   |
| Switches (ON/OFF)       | 4 Nos.                  |
| Panel material          | Mild steel              |

### 3.2.2.9 Skid structure

The skid was fabricated from 40×40 mm square SS 304 pipe having thickness of 2 mm. The channels were precisely cut into required lengths of pieces using wheel cutting and the angled frame was constructed with SS 304 for supporting the entire assembly. The dimensions of the frame were 3200 × 1650 × 2100 mm skid with a ground clearance of 240 mm. The sanitary and hygienic considerations were taken into consideration while fabricating the skid structure. All corner joints of skid were ground to minimum 6.35 mm radius of curvature as per the sanitary standards (Schmidt and Daniel, 2004).

The feed tank, feed pump, flowmeter, PHEs, hot water generator, hot water pump, control panel and temperature sensors were assembled together by clamps, bends, pipelines, unions and valves on the skid structure (Table 3.6).

**Table 3.6 Specifications of PHE module components**

| S. No. | Description    | Quantity<br>(Nos.) | Material | Size (mm) |
|--------|----------------|--------------------|----------|-----------|
| 1      | SMS union      | 24                 | SS 304   | 25        |
| 2      | Pipe (6m long) | 2                  | SS 304   | 25        |
| 3      | Bend           | 19                 | SS 304   | 25        |

|   |                               |        |        |         |
|---|-------------------------------|--------|--------|---------|
| 4 | Pipe clamp                    | 48     | SS 304 | 51      |
| 5 | Square pipe support (6m long) | 5      | SS 304 | 40×40×2 |
| 6 | Wheel                         | 4      | Teflon | 76.20   |
| 7 | Ball valves                   | 11     | SS 304 | 25      |
| 8 | Gaskets in valves and unions  | 1 Pack | EPDM   | 3       |

### **3.2.2.10 Hydraulic testing**

All fabricated components of PHE module were tested for leakage and mechanical strength by standard hydraulic pressure testing (Jousten, 2008; ASME, 2010). Water was filled in the PHE and the pressure was increased to 300 kPa by using hydraulic test rig. The pressure was maintained for 24 h and after that test period, the pressure drop was measured. Drop-in pressure, if any, was identified as a possibility of potential leakage and appropriate corrective measures were taken to rectify leaky points.

### **3.2.2.11 Design and layout of power and control panel circuit**

Three phase 415V - 50 Hz -63A power circuit was designed and the wiring diagram was prepared using electrical CAD software for control of electric heater in the hot water generator. The power circuit wiring diagram is shown in Fig. 3.9.

The control panel was wired as per the wiring diagram (Fig. 3.9) using universal colour code applied for wiring. Multi-stranded, annealed, PVC insulated, copper conductor (Make- Finolex) of different diameters were selected based on their loading conditions required by the instruments and rotating components of the developed module.

## **3.3 Surface Coating Process**

Nine discs of 50 mm diameter were cut from a 0.5 mm thick stainless steel (316 grade) sheet by laser cutting. All the discs were sand blasted to 6 Ra, to provide good grip for the surface coatings, and were cleaned with ethanol (AR grade purity, HiMedia). A base coat of PTFE added with binder was applied on each disc to a thickness of 8-10  $\mu$  by using high volume low pressure (HVLP) spray gun (0.3 MPa), followed by curing in hot air oven at 100°C for 5 min and cooled to room temperature. Then the final coat of nano-emulsion of PTFE-TiO<sub>2</sub> was prepared in different proportions and coat thicknesses, as indicated in Table 3.7 and was applied on the discs. The thicknesses of the coating were measured using

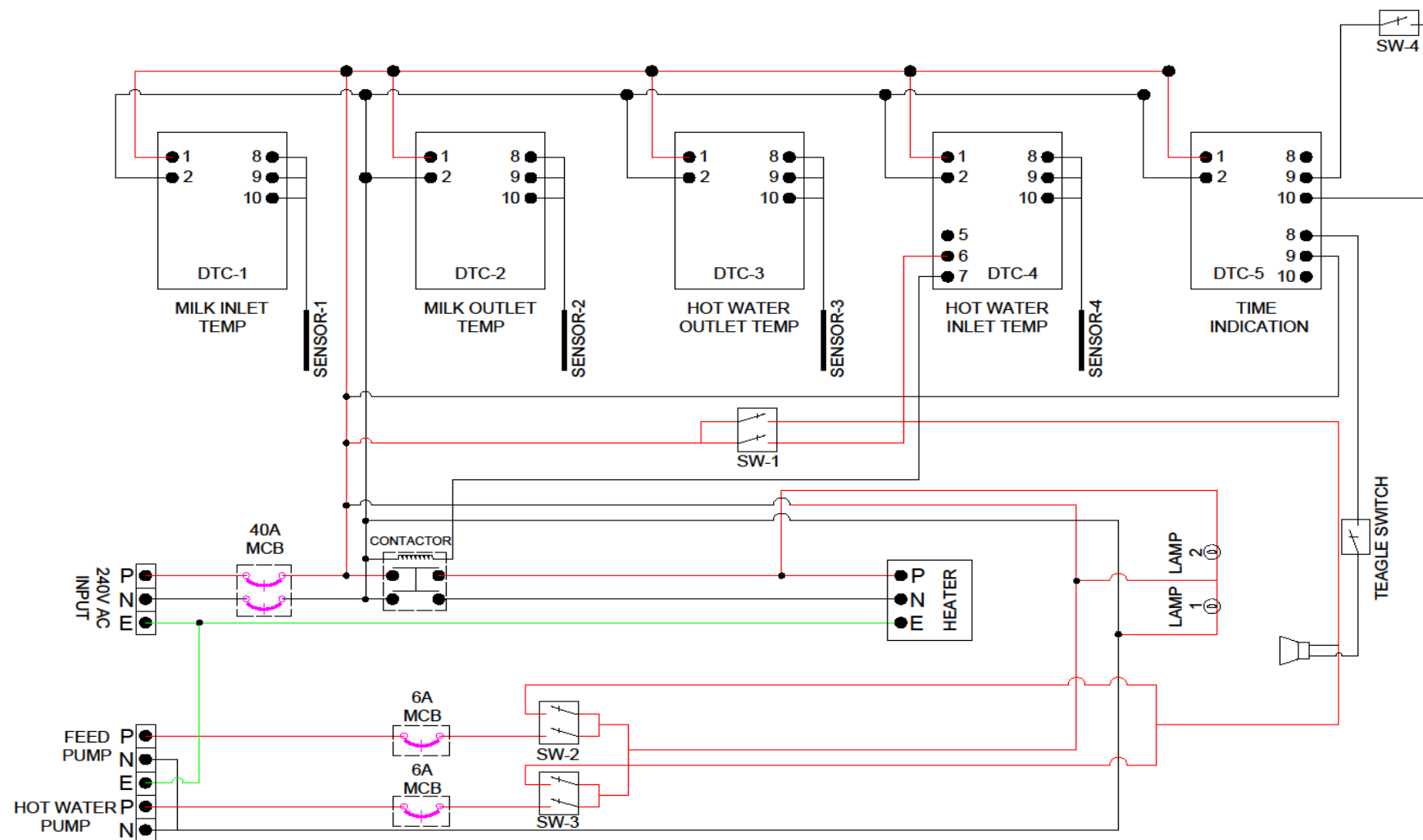


**Fig. 3.9. Wiring Diagram of Control Panel**

a robust coating thickness gauge (Model: MiniTest 650, Make: ElektroPhysik, Germany). The coated discs were again annealed at  $410 \pm 10^\circ\text{C}$  for 5 min, which was above the melting point of PTFE ( $342^\circ\text{C}$ ) and were cooled to room temperature. After cooling, all the discs were shrink wrapped using polystyrene until further studies were carried out. The best combination of coating material proportion and coating thickness was selected on the basis of thermal conductivity of the coated discs. The process sequence of coating is shown in the Fig. 3.10.



**Circular plates**



**Nano-emulsion mixing**



**Spraying**



**Curing**



**Thickness measurement**

**Fig. 3.10 Process Sequence for Nanoparticle Coating**

**Table 3.7 Combinations of coating compositions and thicknesses**

| Discs  | PTFE: TiO <sub>2</sub> | Coating Thickness (μ) |
|--------|------------------------|-----------------------|
| Disc-1 | 88:12                  | 10                    |
| Disc-2 | 86:14                  | 10                    |
| Disc-3 | 84:16                  | 10                    |
| Disc-4 | 88:12                  | 20                    |
| Disc-5 | 86:14                  | 20                    |
| Disc-6 | 84:16                  | 20                    |
| Disc-7 | 88:12                  | 30                    |
| Disc-8 | 86:14                  | 30                    |
| Disc-9 | 84:16                  | 30                    |

### **3.3.1 Adhesion strength**

The adhesion strength between the coating and the stainless steel substrate was checked by using cross-cut tape test according to the standard test method (ASTM: D3359, 1997). The coated plates were cleaned and gently wiped with a cotton cloth without damaging the coating integrity. The cleaned plates were then fixed on a firm base under an

illuminated magnifier and 11 parallel cuts with a spacing of approximately 1 mm were made on it with the aid of a guide and a knife. Same numbers of parallel cuts with the same spacing were made at right angles to earlier set of cuts forming 100 squares on the plate. The detached flakes or ribbons of coatings formed due to cuts were removed with a soft brush. A transparent adhesive tape was placed over the grid of cuts covering all the 100 squares and was rubbed with a fingernail to get maximum contact. After an interval of 90 s, the tape was removed by seizing the free end and pulling rapidly without jerk. The surface was inspected and the number of squares that detached along with the adhesive tape was noted. According to the size of the removed area (expressed as %) the samples were divided into the following classification scale: 5 = 0%; 4  $\leq$  5%; 3 = 5-15%; 2 = 15-35%; 1 = 35-65%; 0  $\geq$  65%.

### **3.4 Characterization of Coated Surfaces**

Among the different coated surfaces, the best combination of PTFE-TiO<sub>2</sub> and thickness of coating was selected based on the thermal conductivity of the coated plate. The surface modified with selected coating was subjected to surface characterization using various techniques described below and were compared with the non-coated surface (SS 316).

#### **3.4.1 Thermal conductivity**

The thermal conductivity of the coated and non-coated discs was measured using thermal conductivity meter (Model: Unitherm<sup>TM</sup> 2022, Anter Corporation, Pittsburgh, PA) shown in Fig. 3.11, as per ASTM E-1530 standard (1999). It is able to measure the thermal conductivity of materials in the range of 0.1–40 W/mK. Circular discs of 50 mm diameter were tested for thermal conductivity. The disc was held under a uniform compressive load between two parallel polished surface plates maintained at different temperatures. The lower surface was part of a calibrated heat flow transducer. An axial temperature gradient in the stack was established by the heat flow from the upper surface plate, through the sample, to the lower surface plate. The temperature difference across the sample was measured along with the output from the heat flow transducer, after reaching thermal equilibrium. The heat flow and temperature gradient were recorded by sensors attached to the plates and thermal conductivity of the disc was calculated using the Fourier's law of heat conduction (Eq. 3.16). The thermal resistance was calculated between the upper and lower surfaces from the heat

flux (Q) and the temperature difference between the plates ( $T_1-T_2$ ). By substituting the thickness ( $\delta x$ ) and cross-sectional area of the discs (A), the thermal conductivity (k) of the discs was calculated using the following equations (Eqs.3.17-3.18).

$$Q = kA \frac{(T_1 - T_2)}{\delta x} \quad (3.16)$$

$$\text{The thermal resistance of the disc } R = \frac{(T_1 - T_2)}{Q/A} \quad (3.17)$$

$$\text{Thermal conductivity } k = \frac{\delta x}{R} \quad (3.18)$$



**Fig. 3.11. Thermal Conductivity Meter**

### **3.4.2 Roughness**

The surface roughness of SS 316 disc and PTFE-TiO<sub>2</sub> composite coated surface was measured using non-contact optical profilometer as shown in the Fig. 3.12 (Model: TalySurf CCI Lite, Make: Taylor Hobson Precision, Leicester, UK) with a TalyMap Platinum software (TalySurf, UK). This uses coherence correlation interferometry measurement technique and a high resolution digital camera array to measure the 3D surface topography of the discs. The 3D image of the surface was generated by scanning the surface in 'Z' direction (height)

over an area of 'X' and 'Y' lateral dimensions. Four profilometric scans of the discs were taken at different positions on the surface. The 2D texture parameters of the surfaces were obtained from the resulting cross-sectional profile. The parameters such as arithmetic mean deviation ( $R_a$ ), total height ( $R_t$ ), maximum profile peak height ( $R_p$ ), maximum peak to valley height ( $R_z$ ), mean height ( $R_c$ ), maximum profile valley depth ( $R_v$ ), root-mean-square deviation ( $R_q$ ), relative material ratio ( $R_{mr}$ ) of the roughness profile were extracted according to ISO 4287 (1977) and the mean and the standard deviation were calculated.



**Fig. 3.12. Optical Profilometer**

### **3.4.3 Contact angle**

The liquid solid interfacial tension or water repellency of the PTFE-TiO<sub>2</sub> coated plate was compared with the uncoated SS 316 disc surface by measuring the contact angle. The water contact angle was determined by an optical contact angle goniometer (Model: Kyowa DM501, Kyowa Interface Science Co. Ltd., Japan) equipped with FAMAS software (Fig. 3.13). For the measurement of the static angles, the sessile drop method was followed. The computer controlled automatic dispenser discharged a precise volume of liquid (droplet of 1 $\mu$ L). The syringe holding the droplet at its tip was moved down by operating its vertical

knob until the droplet touched the disc surface. The syringe was then moved back in upward direction leaving the droplet on the disc surface. Still images were captured using charge-coupled device (CCD) camera, and the measurements were performed after one second of deposition of droplet on the disc surface.

Five measurements were carried out for each surface from different locations and the average was taken. High-precision drop shape analysis was adopted during the measurements using the FAMAS software to determine the contact angles. In general, the wetting behavior can be classified into four different regimes on the basis of water contact angle (WCA). WCA in the range of  $0^\circ < \theta < 10^\circ$ ,  $10^\circ < \theta < 90^\circ$ ,  $90^\circ < \theta < 150^\circ$  and  $150^\circ < \theta < 180^\circ$  can be termed as superhydrophilic, hydrophilic, hydrophobic and superhydrophobic, respectively (Marmur, 2012). The contact angles of distilled water, milk and paneer whey were measured as the ability of water-repellency on coated and non-coated surfaces. From the contact angle, the work of adhesion was computed using Young-Dupré's equation (Eq. 3.19).

$$W_a = \gamma(1 + \cos\theta) \quad (3.19)$$

where,  $W_a$  is the work of adhesion, ' $\gamma$ ' is the surface tension of the liquid and ' $\theta$ ' is the contact angle. The surface tension of the liquids was measured using stalagmometer.

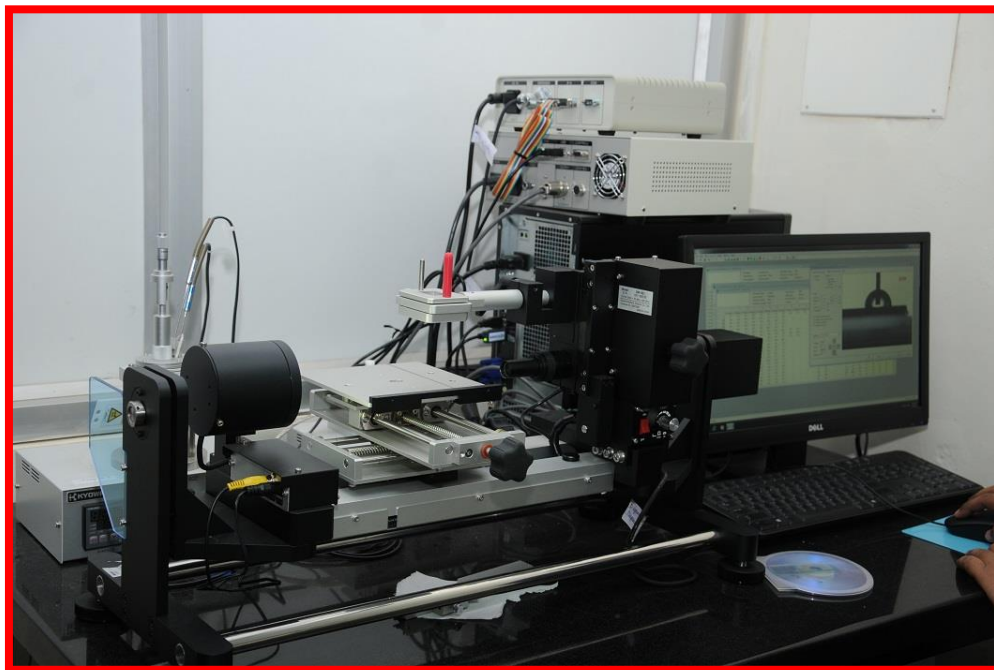


**Fig. 3.13. Contact Angle Meter**

#### **3.4.4 X-Ray diffraction (XRD)**

The crystalline nature of PTFE-TiO<sub>2</sub> coated and uncoated SS 316 discs was analyzed in an X-ray diffractometer (Model: Rigaku, SmartLab XRD, Japan) (Fig. 3.14) The CuK $\alpha$  of wavelength 1.54059Å was used as the X-ray source and was operated at 40 kV and 30 mA. The detector used was D/teX Ultra. The scan speed and time were set at 5 and 4°/min for the coated and uncoated surfaces, respectively with 150 mm distance between the sample and the detector. All the samples were scanned at room temperature in the 2 $\theta$  range from 10 to 90° using a step size of 0.02°. The crystallite sizes were estimated by Scherrer's formula (Eq. 3.20) and the inter-planar spacing between atoms was calculated using Bragg's Law (Eq. 3.21).

$$D = \frac{K\lambda}{\beta \times \cos\theta} \quad (3.20)$$

$$2 \times d \times \sin\theta = n \times \lambda \quad (3.21)$$

where, 'D' is the crystallite size, 'K' is Scherrer's constant, ' $\lambda$ ' is the wavelength of X-ray, ' $\beta$ ' is the full width at half maximum (FWHM) of the peaks, ' $\theta$ ' is the Bragg angle, 'n' is the order of reflection and 'd' is the inter-planar spacing.



**Fig. 3.14. X-Ray Diffractometer**

### **3.4.5 Atomic force microscopy (AFM)**

Atomic force microscope (Model: Scan Asyst, Bruker, Santa Barbara, CA, USA) was used to measure the roughness and morphology of PTFE-TiO<sub>2</sub> coated and control surfaces (10 × 10 μm area). They were analyzed in 2D and 3D for quantifying roughness of the surfaces by arithmetic average of the absolute values (Ra) of the vertical differences (μm) (Fig. 3.15). AFM measured the surface height at point locations by using class 2M reflected laser beam in the quadrant photo detector and generated a surface topographical map that was used to calculate the surface roughness values. The surface area of the image was from -165 to 165 μm and the height of sensor over the surface was 10 nm.

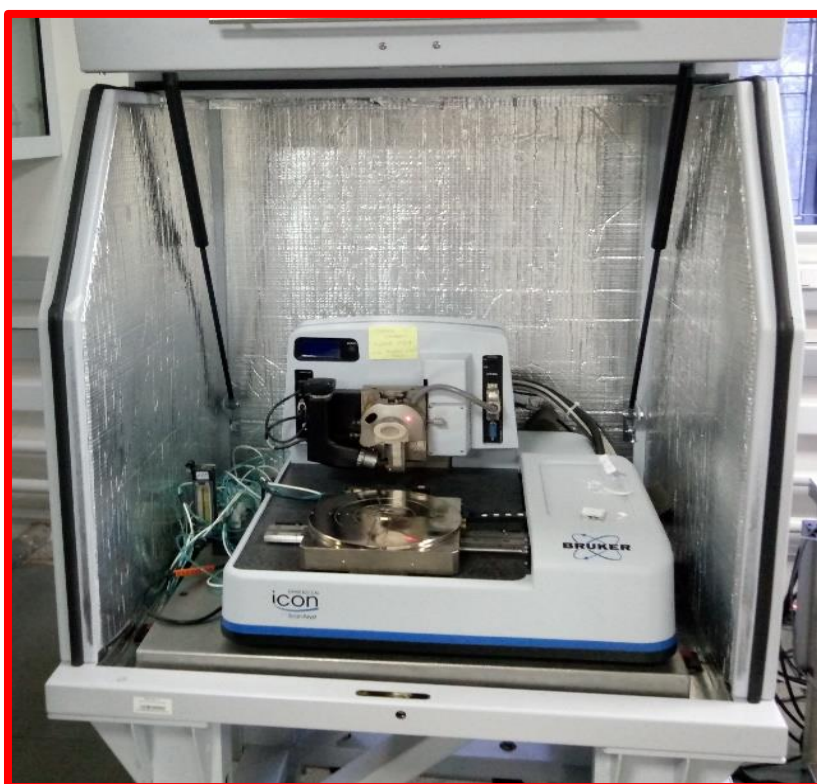


**Fig. 3.15. Atomic Force Microscope**

### **3.4.6 Field emission scanning electron microscope (FESEM)**

The microstructure of the coated and non-coated surfaces (control) was examined by using Field Emission Scanning Electron Microscope (Model: FESEM Tescan-Mira 3 LMH, Czech Republic) (Fig. 3.16). For the modified and control surfaces, the surface chemistry and the distribution of elements in the coating matrix were determined by energy dispersive spectroscopy (EDS) (Model: Bruker Quantax 200, Ettlingen, Germany). The

number and the intensity of the signals in the EDS spectrum were analyzed to quantify the surface composition.



**Fig. 3.16. Field Emission Scanning Electron Microscope – EDS**

### **3.5 Fouling Experiment**

#### **3.5.1 Process fluid**

Milk and paneer whey were selected to investigate the performance of the modified and control surfaces against fouling. The raw milk was standardized to 3.0% fat and 8.5% SNF (toned milk). The fat content was determined by Gerber method (BIS, 1977a). The titratable acidity of milk and whey was measured before starting the experiment (Method 947.05 AOAC, 1990).

##### **3.5.1.1 Physical properties of water**

The physical properties of water such as density, viscosity, thermal conductivity and specific heat at bulk mean temperature were estimated (Incropera and DeWitt, 1996).

### **3.5.1.2 Physical properties of milk and paneer whey**

The physical properties of water and paneer whey such as density, viscosity, thermal conductivity and specific heat were measured for the mean bulk temperature using the following techniques.

Thermal conductivity of milk and paneer whey was measured using Thermal Properties Analyser (KD2 Pro, Decagon Devices, Inc., USA) using single needle KS-1 sensor which is 60 mm long and 1.3 mm diameter. Before taking the measurement, the equipment was calibrated for its accuracy. The calibration was performed with glycerol whose thermal conductivity was 0.285 W/m K at 20°C. The specific heat capacity of milk and whey was taken from the literature (Rao, *et al.*, 2005; Rahman, 2009).

Viscosity of milk and paneer whey was determined using Ostwald viscometer. The time required for milk to flow through a capillary of a known diameter of a certain factor between two marked points was measured. By multiplying the time taken by the factor of the Ostwald viscometer, the kinematic viscosity was obtained. Dynamic viscosity was obtained by multiplying kinematic viscosity with density of milk. Density of milk and paneer whey was measured using specific gravity bottle at 20°C.

### **3.5.3 Preparation of setup**

Preliminary experiments were carried out with water to validate the experimental set-up for temperature and flow rate. The set-up was also validated to ensure that the flow rates and temperatures were same in PHE-1 and PHE-2.

#### **3.5.3.1 Experimentation**

The flow loop of the experimental set up is shown in Fig.3.10. The heating medium (distilled water) and the milk were circulated in a closed flow loops. The flow rates of the milk and heating medium were 25 and 75 L/h, respectively. For the fouling experiments, the experimental setup was thermally stabilized using milk/paneer whey in recirculation mode. After achieving thermal equilibrium, the timer was set up for 480 minutes. The process fluid was heated to the final outlet temperature of 75°C in both the PHEs. The inlet and outlet temperatures of the process fluid and hot water were noted at an interval of 10 min. After a run time of 480 min, the processing was stopped and the setup was flushed with

soft water. The PHEs were dismantled and visually inspected to examine for the fouling deposition. The PHE was re-assembled and cleaned as per the CIP regime.

### **3.6 Visual Inspection of Fouling Deposition**

The fouling deposition on the SS 316 uncoated and PTFE-TiO<sub>2</sub> coated surfaces was done preliminarily through visual inspection of the uncoated and coated plates for milk and paneer whey. The milk or paneer whey was processed for continuous 8 h long experimental trial and the plates of PHEs fitted with coated and uncoated surfaces were removed and observed visually. The colour of deposits, pattern of deposition, adherence to the surface, etc. were studied for both the coated and uncoated surfaces.

### **3.7 Fouling Measurement Techniques**

Fouling deposition on the experimental surfaces was monitored by both invasive and non-invasive techniques.

#### **3.7.1 Invasive technique -Amount of fouling deposits**

The build-up of fouling deposits on a processing surface adds to the weight of the processing surface, which can be used to monitor the fouling deposition process. Hence, the experimental (modified and control) surfaces were weighed before and after fouling experiments. The difference in mass was calculated by deducting initial weight of the plate from final weight of the plate. The weight of the fouling deposit was then normalized to the effective heat transfer area and to the quantity of milk used for fouling. Thus, the amount of the fouling deposits was calculated and expressed as g/m<sup>2</sup>.

#### **3.7.2 Non-invasive technique – Fouling Resistance (R<sub>f</sub>)**

The build-up of fouling deposits over a period of time on heat transfer plates acts as an additional surface for heat transfer and decreases the thermal performance of the processing equipment, resulting in to decreased the overall heat transfer coefficient. This was evaluated in terms of Fouling Resistance (R<sub>f</sub>) as follows.

$$R_f = \frac{1}{U_t} - \frac{1}{U_0}$$

where, 'U<sub>t</sub>' is the value of overall heat transfer coefficient at time 't' and 'U<sub>0</sub>' is the value of overall heat transfer coefficient at time, 't=0'.

### **3.8 Analytical Characterization of Fouling Deposits**

The migration of coating material from the coated surface to the milk was studied using X-Ray Photoelectron Microscopy (XPS) (Fig. 3.17). XPS analysis was performed on a Kratos Axis Ultra DLD spectrometer (Kratos Analytical, Manchester, UK) using a monochromatic Al K $\alpha$  X-ray source ( $h\nu = 1486.6$  eV). The emission voltage and the current of this source were set to 15 kV and 10 mA, respectively. The pressure in the analyzing chamber was maintained at  $10^{-7}$  Pa, and the size of the analyzed area was  $300 \times 700 \mu\text{m}^2$ , with a depth of 10 nm. Survey (0-1300 eV) and high-resolution spectra were recorded at pass energies of 20 eV with a step size of 0.1 eV (the surveys were recorded at pass energies of 160 eV with a step of 1 eV). Data treatment and peak-fitting procedures were performed using Casa XPS software. Obtained spectra were rescaled by shift of C1s C-C at 284.6 eV. The Ca2p peaks were decomposed using Gaussian-Lorentzian peak shapes.

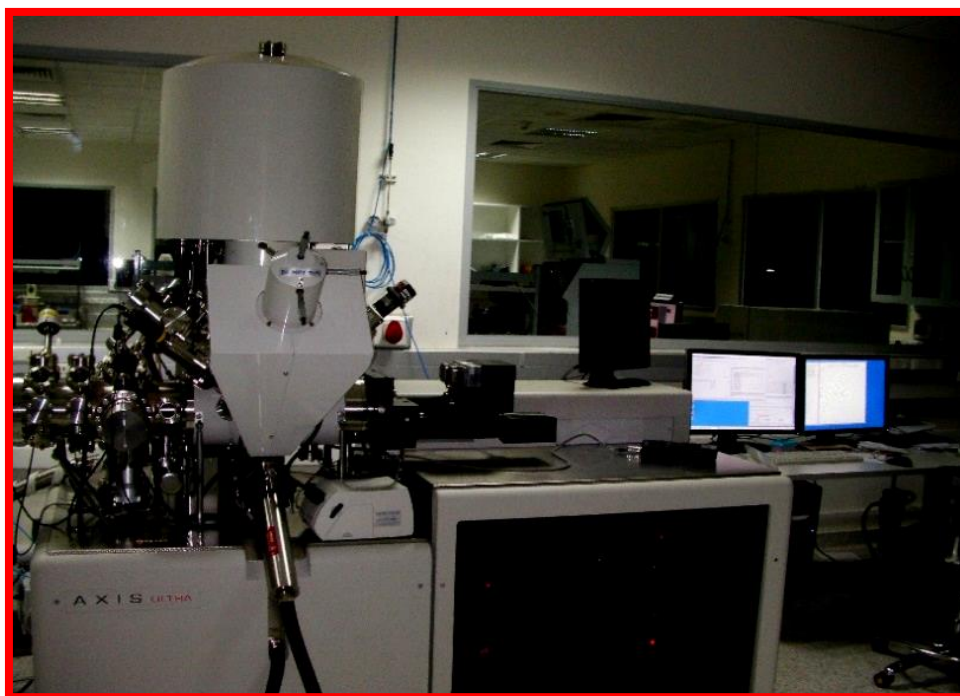


**Fig. 3.17. X-Ray Photoelectron Spectroscopy (XPS)**

### **3.9 Cleaning Procedure**

The modified and control surfaces were cleaned before each fouling experiment as per the CIP regime presented in Table 3.8. The cleaning solutions were circulated through the experimental set-up to clean the surfaces.

**Table 3.8 CIP programme used for cleaning**

| Steps in CIP                 | Concentration | Temperature (°C) | Time (min) |
|------------------------------|---------------|------------------|------------|
| Water rinse                  | —             | 65               | 10         |
| Nitric acid circulation      | 1.5%          | 65               | 20         |
| Water rinse                  | —             | 65               | 10         |
| Sodium hydroxide circulation | 1.5%          | 75               | 30         |
| Final rinse with soft water  | Soft water    | 35               | 10         |

### 3.10 Evaluation of Performance of the Developed PHE

#### 3.10.1 Effectiveness

The maximum heat transfer possible in a heat exchanger is given by the minimum heat capacity rates (mass flow rate multiplied by the specific heat) between the milk and the hot water, as given in Eqs. (3.22) and (3.23).

$$C_{\min} = \text{Min} (m_m C_m, m_w C_w) \quad (3.22)$$

$$Q_{\max} = C_{\min} (T_i - T_o) \quad (3.23)$$

where, ‘ $m_m$ ’ is the mass flow rate of milk, ‘ $C_m$ ’ is the specific heat of milk, ‘ $m_w$ ’ is the mass flow rate of water, ‘ $C_w$ ’ is the specific heat of water and ‘ $T_i$ ’, and ‘ $T_o$ ’ are the inlet and outlet temperatures of hot water and milk respectively.

The effectiveness ( $\epsilon$ ) of the PHE, defined as the closeness of heat transfer to the maximum heat transfer possible with given set of operational parameters and conditions, was calculated by using Eq. 3.24.

$$\epsilon = \frac{m c_p (T_{wi} - T_{wo})}{Q_{\max_{\text{hot}}}} = \frac{m c_p (T_{mo} - T_{mi})}{Q_{\max_{\text{cold}}}} \quad (3.24)$$

where, ‘ $m_m$ ’ is the mass flow rate of milk, ‘ $C_m$ ’ is the specific heat of milk, ‘ $m_w$ ’ is the mass flow rate of water, ‘ $C_w$ ’ is the specific heat of water and ‘ $T_i$ ’, and ‘ $T_o$ ’ are the inlet and outlet temperatures of hot water and milk respectively.

### 3.10.2 Overall heat transfer coefficient

The actual overall heat transfer coefficient (U) was determined by equating the heat gained by the process fluid with the rate of heat transfer by measuring the inlet and outlet temperatures of the process fluid and hot water. The actual U value (Eq. 3.26) was obtained by substitution and simplification of Eqs. (3.4) and (3.5).

$$Q_m = Q_r \quad (3.25)$$

$$U = \frac{C_m (T_{mi} - T_{mo}) \ln \left[ \frac{(T_{wi} - T_{mo})}{(T_{wo} - T_{mi})} \right]}{A (T_{wi} - T_{mo}) - (T_{wo} - T_{mi})} \quad (3.26)$$

### 3.10.3 Energy consumption

The mass flow rate and temperature of the water at inlet and outlet of PHE were noted at 10 min interval during the 8 h processing period of each run. The thermal energy consumption was calculated from mass flow rate, specific heat and drop in temperature of water, and was averaged over the run time (8 h). All the energy requiring components (milk pump, hot water pump and hot water generator) of the developed module basically run with electrical power. Hence, the overall electrical energy consumption of the unit was also measured using digital power monitor (Make: HTC Instruments, Mumbai; Model: PM03).

### 3.11 Statistical analysis

Statistical analysis was carried out using Statistical Package for the Social Sciences (SPSS) software (SPSS for Windows, ver.17, Chicago, IL, USA). Student's t-test was performed on each data set to determine statistical significance ( $p < 0.05$ ).

### 3.12 Pasteurization Efficiency Test

The pasteurization efficiency of milk was evaluated by using alkaline phosphatase activity test (BIS, 1977b). The test is an indicator for the presence or absence of alkaline phosphatase in the milk. The enzyme is destroyed by the same heat treatment necessary for the destruction of most of the heat resistant pathogens likely to be present in milk. When the heat treatment is lower than that specified above, some of the phosphatase remains active

and liberates para nitro phenol from disodium p-nitrophenyl phosphate in a buffered solution at pH 9.5. The presence of free p-nitrophenol was determined by Lovibond Comparator.

The standardized raw milk sample, subjected to heat treatment at 75°C, was analysed for pasteurization efficiency. Exactly 5 mL of buffer substrate was taken into a clean and dry test tube. 1 mL of the milk sample was added to the buffer. Then the test tube contents were mixed by inversion and placed in a water bath maintained at 37-38°C. Another test tube containing the same quantity of buffer substrate and 1 mL of boiled milk was placed in water bath (control). After 2 h, the tubes from the bath were taken out, inverted and the colour developed was read using the comparator and special disc. The tube which contained the boiled milk as control and the test sample were placed on the LHS and RHS of the stand, respectively. Readings were taken by looking down on to the two apertures with the comparator disc facing a good sunlight; the disc was revolved until the sample was matched; readings falling between two standards were recorded to the nearest reading. If the readings are between 0 and 10, then it is considered as properly pasteurized milk. If the reading is more than 10, then it is under pasteurized milk.



# CHAPTER - 4

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## RESULTS AND DISCUSSIONS

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## 4. RESULTS AND DISCUSSION

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This chapter details the coating of PTFE-TiO<sub>2</sub> on SS 316 PHE plate, interpretation of the experimental measurements of characterization of PTFE-TiO<sub>2</sub> coated surface and uncoated SS 316 surface, fouling experimentation using milk and paneer whey as process fluids and performance of the developed PHE module.

### 4.1 Design of PHE Module

The designing procedure of a plate heat exchanger was primarily aimed at achieving the processing capacity of 25 L/h. The heat duty for this capacity was calculated using Eq. (3.1) as 1.17 kW. Corresponding heat rejection from the heating medium (hot water), assuming a ratio of 1:3 between the milk and hot water flowrates was verified for possible range of temperature (83 to 73°C) using Eq. 3.2. The heat requirement fulfilled by the heat supply provided enough heat transfer area is available. The required heat transfer area was obtained by equating Eqs. 3.1 and 3.5. A plate width of 120 mm and a plate spacing of 2.5 mm were assumed for single channel per pass configuration for proposed capacity. Eq. 3.14 and 3.15 yielded channel velocity of 0.2 m/s resulting in the Reynolds number of 84.7. The empirical correlation (Eq. 3.9) recommended for  $Re \leq 400$  was applied using above estimated parameters and convective heat transfer coefficient for milk side was estimated to be 1113.05 W/m<sup>2</sup>K. Following the same steps and using the properties of water at respective temperatures, the convective heat transfer coefficient for water side was estimated to be 2066 W/m<sup>2</sup>K. Substituting the values of convective heat transfer on both the sides, thermal conductivity of plate (16.5 W/mK) and thickness of 0.5 mm in Eq. 3.7 produced the overall heat transfer coefficient of 707.83 W/m<sup>2</sup>K. The log mean temperature was calculated using Eq. 3.6 to be 19.57°C and the required minimum heat transfer area was 0.085 m<sup>2</sup>. The estimated area was held as the lower limit and nearest upper size of the plate (considering 3 plates) after applying an upper margin of 20%, available in the market was chosen.

The height of the feed tank was fixed as 481 mm and its inner diameter was fixed as 376 mm to get the height to diameter ratio of nearly 1 after application of insulation along with external SS cladding. The thickness of mineral wool insulation was estimated as 20 mm and was applied to the cylindrical wall and bottom of the feed tank.

The capacity of the hot water generator was estimated considering the heat demand of raising the temperature of required quantity of water from room temperature to nearly 85°C and then for making up the heat loss was calculated by Eq. 3.2. The required heating power was found to be around 1.8 kW. Considering heat loss and a safety margin, an induction heater coil of 2.0 kW was selected as primary heat source in the hot water generator. The coil was placed in a cylindrical SS housing having a height of 139 mm and diameter of 274 mm. A cylindrical vessel for water was designed with a base compatible for induction heating was placed above the heating coil housing. The water vessel had the same diameter (274 mm) and 236 mm height to hold 10 L water. The hot water generator including heating coil housing, water vessel, insulation with cladding and lid together had a height of 425 mm, which was insulated by 20 mm thick layer of mineral wool insulation covered externally with a stainless steel cladding. A mechanical type thermostat was provided to the hot water generator for close temperature control.

#### **4.2 Fabrication of the PHE Module**

The skid mounted PHE module comprising two identical PHEs, one of which was fitted with uncoated SS 316 plates and another with PTFE-TiO<sub>2</sub> coated plates, feed tank, hot water generator, pumps, pipe network and process control loop was fabricated as described in Section 3.2.2. All the fabrication operations were performed as per the principles of hygienic design of equipment. A view of the fabricated PHE module is as shown in Fig. 4.1.

#### **4.3 Selection of PTFE-TiO<sub>2</sub> Coating for SS 316 PHE Plate**

The coating proportion (PTFE:TiO<sub>2</sub>) and thickness were selected based on the thermal conductivity of the coated disc.

##### **4.3.1 Thermal conductivity**

Thermal conductivities of PTFE-TiO<sub>2</sub> coated SS 316 discs were measured using thermal conductivity meter. PTFE is a semi-crystalline polymer and its heat transfer depends upon the vibration of the crystal lattice. It is also a good coating material, but possess inherently low thermal conductivity because of phonon scattering at the boundary of the lamellar crystal and intermolecular amorphous region in the polymer (Chen *et al.*, 2016). Generally, the thermal conductivity of a polymer coated surface is reported to be lower as compared to the uncoated metal substrate, because of the inherently low thermal conductivity

of polymers as compared to metals. It is one of the major drawbacks of nano-coating over heat transfer surfaces. Thus, to enhance the thermal conductivity of the polymer coating material (PTFE), filler material ( $\text{TiO}_2$ ) at different ratios was 88:12, 86:14, 84:16 incorporated. It was observed that as the amount of filler material increased, the thermal conductivity of the coating material also increased (Table 4.1). The highest thermal conductivity was observed for 20  $\mu\text{m}$  coating thickness with 84:16 (PTFE:  $\text{TiO}_2$ ) as 0.281 W/mK. This combination of coating thickness and coating ratio was selected for the final coating over the SS 316 PHE plate surfaces.

**Table 4.1 Thermal conductivity of discs coated with PTFE- $\text{TiO}_2$**

| Coating Thickness ( $\mu\text{m}$ ) | Coating ratio (PTFE: $\text{TiO}_2$ ) |       |       |
|-------------------------------------|---------------------------------------|-------|-------|
|                                     | 88:12                                 | 86:14 | 84:16 |
|                                     | Thermal conductivity (W/mK)           |       |       |
| 10                                  | 0.177                                 | 0.186 | 0.278 |
| 20                                  | 0.179                                 | 0.202 | 0.281 |
| 30                                  | 0.155                                 | 0.150 | 0.167 |

#### 4.3.2 Adhesion strength

The adhesion strength of the (PTFE- $\text{TiO}_2$ ) coating was measured by a cross-cut tape test method and the resultant surface is shown in Fig.4.2. It can be seen that the edges of the cuts were completely smooth and there was no sign of detachment of any squares from the lattice. These observations confirmed to rating 5 of the standard test B (ASTM: D3359, 1997) suggest strong adhesion strength between the PTFE- $\text{TiO}_2$  coating and the SS 316 substrate. Similar observation was noted by Horkavcova *et al.* (2008) while testing the adhesion of bioactive layer of dried gel  $\text{Na-TiO}_x \cdot n\text{H}_2\text{O}$  on titanium alloy substrate and by Lakshmi and Aruna (2017) for silica-titania hybrid coatings embedded with silica nanoparticles on aluminium alloy (AA2024-T3) and the respective coatings were rated as 5B. Xu *et al.* (2010) also used the same technique to confirm the adhesion of superhydrophobic coating.

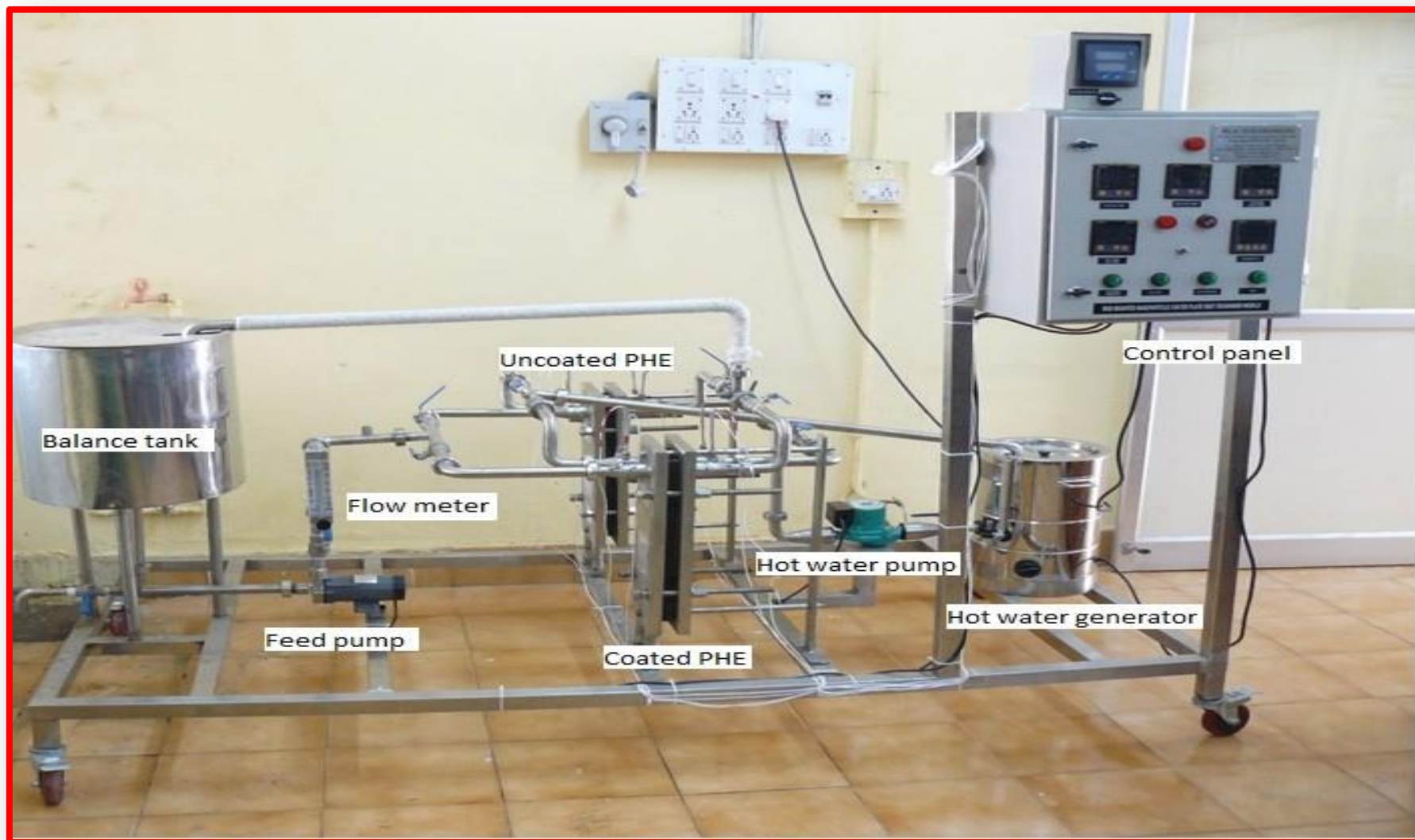


**Fig. 4.1 Skid Mounted PHE Module**

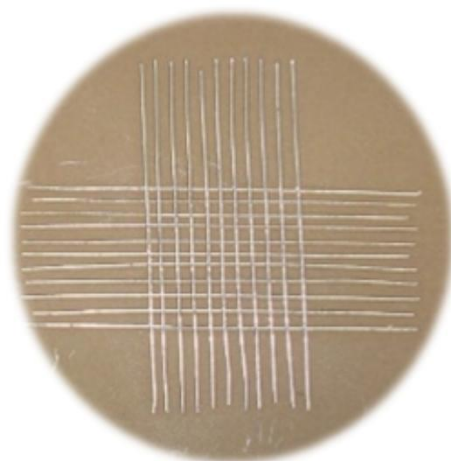


**Fig.4.2 Cross-Cut Tape Test of PTFE-TiO<sub>2</sub> Coated Surface**

#### **4.3.3 PTFE-TiO<sub>2</sub> Coating Application on SS 316 PHE Plate**

The thickness of coating as 20  $\mu\text{m}$  and coating ratio (PTFE: TiO<sub>2</sub>) of 84:16 were selected for final coating over the SS 316 PHE plate surfaces. The native SS 316 plates were sand blasted followed by coating application using spray coating technique. The sandblasting produced visually rough surface favourable for coating application. The photographs of the SS 316 (uncoated), sand blasted and PTFE-TiO<sub>2</sub> coated plate are shown in Fig. 4.3 (a, b & c).

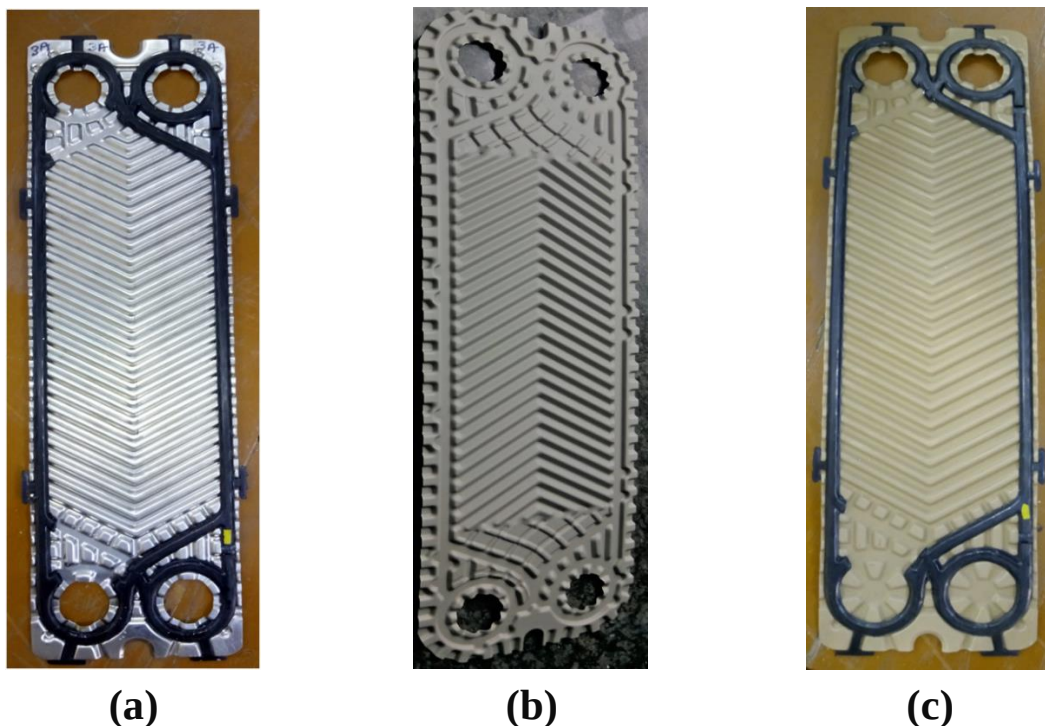


**Fig.4.3 Visual change in the appearance of the surface of the (a) native SS 316 (b) sand blasted (c) PTFE-TiO<sub>2</sub> coated plates**

#### 4.4 Characterization of Uncoated (SS 316) and Coated (PTFE-TiO<sub>2</sub>) Surface

The surface morphology, elemental composition, microstructure, wettability, roughness and topography were studied for uncoated (SS 316) and coated surface (PTFE-TiO<sub>2</sub>) by using different techniques. The salient findings are discussed below along with possible reasons and indications thereof.

##### 4.4.1 Surface roughness by optical profilometer

The roughness of the uncoated SS 316 and PTFE-TiO<sub>2</sub> coated surfaces was measured by optical profilometer and the results are presented in Table 4.2 and Fig. 4.4 and 4.5. It was observed that the average roughness value ( $R_a$ ) for SS 316 uncoated surface ( $1.67 \times 1.67 \text{ mm}^2$ ) measured at different locations was  $0.20 \pm 0.02 \text{ }\mu\text{m}$  whereas for PTFE-TiO<sub>2</sub> coated surface, it was  $0.74 \pm 0.09 \text{ }\mu\text{m}$ . It is quite clear from observed data that the surface roughness of the coated surface was more than the SS 316 uncoated surface.

**Table 4.2 Roughness/Textural parameters of uncoated and coated surfaces**

| <b>Amplitude Parameters-Roughness profile (<math>\mu\text{m}</math>)</b> | <b>SS 316<br/>(Uncoated)</b> | <b>PTFE-TiO<sub>2</sub><br/>(Coated)</b> |
|--------------------------------------------------------------------------|------------------------------|------------------------------------------|
| $R_p$ : Maximum profile peak height                                      | $0.56 \pm 0.07$              | $2.33 \pm 0.38$                          |
| $R_v$ : Maximum profile valley depth                                     | $1.95 \pm 0.13$              | $3.12 \pm 0.36$                          |
| $R_z$ :Maximum peak to valley height                                     | $2.50 \pm 0.18$              | $5.45 \pm 0.64$                          |
| $R_c$ :Mean height                                                       | $0.69 \pm 0.07$              | $2.22 \pm 0.29$                          |
| $R_t$ :Total height                                                      | $2.59 \pm 0.19$              | $5.54 \pm 0.63$                          |
| $R_a$ :Arithmetic mean deviation                                         | $0.20 \pm 0.02$              | $0.74 \pm 0.09$                          |
| $R_q$ :Root-mean-square deviation                                        | $0.33 \pm 0.03$              | $1.12 \pm 0.12$                          |
| $R_{sk}$ :Skewness                                                       | $-2.83 \pm 0.20$             | $-0.5 \pm 0.31$                          |
| $R_{ku}$ : Kurtosis                                                      | $15.36 \pm 1.58$             | $3.63 \pm 0.38$                          |
| <b>Material Ratio parameters - Roughness profile</b>                     | <b>SS 316</b>                | <b>PTFE-TiO<sub>2</sub></b>              |
| $R_{mr}(\%)$ : Relative material ratio                                   | $91.56 \pm 1.64$             | $10.67 \pm 4.06$                         |
| $R_{dc}$ : Profile section height                                        | $0.26 \pm 0.04$              | $10.51 \pm 0.18$                         |

Both the SS 316 and PTFE-TiO<sub>2</sub> surfaces could fulfill the criteria of roughness ( $R_a$ ) less than 0.8  $\mu\text{m}$  for food contact surfaces to be hygienic as suggested by Flint *et al.* (1997). It could be noted that the PTFE-TiO<sub>2</sub> coating significantly modified the surface roughness which would be helpful in reducing the fouling deposition during thermal processing of milk/paneer whey. The various amplitude and roughness ratio parameters for both the coated and uncoated surfaces are presented in Table 4.2. Roughness alone will not determine the hydrophilic or hydrophobic surface, will be the surface material characteristic.

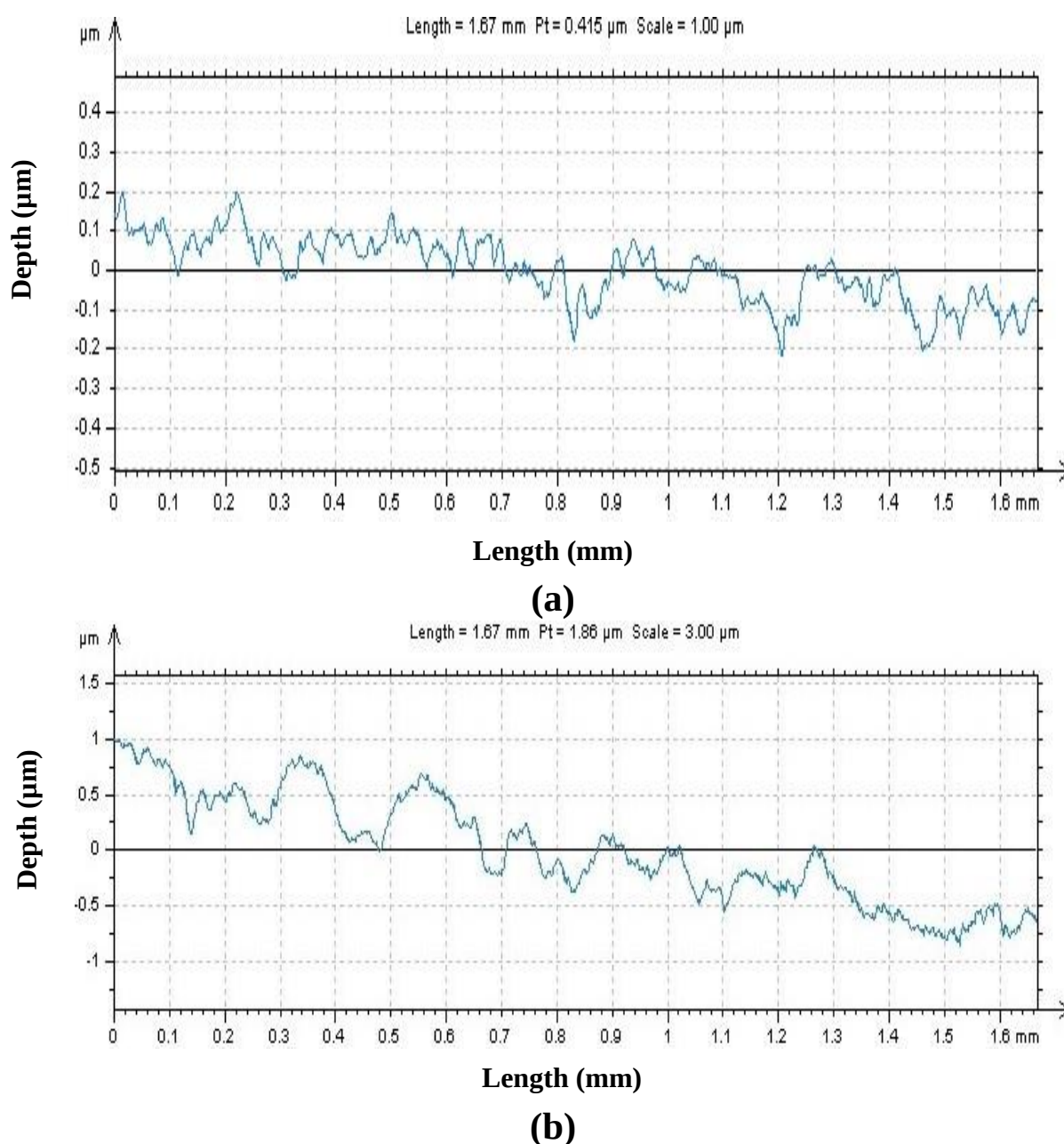
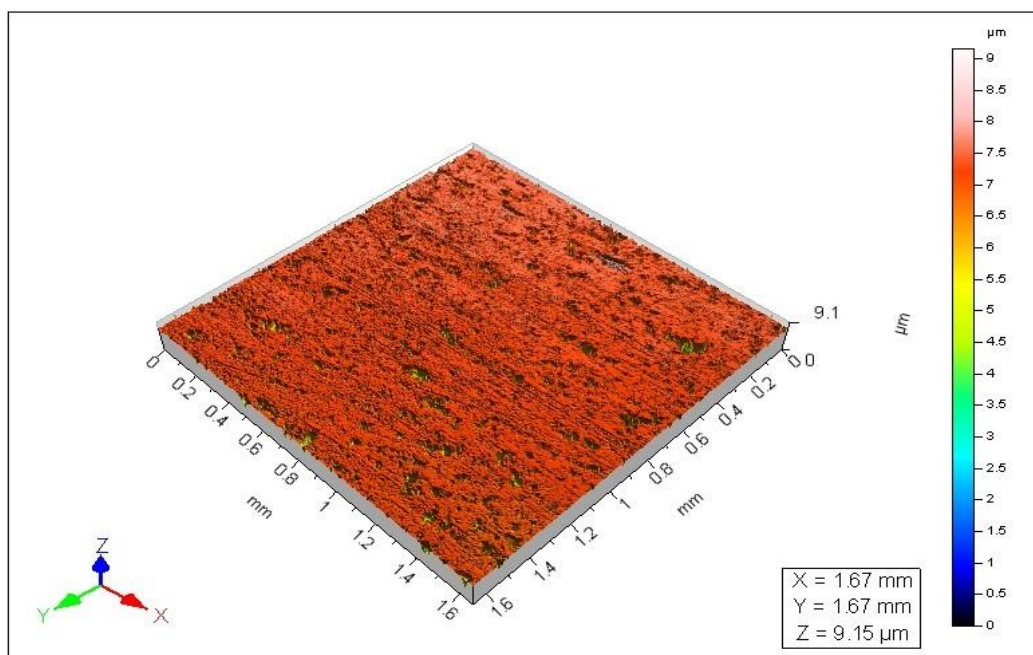
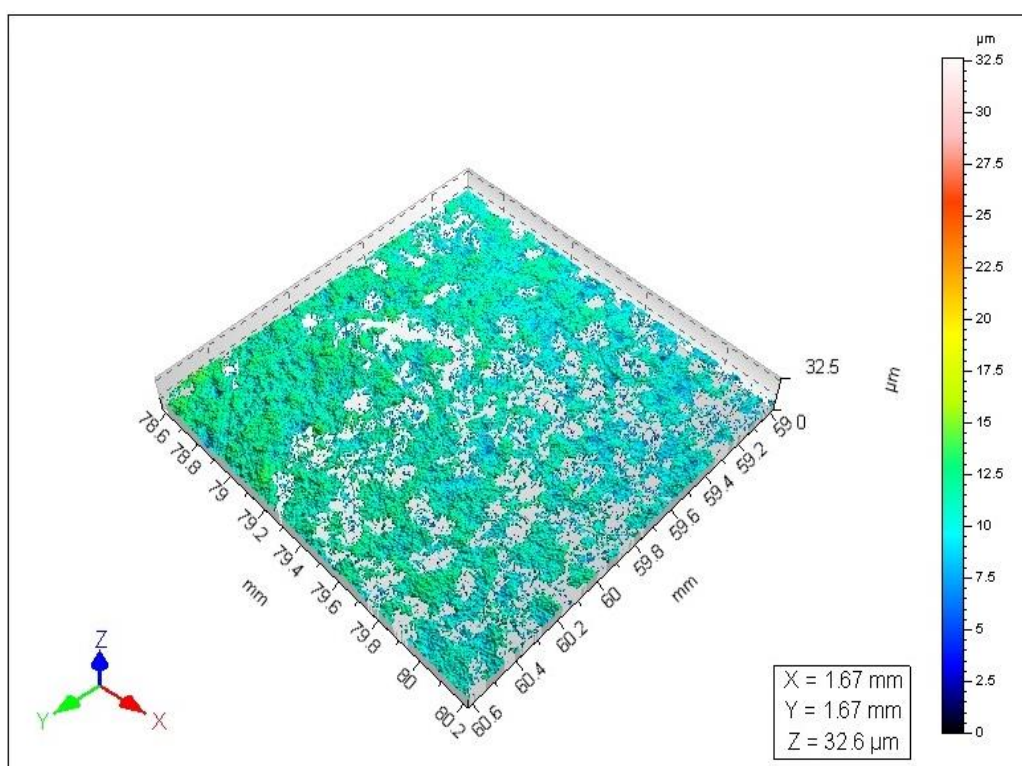


**Fig. 4.4. Roughness profile of (a) SS 316 and (b) coated with PTFE-TiO<sub>2</sub> surfaces**



(a)



(b)

**Fig. 4.5 3D Roughness profile of (a) SS 316 and (b) coated with PTFE-TiO<sub>2</sub> surfaces**

#### 4.4.2 Contact angle

Fig 4.6 (a-f) shows the images of droplets captured by the contact angle meter and used for the contact angle measurements on the SS 316 uncoated and PTFE-TiO<sub>2</sub> coated surfaces for distilled water, milk and paneer whey. The measured values of contact angle for SS 316 uncoated and PTFE-TiO<sub>2</sub> coated surfaces for distilled water were  $66.8 \pm 6.3^\circ$  and  $112.8 \pm 0.8^\circ$ , whereas for milk the values were  $61 \pm 6.1^\circ$  and  $97.5 \pm 1.1^\circ$ , respectively. The paneer whey showed the contact angles of  $82.44 \pm 2.11^\circ$  and  $103.8 \pm 1.03^\circ$  for SS 316 and PTFE-TiO<sub>2</sub> coated surfaces, respectively. According to the classification made by Marmur (2012), the PTFE-TiO<sub>2</sub> coated surfaces were designated as hydrophobic surface. The PTFE-TiO<sub>2</sub> coatings on the SS 316 surface significantly enhanced the contact angle values for all the three liquids studied i.e. water, milk and paneer whey. This ultimately would help to reduce the interaction between the fluid and the coated surface, thereby reduce the extent of fouling deposition during thermal processing. Enhanced contact angle values improved the hydrophobicity of the coated surface as compared to the uncoated SS 316 surface, which further facilitated in ease of removal of fouling deposits. It was also observed that contact angle for milk was lesser than that of paneer whey for both types of the surfaces. It could be due to the lower surface tension values of milk ( $51.19 \pm 0.34$  mN/m) and paneer whey ( $49.45 \pm 1.78$  mN/m) as compared to water (72 mN/m). Adhikari *et al.* (2001) stated that lower the contact angle of liquid on a solid surface, stronger the attraction and greater the forces required to separate these surfaces. Thus, the milk would be attracted and bound to the SS 316 uncoated and PTFE-TiO<sub>2</sub> coated surfaces more strongly than paneer whey. The removal of paneer whey deposits would be easier when compared to that of milk. Uncoated stainless steel materials used in industries are inherently hydrophilic in nature, which possess lower contact angle for water ( $<90^\circ$ ), facilitating greater degree of wetting, while PTFE-TiO<sub>2</sub> coated SS 316 surfaces were hydrophobic to facilitate lesser degree of wetting by the processed fluids. The contact angles for water obtained in this study on SS 316 and TiO<sub>2</sub>-PTFE coated surface were very close to the values reported by Zhang *et al.* (2019), which were  $68.8 \pm 0.4^\circ$  and  $92.7 \pm 1.7^\circ$ , respectively. The contact angle for milk on SS 316 was also on par with the reported values of  $69.6^\circ$  by Kananah *et al.* (2009). The work of adhesion for water, milk and paneer whey was 100.36, 75.54 and 55.95 mN/m on SS 316 surface, whereas it was 44.10, 44.50 and 37.65 mN/m on PTFE-TiO<sub>2</sub> coated surface, respectively. The work of adhesion of fluids on the PTFE-TiO<sub>2</sub> coated surface was significantly lesser than that on the uncoated

surface indicating weaker bonding because of the PTFE-TiO<sub>2</sub> coating application. Miwa *et al.* (2000) suggested that contact angle of greater than 150° on any solid surface indicates a super hydrophobic surface. The results indicated that PTFE-TiO<sub>2</sub> coating on the SS 316 surface did not improve the contact angles to such extent to induce super hydrophobicity in the surface but it modified the surface characteristics to hydrophobicity.

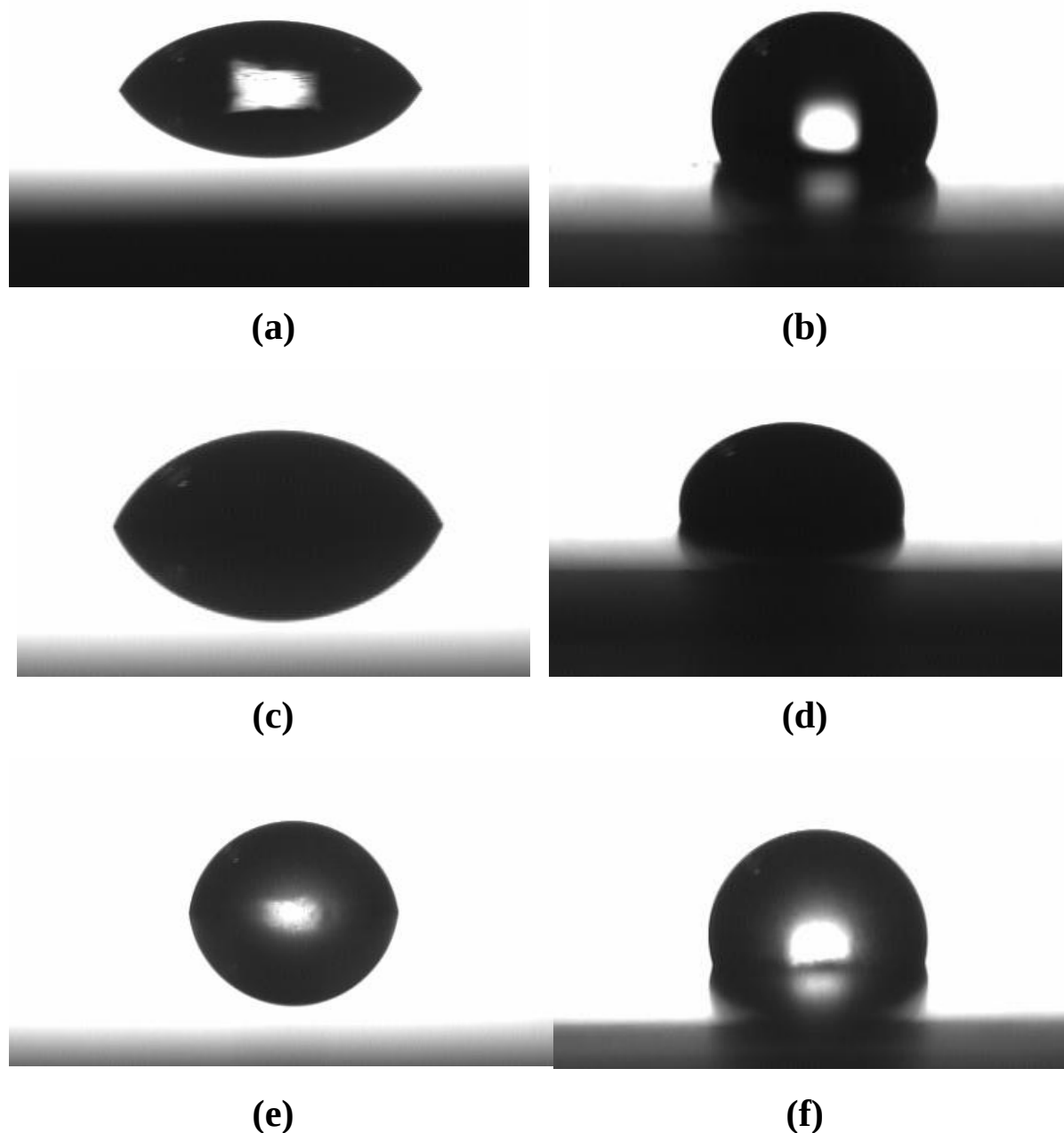


**Fig. 4.6** Contact angle for (a) water on SS 316 (b) water on PTFE-TiO<sub>2</sub> coated (c) milk on SS 316 (d) milk on PTFE-TiO<sub>2</sub> coated (e) paneer whey on SS 316 and (f) paneer whey on PTFE-TiO<sub>2</sub> coated surfaces

#### 4.4.3 X-Ray Diffractometric Analysis (XRD)

The X-ray diffraction pattern of SS 316 and PTFE-TiO<sub>2</sub> coated surfaces is shown in Fig. 4.7. From the diffractogram of SS 316 surface, the diffraction peaks at approximately  $2\theta = 44.11^\circ$ ,  $51.37^\circ$  and  $75.61^\circ$  correspond to (111), (200) and (220) crystal planes, respectively were observed. These peaks were in accordance with the positions reported by Totten *et al.* (2011). SS 316 crystallized in cubic structure with lattice parameter of 3.783 Å. Peak shifts observed in the coated surface with intense peaks at  $18.10^\circ$  and  $25.24^\circ$  corresponded to PTFE and TiO<sub>2</sub>, respectively. The peaks for PTFE and TiO<sub>2</sub> were confirmed with the reported values of d'Amorim *et al.* (2013) and Castro *et al.* (2017), respectively. The observed inter-planar spacing between atoms (d-spacing) was in good agreement with the standard values with ICDD No. 01-086-1157 for TiO<sub>2</sub> anatase and 00-047-2217 for PTFE. The crystallite size ranged from 56.25 to 135.51 nm with an average of 82.35 nm on SS 316 surface, whereas it ranged from 4.19 to 173.10 nm with an average of 49.62 nm for the PTFE-TiO<sub>2</sub> coated surface. SEM observations also confirmed that the size of particles was in good agreement with the XRD results.

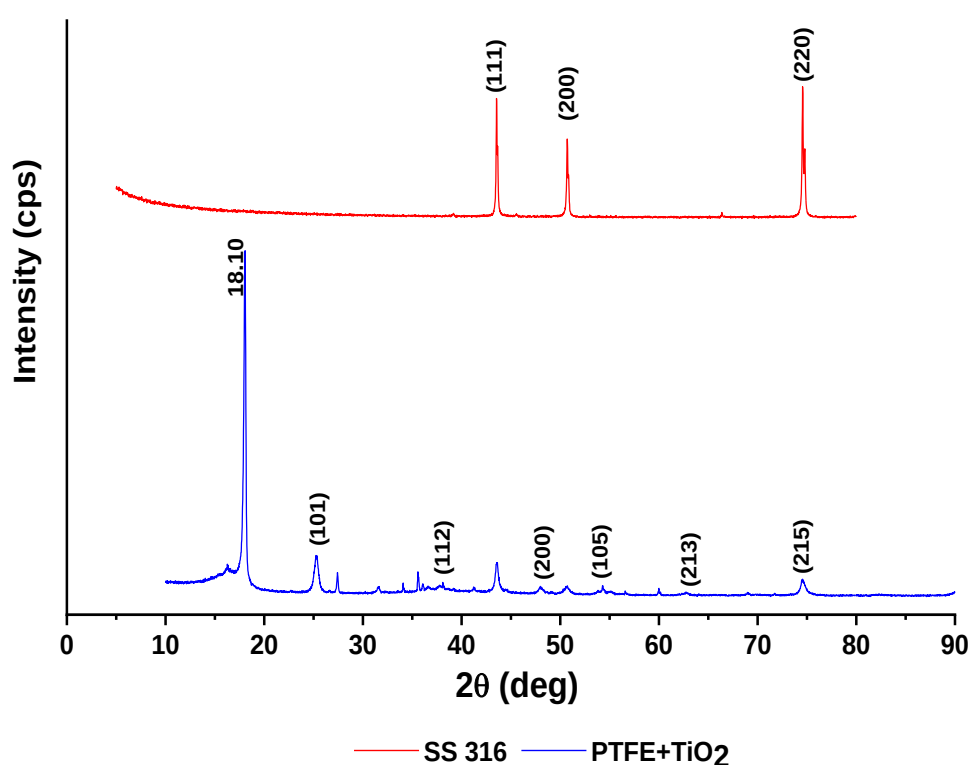
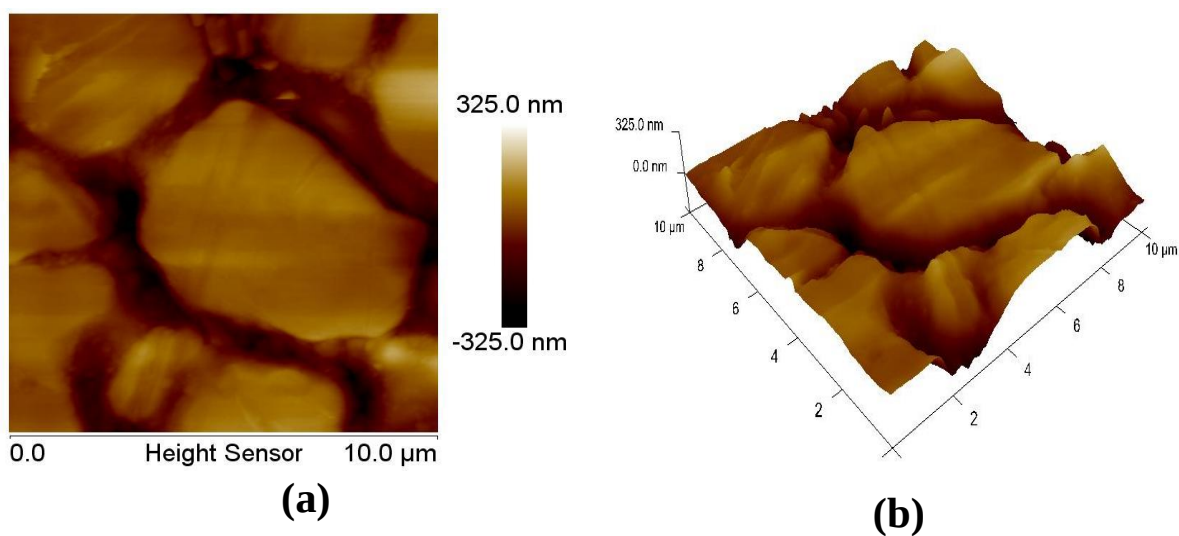


Fig. 4.7 X-Ray diffractogram of SS 316 and PTFE-TiO<sub>2</sub> coated surfaces

#### 4.4.4 Atomic Force Microscopic Analysis (AFM)

Atomic force microscopic (AFM) analysis for SS 316 uncoated and PTFE-TiO<sub>2</sub> coated surfaces are depicted in Fig. 4.7. The uncoated SS 316 surface showed an average surface roughness of 65.5 nm, owing to the typical surface micro cracks clearly visible in Fig 4.8 (a & b) which resulted in a relatively higher roughness when compared to the coated surface. These images were supported by the SEM images for uncoated SS 316 surface. Roughness is an important parameter while designing an antifouling surface. de Jong (1997) expressed that rough surface promoted higher degree of adhesion of the fouling deposits. Upon coating with PTFE-TiO<sub>2</sub> composite over SS 316 surface, further smoothing of the surfaces was observed (Fig. 4.8 c & d). The surface roughness value of the PTFE-TiO<sub>2</sub> coated surface was found to be 33.9 nm.

The surface roughness obtained by AFM was not comparable to the surface roughness ( $R_a$ ) obtained using the optical profilometer. This disagreement might be because of the difference of their spatial frequencies and area covered in X-Y plane. The AFM covered an area of  $10 \times 10 \mu\text{m}^2$  whereas the profilometer covered  $1.67 \times 1.67 \text{ mm}^2$ . Further, the non homogeneity of the surface composition (coating composition) and shiny surface may distract the optical measurement of profilometer. The AFM was found to be more reliable in nanoscale by Verran *et al.* (2000) for measurement of the surface roughness of the stainless steel surface.



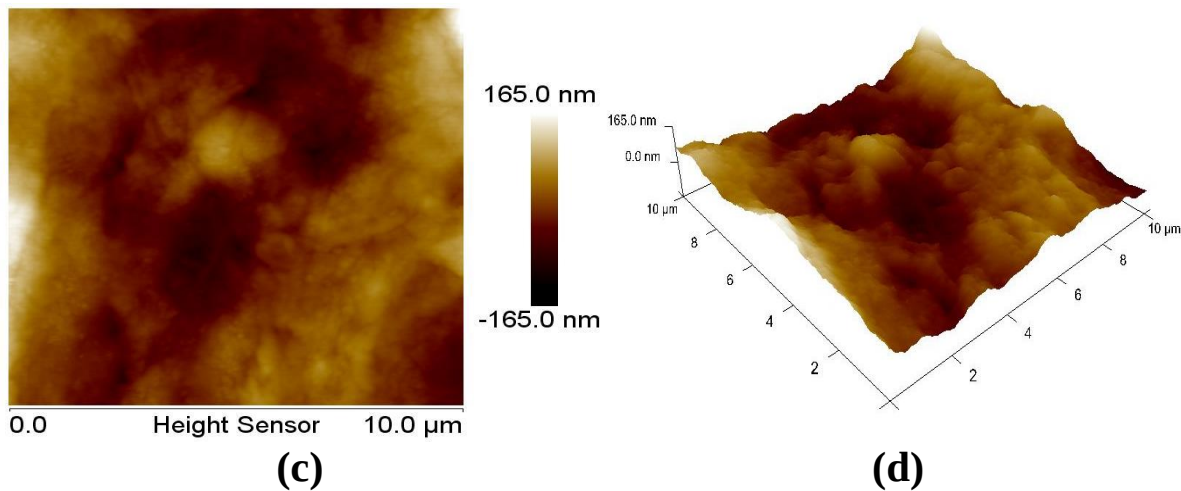


**Fig.4.8 AFM Images of (a) SS 316 2D view (b) SS 316 2D view (c) PTFE-TiO<sub>2</sub> coated surface 2D view and (d) PTFE-TiO<sub>2</sub> coated surface 3D view**

#### 4.4.5 SEM analysis

The surface morphology of uncoated SS 316 plain (Fig. 4.9 a & b) and PTFE-TiO<sub>2</sub> coated SS 316 substrates (Fig. 4.9 c & d) was examined by SEM. It was observed from the images obtained at higher magnification (Fig. 4.9 b) that the uncoated SS 316 plate surface exhibited heterogeneous surface with uneven cracks. Similar observation was made by Santos *et al.* (2004) and Barish and Goddard (2013). On the contrary, the images of the surface coated with composite (PTFE-TiO<sub>2</sub>) on the SS 316 surface were free from cracks (Fig. 4.9 c). This could be due to the uniform application of coating materials on the SS 316 substrate. It is seen from the Fig. 4.8 d, that the nanosize bumps could be due to the uniformly distributed aggregates of TiO<sub>2</sub> nanomaterial. The mean particle diameter of TiO<sub>2</sub> nanoparticles ranged from 62 to 85 nm, which was further supported by AFM results. Barish and Goddard (2013) indicated higher level of micro-cracks with separate boundaries in SS 316, whereas the EN-PTFE-SS316 presented a surface with uniformly dispersed nanoparticles and no evident of surface cracks. Similarly, Basu and Kumar (2011) reported that the PTFE-HMS composite coatings were free from cracks and had a lotus-leaf-like microstructure with microscale bumps and clusters.

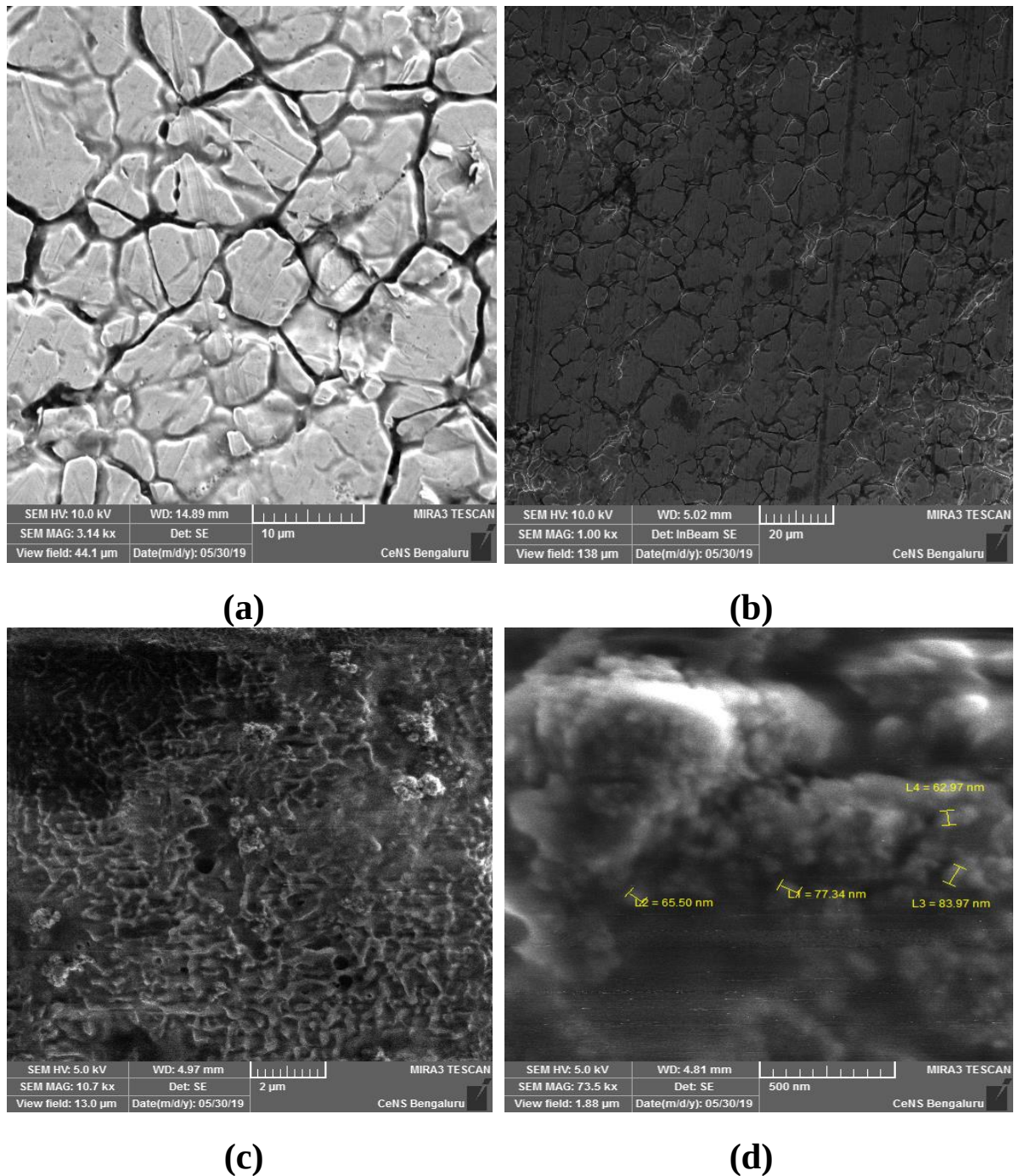


**Fig. 4.9 SEM images of (a) & (b) SS 316 plain surface (c) & (d) surface coated with PTFE-TiO<sub>2</sub>**

#### 4.4.6 SEM-EDS analysis

The elemental composition of SS 316 and PTFE-TiO<sub>2</sub> coated surface measured using SEM-EDS technique is shown in Fig. 4.10 (a & b). The major elements on the coated surface were titanium, carbon, fluorine, iron and oxygen. The SEM-EDS analyses revealed that the coated composite was distributed over entire surface of the substrate (SS

316) as observed in SEM images also. The surface elemental composition of SS 316 uncoated and PTFE -TiO<sub>2</sub> coated surfaces is presented in Table 4.3. It was observed that 65.42 and 6.31% by weight of the surface constituent in the coated surface was fluorine and titanium, which had come from PTFE and TiO<sub>2</sub> nanoparticles, respectively.

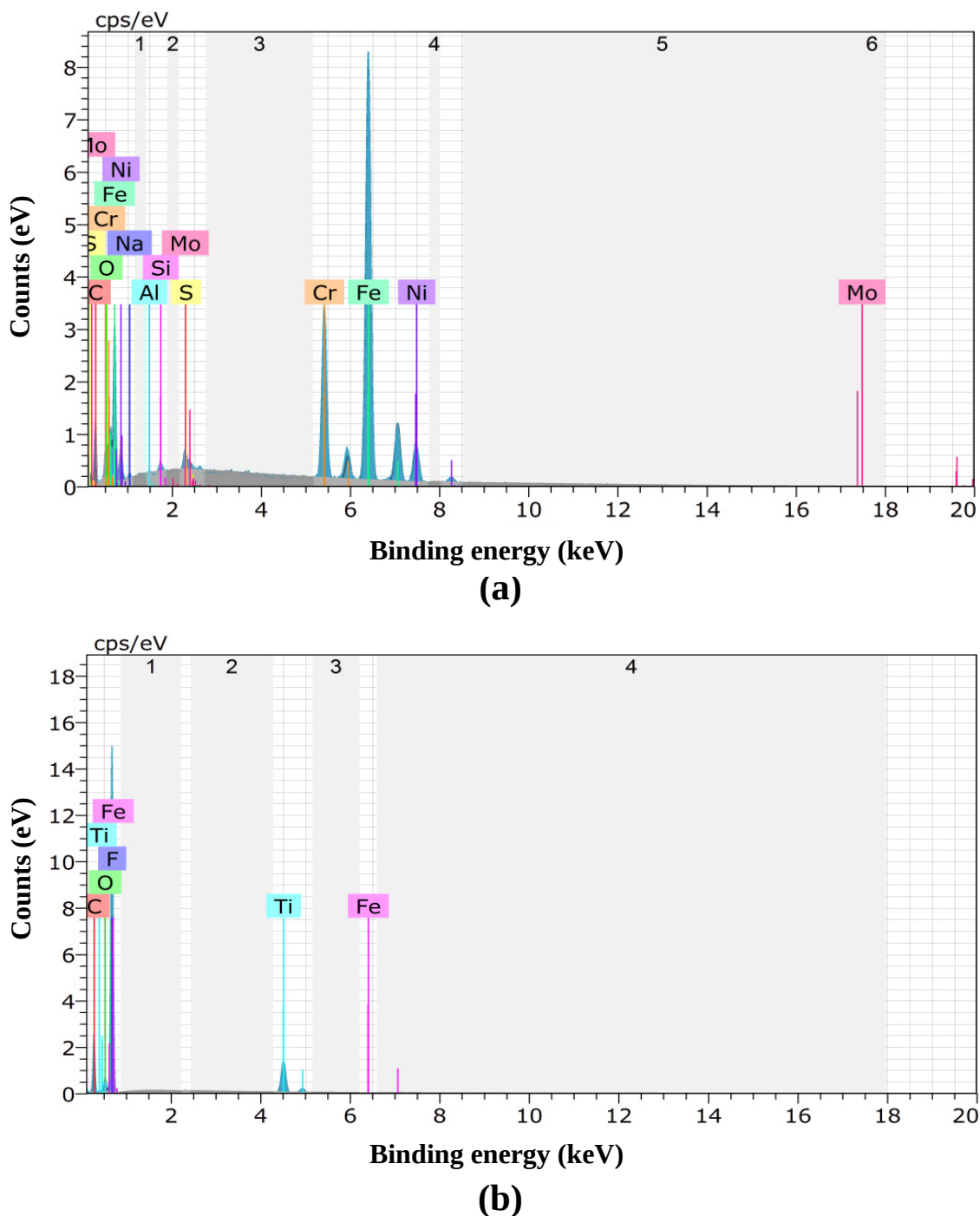


**Fig 4.10 EDS spectra of (a) SS 316 surface and (b) surface coated with PTFE-TiO<sub>2</sub>**

Zhang *et al.* (2019) reported similar findings when stainless steel was coated with the PTFE and TiO<sub>2</sub> nanoparticles. The presence of chromium in the EDS spectra could be due to the exposure of stainless steel surface because of non-uniform coating. In our study, chromium was not found in the coated surface confirming the uniform coating of the PTFE-TiO<sub>2</sub> on the SS 316 surface.

**Table 4.3 Elemental composition of SS 316 and PTFE-TiO<sub>2</sub> coated surfaces**

| Elements   | SS 316 surface |         | PTFE-TiO <sub>2</sub> coated surface |         |
|------------|----------------|---------|--------------------------------------|---------|
|            | Wt. %          | Atom. % | Wt. %                                | Atom. % |
| Carbon     | 5.97           | 22.00   | 23.03                                | 33.03   |
| Oxygen     | 1.38           | 3.83    | 4.58                                 | 4.53    |
| Sodium     | 0.40           | 0.76    | 0.40                                 | 0.76    |
| Aluminum   | 0.12           | 0.20    | -                                    | -       |
| Silicon    | 0.36           | 0.58    | -                                    | -       |
| Chromium   | 14.74          | 12.54   | -                                    | -       |
| Iron       | 65.45          | 51.87   | 0.26                                 | 0.08    |
| Nickel     | 9.82           | 7.41    | -                                    | -       |
| Molybdenum | 1.76           | 0.81    | -                                    | -       |
| Fluorine   | -              | -       | 65.42                                | 59.34   |
| Titanium   | -              | -       | 6.31                                 | 2.26    |

#### 4.5 Physical Properties of Milk and Paneer Whey

The physical properties of the milk and water at mean temperature at an interval of 10 min during the experimental trials were required for the purpose of calculations. The estimated values along with the mean temperature are given in Tables 4.4 and 4.5. Additionally, select compositional properties and the surface tension of milk and paneer whey was determined for the purpose of calculating the work of adhesion of these liquids with uncoated SS 316 and PTFE-TiO<sub>2</sub> coated surfaces. The mean values are shown in Table 4.6.

**Table 4.4 Physical properties of milk**

| Run | Mean temperature (°C) | Specific gravity | Specific heat (J/kg°C) | Dynamic viscosity (mPa.s) | Thermal conductivity ( $\times 10^{-2}$ W/mK) |
|-----|-----------------------|------------------|------------------------|---------------------------|-----------------------------------------------|
| 1   | 61.72                 | 1.0011           | 3870.74                | 0.78                      | 60.517                                        |
| 2   | 60.51                 | 0.9958           | 3870.26                | 0.80                      | 60.419                                        |
| 3   | 70.24                 | 0.9925           | 3874.21                | 1.08                      | 61.026                                        |
| 4   | 69.25                 | 0.9973           | 3873.50                | 0.72                      | 60.953                                        |
| 5   | 67.78                 | 0.9987           | 3872.62                | 0.73                      | 60.855                                        |
| 6   | 67.26                 | 0.9936           | 3875.61                | 0.69                      | 61.171                                        |
| 7   | 70.16                 | 0.9962           | 3874.13                | 0.71                      | 61.018                                        |

Each value of the property is the mean of 48 readings taken at interval of 10 min during the experimental runs of 8 h each

**Table 4.5 Physical properties of water**

| Run | Mean temperature (°C) | Specific gravity | Specific heat (J/kg°C) | Dynamic viscosity (mPa.s) | Thermal conductivity ( $\times 10^{-2}$ W/mK) |
|-----|-----------------------|------------------|------------------------|---------------------------|-----------------------------------------------|
| 1   | 78.95                 | 0.97             | 4176.12                | 1.00                      | 66.843                                        |
| 2   | 79.26                 | 0.97             | 4203.62                | 1.00                      | 66.866                                        |
| 3   | 80.83                 | 0.97             | 4204.11                | 1.00                      | 66.973                                        |
| 4   | 79.61                 | 0.97             | 4176.12                | 1.00                      | 66.889                                        |
| 5   | 78.56                 | 0.97             | 4176.12                | 1.00                      | 66.814                                        |
| 6   | 80.86                 | 0.97             | 4176.12                | 1.00                      | 66.975                                        |
| 7   | 80.62                 | 0.97             | 4176.12                | 1.00                      | 66.957                                        |

Each value of the property is the mean of 48 readings taken at interval of 10 min during the experimental runs of 8 h each

**Table 4.6 Composition and surface tension of milk and paneer whey**

| Properties                    | Milk       | Paneer whey |
|-------------------------------|------------|-------------|
| Fat content (%)               | 3.0±0.34   | --          |
| SNF content (%)               | 8.5±0.11   | --          |
| Total solids (%)              | 11.5±0.37  | 6.1±0.27    |
| Titrateable acidity (% L. A.) | 0.16±0.02  | 0.43±0.12   |
| Surface tension (mN/m)        | 51.19±0.34 | 49.45±1.78  |

Each value is the mean of 5 readings

#### **4.6 Visual Inspection of Fouling Deposition**

The experimental setup was tested for fouling deposition on SS 316 uncoated and PTFE-TiO<sub>2</sub> coated surfaces by processing of milk and paneer whey up to pasteurization temperature at constant flow rate of 25 L/h using hot water as heating medium. After processing for 8 h, the plates were dismantled and observed visually. As seen from the Fig.4.11, the uncoated SS 316 plate gathered more deposition than coated PTFE-TiO<sub>2</sub>. The deposition on both the coated and uncoated plates was white in colour, soft and apparently spongy. The foulants deposited on SS 316 plate were found to be densely spaced, almost as a layer and adhered strongly to the surface. In contrast, on PTFE-TiO<sub>2</sub> coated plate the foulant was sparsely spaced and adhered loosely to the surface. Similar observation was noticed by Balasubramanian and Puri (2008), while using Ni-P-PTFE coated surfaces for whey pasteurization (75-77°C) for a duration of 8 h continuously.

#### **4.7 Thermal Performance of PHE Module**

The thermal performance of PHE with coated surfaces (plates) in comparison to uncoated surfaces during heat treatment of milk and paneer whey as evaluated in terms of fouling deposition and overall heat transfer coefficients is discussed below.

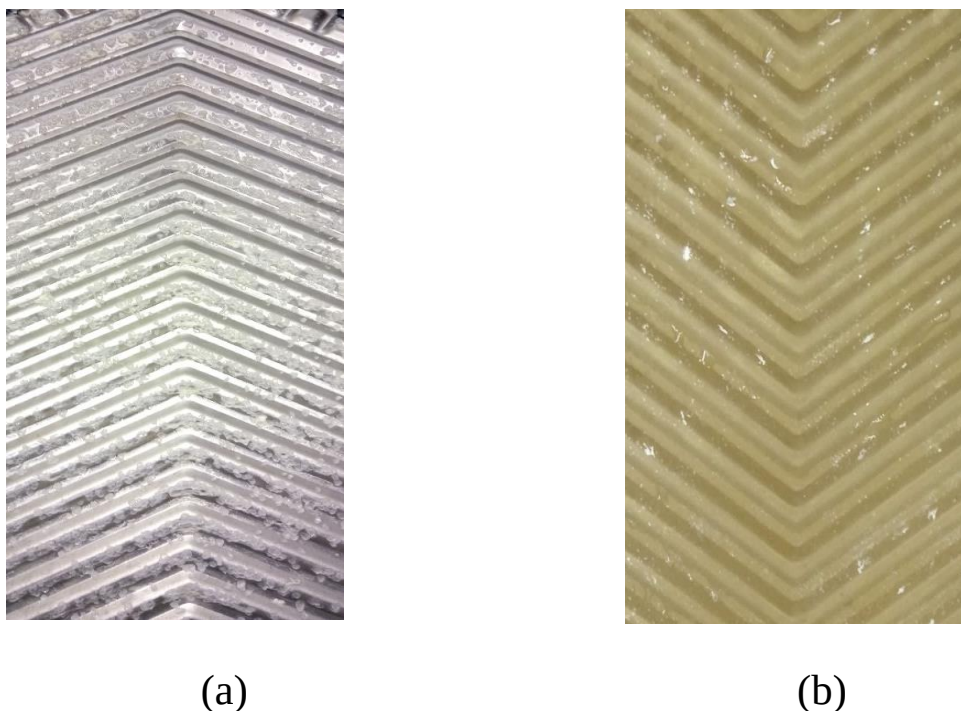


**Fig. 4.11 Fouling deposition on (a) SS 316 uncoated and (b) PTFE-TiO<sub>2</sub> coated surfaces**

#### **4.7.1 Overall heat transfer coefficient during heat treatment of milk**

The overall heat transfer coefficients computed during heat treatment of milk using PHEs with uncoated and coated surfaces are shown in Table 4.7 and Fig. 4.12. Table 4.7 displays the mean values of overall heat transfer coefficients for the complete duration of the individual trial and the Fig. 4.12 shows the values at an interval of 20 min (mean of seven trials). The overall heat transfer coefficients for uncoated surfaces ranged from 361.36 to 969.26 W/m<sup>2</sup>K, whereas for coated surfaces, it ranged from 468.53 to 593.9 W/m<sup>2</sup>K. The lower values of the overall heat transfer coefficient for coated surfaces could be due to the thermal barrier imposed by the coating layer of PTFE-TiO<sub>2</sub> between the heating medium and the process fluid that was being heated. The coating materials, especially the polytetrafluoroethylene possessed low thermal conductivity (0.272 W/mK) compared to that of the SS 316 (16.5 W/mK). It could be argued that the application of PTFE-TiO<sub>2</sub> coating decreased the thermal conductance of the plate resulting in lower heat transfer coefficient.

**Table 4.7 Overall heat transfer coefficient during heat treatment of milk and paneer whey for PHEs with uncoated and coated plates**

| Trial No. | Processing fluids                                      |               |                 |               |
|-----------|--------------------------------------------------------|---------------|-----------------|---------------|
|           | Milk                                                   |               | Paneer whey     |               |
|           | Overall heat transfer coefficient (W/m <sup>2</sup> K) |               |                 |               |
|           | Uncoated plates                                        | Coated plates | Uncoated plates | Coated plates |
| 1         | 643.66                                                 | 511.4         | 511.34          | 371.76        |
| 2         | 665.20                                                 | 493.13        | 504.52          | 457.92        |
| 3         | 622.90                                                 | 544.45        | 481.25          | 364.28        |
| 4         | 672.44                                                 | 545.16        | 451.53          | 385.00        |
| 5         | 709.97                                                 | 537.85        | 454.69          | 359.67        |
| 6         | 707.69                                                 | 553.91        |                 |               |
| 7         | 653.58                                                 | 543.39        |                 |               |

Each value is the mean of 24 observations taken at 20 min interval during experimental run of 8 h

As seen from the Fig. 4.12, the overall heat transfer coefficient at the beginning of the trial was higher for uncoated surface and it remained relatively stable up to 90 min indicating this duration as the induction period. After 90 min of processing time, remarkable decrease was observed, i.e. post induction period, leading to significant drop in the overall heat transfer coefficients after crossing over of the coated surface graph. Over a period of 8 h run, the overall heat transfer coefficient for uncoated surface dropped by more than 62% of its value observed at the beginning. On the other hand, the overall heat transfer coefficient for (PTFE-TiO<sub>2</sub>) coated plates showed very moderate decline over the processing time of 8 h. It was found that the drop in the overall heat transfer coefficient for coated surface over 8 h of processing time was merely 21.21% of its value observed at the beginning the trends of the overall heat transfer values obtained were in line with the findings of Beuf *et al.* (2003). The authors reported a drop in the overall heat transfer coefficients for reference stainless steel plates of PHE and the plates coated with six different materials as 17 and 9.75 to 13.7%, respectively for 90 min of processing. Barish

and Goddard (2013) reported a reduction of heat transfer from 180 to 60 W through a SS plate of  $8 \times 12 \text{ cm}^2$  PHE while pasteurization of raw milk over a period of 480 min.

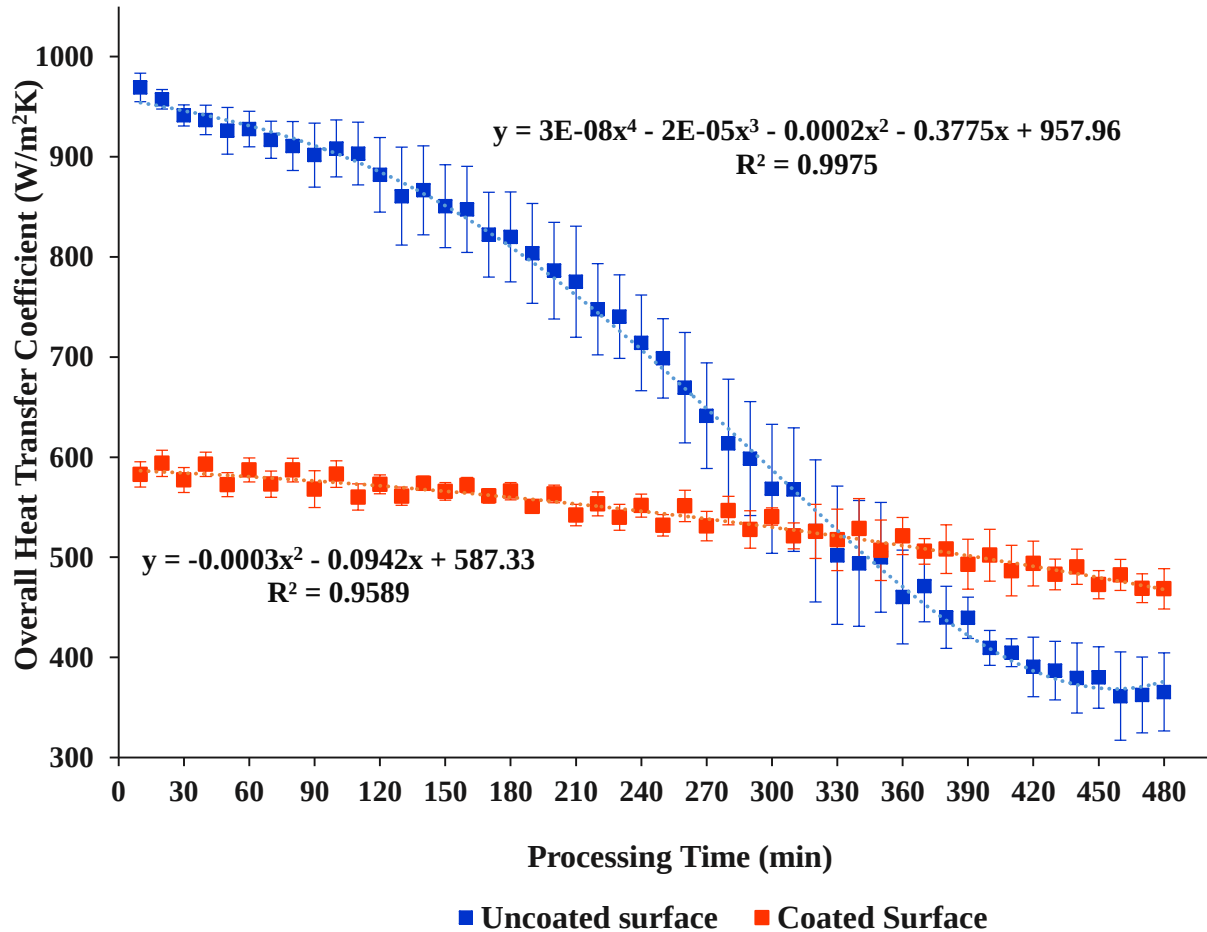


**Fig. 4.12 Overall heat transfer coefficient as a function of processing time during heat treatment of milk using SS 316 (uncoated) and PTFE-TiO<sub>2</sub> coated surfaces**

The decrease in the overall heat transfer coefficient over processing time is mainly due to fouling deposition over the plates. The deposition over the plate acts as an additional barrier for the heat transfer across the plate surface. Further, the effective thermal conductivity of the plate would be reduced because of milk foulant deposits which are majorly organic materials. Thus, the increased thickness accompanied by decreased effective conductivity of the fouled heat transfer surface would reduce the overall heat transfer coefficient. Corcoran (1996) reported a drop in the heat transfer coefficient from 3.75 to 1.4 kW/m<sup>2</sup>K over a processing period of 240 min in PHE.

#### 4.7.2 Overall heat transfer coefficient during heat treatment of paneer whey

As seen from Table 4.7, the mean overall heat transfer coefficient for uncoated surfaces ranged from 274.91 to 666.99 W/m<sup>2</sup>K, whereas for coated surfaces it ranged from 259.77 to 326.55 W/m<sup>2</sup>K. Similar to the heat treatment of milk, the overall heat transfer coefficient for coated surfaces was lower than the uncoated surfaces in case of paneer whey because of the imposition of thermal barrier by the PTFE-TiO<sub>2</sub> layer as mentioned in the previous Section. However, in comparison to milk, the overall heat transfer coefficients obtained during heat treatment of paneer whey were on the higher side for both coated and uncoated surfaces. This could be attributed to the poor heat transfer characteristics of paneer whey such as higher specific heat and lower thermal conductivity on account of its higher water content as compared to that of the milk. The drop in the values of the overall heat transfer coefficients over uncoated surfaces was 58.78 compared to that on 20.45% in case of PTFE-TiO<sub>2</sub> coated surface.

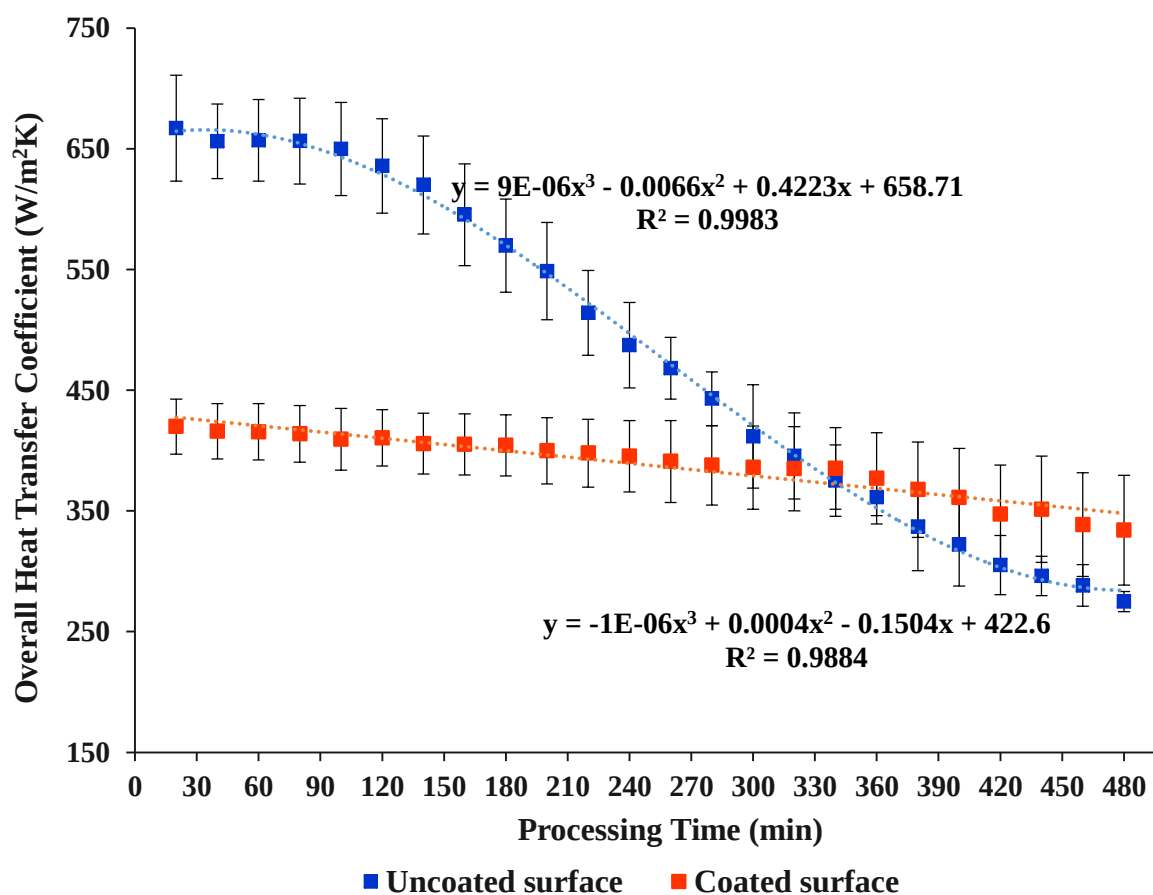


Fig. 4.13 Overall heat transfer coefficient as a function of processing time during heat treatment of paneer whey using SS 316 (uncoated) and PTFE-TiO<sub>2</sub> coated surfaces

Relationship between the mean overall heat transfer coefficients and processing time (Fig. 4.13) revealed a trend resembling to that in case of milk processing. The values were considerably constant up to initial 60-70 min of heat treatment and decreased continuously with time in case of uncoated surface. For coated surface the overall heat transfer coefficients were lower but sustained longer without any considerable drop.

The decrease in the overall heat transfer coefficient over processing time is mainly due to fouling deposition over the plates that hindered the heat transfer. Corcoran (1996) reported a drop in the heat transfer coefficient from 3.75 to 1.4 kW/m<sup>2</sup>K during paneer whey processing for 240 min. The decline in overall heat transfer coefficient (600 to 200 W/m<sup>2</sup>K) obtained was in close agreement with that reported by Fickak *et al.* (2011) during fouling experiment using heat induced whey protein gels for a period of 5500 s.

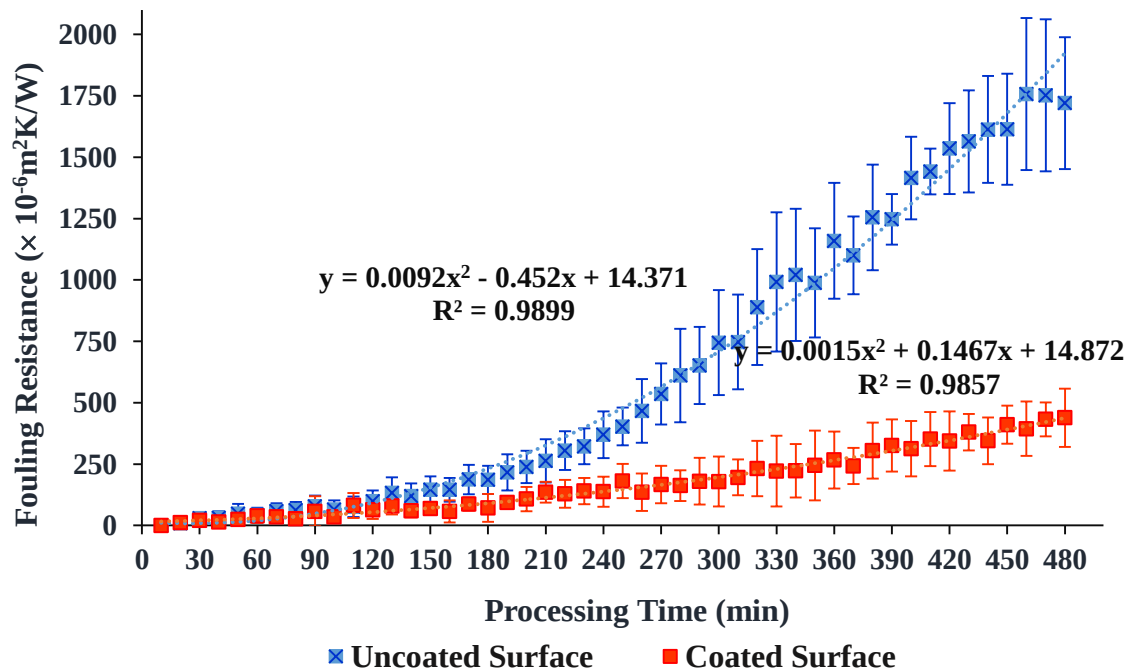


**Fig. 4.14 Fouling resistance ( $R_f$ ) as a function of processing time during heat treatment of milk using SS 316 (uncoated) and PTFE-TiO<sub>2</sub> coated surfaces**

#### 4.7.3 Fouling resistance during heat treatment of milk

Fig. 4.14 shows continuous increase in fouling resistance ( $R_f$ ) encountered over the coated and uncoated surfaces during the heat treatment of milk. Initial trends up to 60-80 min indicate negligible fouling on both the surfaces indicating fouling induction period.

During the post induction period, the coated surface showed slightly higher fouling resistance than uncoated surface for a short period followed by a drifting pattern with clear separation at 210 min. Since, fouling deposition on coated surface was remarkably lesser than uncoated surface, this higher resistance could be due to thick boundary layer on the coated surface (because of its lower roughness) rather than fouling deposition. Later 210 min of processing, fouling resistance on uncoated surface increased exponentially indicating severe fouling unlike coated surface showing moderate rise in fouling resistance. The observed ranges of  $R_f$  matched with that reported by Boxler *et al.* (2014) for whey protein deposition on the SS and modified surfaces with DLC, SICAN and SICON.

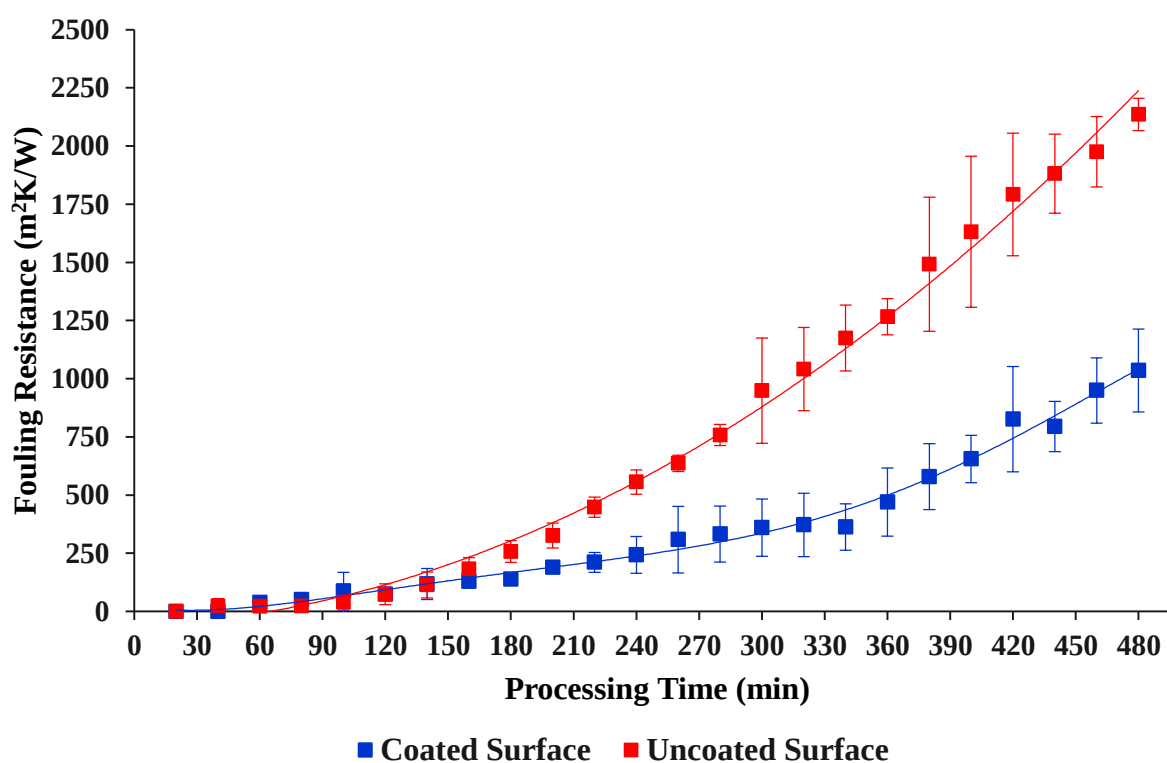


**Fig. 4.15** Fouling resistance ( $R_f$ ) as a function of processing time during heat treatment of paneer whey using SS 316 (uncoated) and PTFE-TiO<sub>2</sub> coated surfaces

#### 4.7.4 Fouling resistance during heat treatment of paneer whey

The fouling resistance ( $R_f$ ) encountered during 8 h long experimental trials on paneer whey using PHE with and without PTFE-TiO<sub>2</sub> coated plates showed continuously rising trends as shown in Fig. 4.15. The period of 60 min in the beginning indicating negligible fouling was interpreted as the fouling induction period for both the surfaces that

was followed by slight upward trends without difference between coated and uncoated surfaces up to 150 min. Thereafter, the coated surface showed rapid enhancement in fouling resistance as compared to the uncoated surface. The observed ranges of  $R_f$  matched with that reported by Boxler *et al.* (2014) for whey protein deposition on the SS and modified surfaces with DLC, SICAN and SICON.

#### 4.7.5 Foulant deposition during heat treatment of milk

The investigation of the fouling deposition on the coated and uncoated surfaces revealed that uncoated SS 316 plates had significantly more ( $P < 0.05$ ) foulant deposits than the coated surface during thermal processing of milk. Mean values of the foulant deposited on coated and uncoated surfaces ranged from 1.14 to 1.39  $\text{mg}/\text{cm}^2$  and 26.07 to 27.77  $\text{mg}/\text{cm}^2$ , respectively (Fig. 4.16). The presence of PTFE- $\text{TiO}_2$  layer prevented the adherence of constituents of milk that reflected in lesser deposition on the coated surfaces. The PTFE- $\text{TiO}_2$  coated surface had approximately 20 times lesser deposits than uncoated SS 316 surface. Rosmaninho *et al.* (2007) reported a reduction of 88% in fouling deposition in Ni-P-PTFE coated over SS 316. Balasubramanian and Puri (2009) observed a reduction of 85 - 87% in fouling with skim milk by adoption of Ni-P-PTFE coating on SS 316 surface. Barish and Goddard (2013) reported that EN-PTFE-SS 316 (coated) surface fouled nearly 30 times less than uncoated SS 316 surface for milk pasteurization.

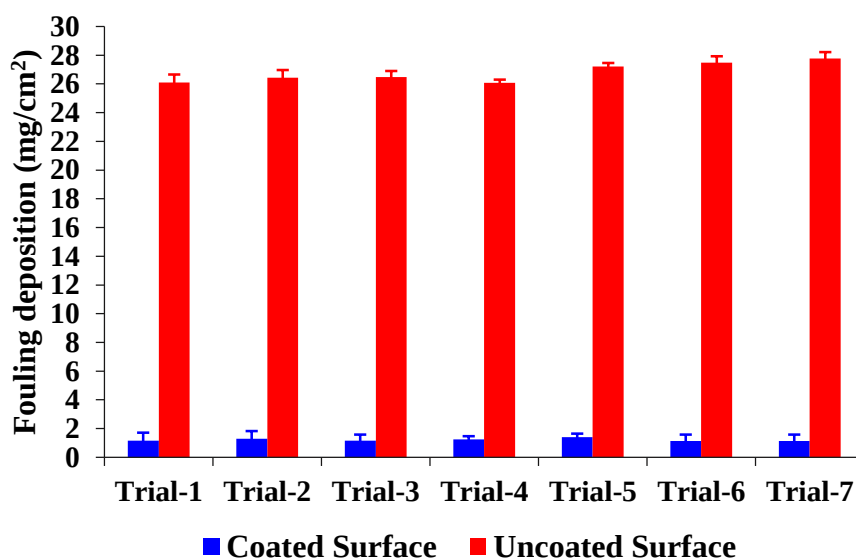


**Fig. 4.16** Foulant deposition on SS 316 (uncoated) and PTFE- $\text{TiO}_2$  coated surfaces during processing of milk

#### 4.7.6 Foulant deposition during heat treatment of paneer whey

The foulant deposition on SS 316 (uncoated) and PTFE-TiO<sub>2</sub> coated surfaces during processing of paneer whey is shown in Fig. 4.17. Similar to milk processing, the SS 316 (uncoated) surface realized significantly lesser ( $P < 0.05$ ) foulant deposition than PTFE-TiO<sub>2</sub> coated surfaces during processing of paneer whey. But, the foulant deposition during paneer whey processing was quite higher than that of milk. The whey proteins, especially  $\alpha$ -la and  $\beta$ -lg, are highly heat sensitive and denature easily. Upon denaturation, first and expose the core containing reactive sulfhydryl groups is exposed, which promote further reactions and fouling deposition (Bansal and Chen, 2006). The coated surfaces after processing of whey for 8 h had a fouling deposition of 8.37 to 10.22 mg/cm<sup>2</sup> against that of 73.76 to 77.63 mg/cm<sup>2</sup> on the uncoated surface. Adhikari *et al.* (2001) stated that lower the contact angle of a liquid on a solid surface, the stronger the attraction and greater the forces required to separate these surfaces.

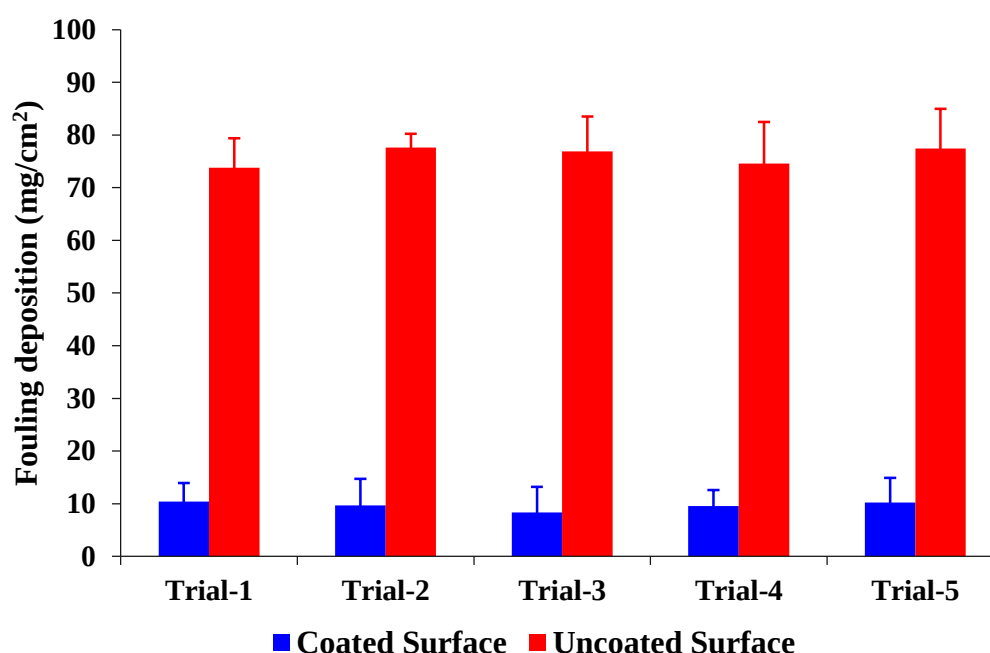


Fig. 4.17 Foulant deposition on SS 316 (uncoated) and PTFE-TiO<sub>2</sub> coated surfaces during processing of paneer whey

## 4.8 Analytical Characterization of Fouling Deposits

### 4.8.1 X-Ray Photo Electron Spectroscopy (XPS) analysis

Fig. 4.18 shows the wide scan survey spectra of the foulant deposits removed from the uncoated stainless steel (SS 316) and PTFE-TiO<sub>2</sub> coated plate surfaces after 8 h of experimental run using milk as process fluid. The major peaks in the spectra were identified as carbon (C) and oxygen (O) with binding energies of 282.8 and 529.4 eV, respectively could be from the milk constituents. Fig. 4.19 (a & b) shows the survey spectra of C 1s and O 1s peaks. Kamegawa *et al.* (2012) reported the existence of fluorine in PTFE and titanium in TiO<sub>2</sub> in the binding energies from 680 to 700 eV and 450 to 470 eV, respectively. Zhang *et al.* (2019) used XPS to validate the presence of PTFE and TiO<sub>2</sub> in coatings and identified the binding energies of 457 and 462.8 eV corresponded to Ti 2p 3/2 and Ti 2p 1/2, respectively. In our study, there was no peak at these binding energies suggesting the absence of PTFE and TiO<sub>2</sub> in the foulant samples. Also, there was neither fluorine (F) nor titanium (Ti) in both the foulant samples suggesting there was no leaching or migration of PTFE or TiO<sub>2</sub> from the plates. Similar observation was reported for Lectrofluor 641 coated PHE for skim milk processing at pasteurization temperature (Balasubramanian and Puri, 2009).

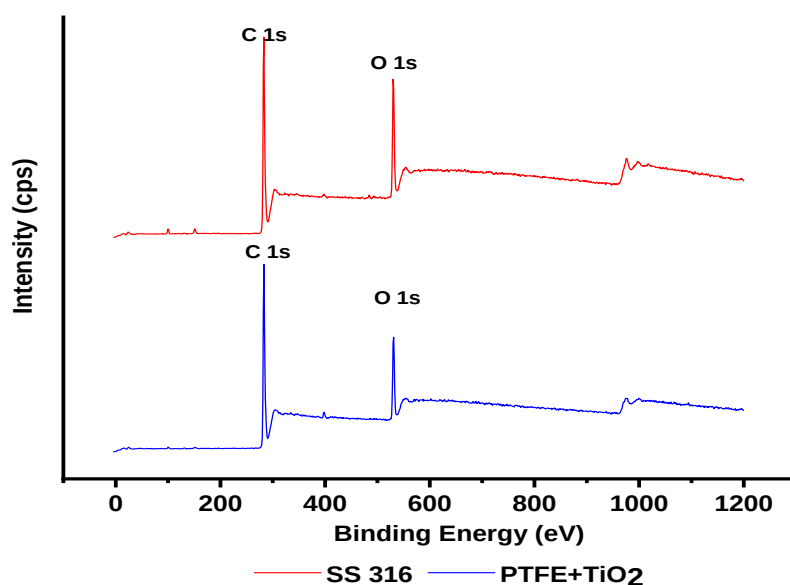


**Fig. 4.18 Comparison of XPS spectra from milk foulants adhering to SS 316 (uncoated) and PTFE-TiO<sub>2</sub> coated surfaces**

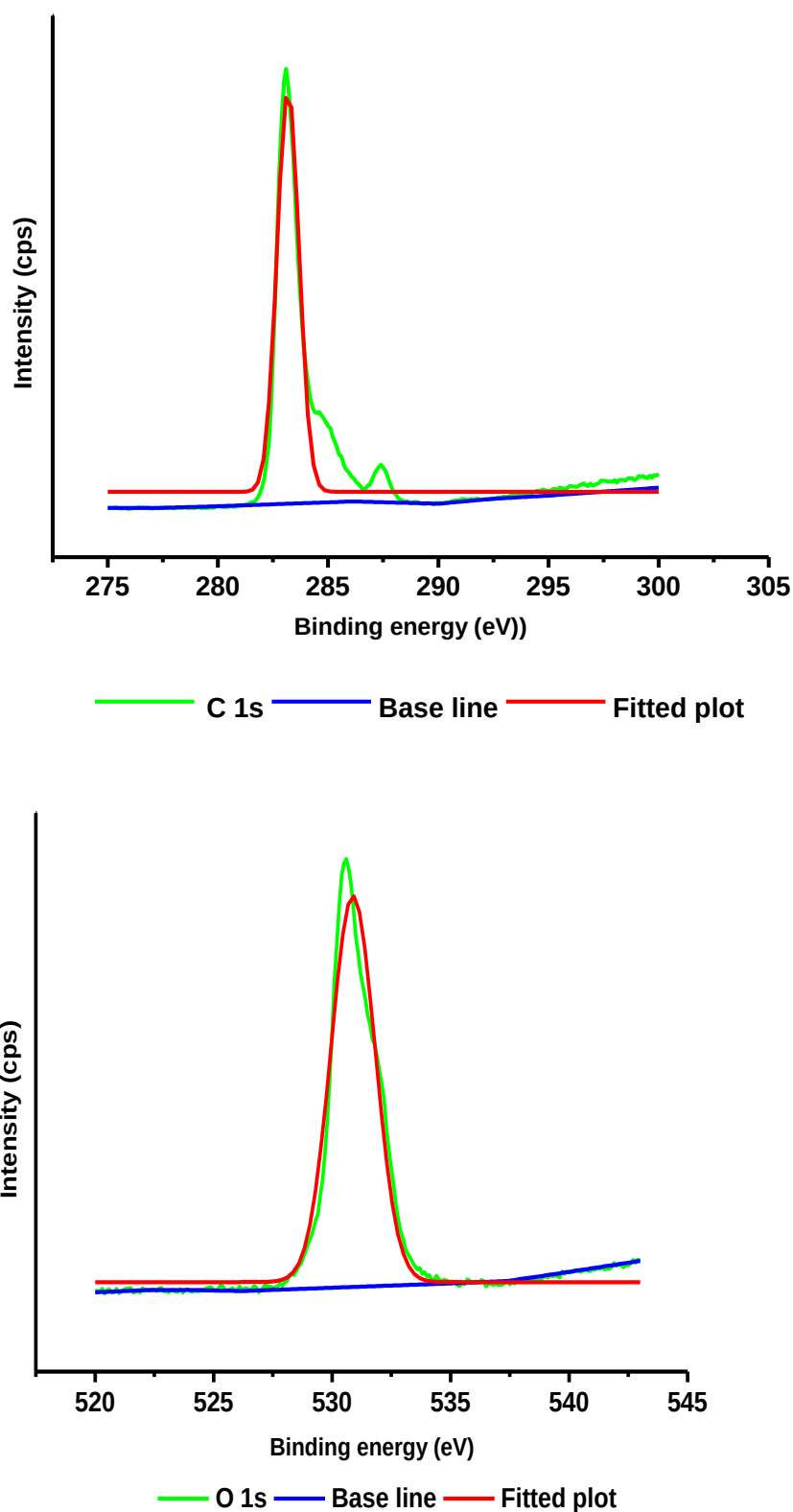


**Fig. 4.19** XPS spectra of milk foulant (a) C 1s and (b) O 1s

## **4.9 Energy Consumption**

### **4.9.1 Effect of PTFE-TiO<sub>2</sub> coating on the thermal energy consumption**

The thermal conditions obtained during each experimental trial during the heating of milk at the rate of 25 L/h in close loop for 8 h are shown in Table 4.8. It can be seen that thermal energy consumption for the PHE fitted with PTFE-TiO<sub>2</sub> coated surfaces was higher than that of the uncoated SS 316 surfaces. The difference in the thermal energy consumption for the PTFE-TiO<sub>2</sub> coated and uncoated SS 316 surfaces ranged from 1.5 to 19% with mean of 9.56. The higher thermal energy consumption in case of PTFE-TiO<sub>2</sub> coated surfaces could be due to its lower thermal conductivity resulting into higher temperature gradient across the plate surface. The log mean temperature difference (LMTD) for coated surfaces was found to be higher than the LMTD for uncoated surface in almost all the trials, which explains the higher thermal energy consumption with coated surface. During each trial of 8 h, the difference of the thermal energy consumption was much higher which diminished with the processing time following the similar trends observed for the overall heat transfer coefficient.

Balasubramanian and Puri (2009) reported 6.81% increased energy consumption during processing of skim milk by using Ni-P-PTFE modified plates in PHE as compared over the uncoated SS 316 plates.

### **4.9.2 Effect of PTFE-TiO<sub>2</sub> coating on total energy consumption**

The energy consumption of the developed module was measured using power monitor for each trial. The measured values accounted for the electrical energy consumed by the milk pump, water pump, hot water generator and the control panel display. It was found that the mean energy consumption for heating 25 L/h of milk from 33 to more than 72°C and to maintain that temperature in closed loop mode for 8 h was around 15.58±0.58 kWh in case of PHE with PTFE-TiO<sub>2</sub> coated plates, whereas the respective values in case of PHE without coating was 14.62±0.59 kWh. Thus, the energy consumption of PHE with PTFE-TiO<sub>2</sub> coated plates was higher than that of the PHE without PTFE-TiO<sub>2</sub> coated plates by 5.7 %. It was understood that the higher thermal energy consumption anticipated in case of the coated plates on account of its reduced thermal conductivity was compensated by the lower pumping energy consumption on account of the less fouling deposition on the same plates.

**Table 4.8 Thermal energy consumption during heat treatment of milk using PHEs with uncoated and coated plates**

| Run | Uncoated SS 316 |                  |        |                      |           | PTFE-TiO <sub>2</sub> coated |                  |        |                      |           | Change in thermal energy (%) |
|-----|-----------------|------------------|--------|----------------------|-----------|------------------------------|------------------|--------|----------------------|-----------|------------------------------|
|     | Flow rate (L/h) | Temperature (°C) |        | Heat consumed (kJ/h) | LMTD (°C) | Flow rate (L/h)              | Temperature (°C) |        | Heat consumed (kJ/h) | LMTD (°C) |                              |
|     |                 | Inlet            | Outlet |                      |           |                              | Inlet            | Outlet |                      |           |                              |
| 1   | 40.16           | 83.23            | 74.66  | 862.44               | 11.15     | 43.39                        | 83.51            | 78.29  | 983.32               | 15.60     | -14.02                       |
| 2   | 37.90           | 83.39            | 75.09  | 735.78               | 12.46     | 50.32                        | 81.67            | 77.35  | 814.45               | 9.80      | -10.69                       |
| 3   | 37.71           | 82.83            | 78.84  | 605.43               | 7.79      | 33.96                        | 82.76            | 77.63  | 720.45               | 8.24      | -19.00                       |
| 4   | 29.90           | 82.00            | 77.21  | 595.71               | 7.57      | 34.17                        | 82.60            | 77.90  | 655.28               | 7.88      | -10.00                       |
| 5   | 33.23           | 81.08            | 76.04  | 673.63               | 7.76      | 48.85                        | 81.76            | 78.38  | 709.02               | 10.00     | -5.25                        |
| 6   | 24.27           | 84.38            | 77.34  | 682.70               | 9.74      | 30.42                        | 82.73            | 77.33  | 692.93               | 7.41      | -1.50                        |
| 7   | 36.87           | 82.72            | 78.51  | 654.49               | 7.68      | 33.85                        | 82.57            | 77.62  | 697.01               | 7.84      | -6.50                        |

#### 4.10 Pasteurization efficiency

After each experimental trial using PHEs with and without PTFE-TiO<sub>2</sub> coated surfaces, the heat treated milk was immediately subjected to alkaline phosphatase test for testing efficiency of pasteurization. The readings of the Lovibond comparator for each trial are shown in Table 4.9.

**Table 4.9 Readings of Lovibond comparator for the milk after heat treatment in PHEs with uncoated and coated plates**

| <b>Trial No.</b> | <b>1</b> | <b>2</b> | <b>3</b> | <b>4</b> | <b>5</b> | <b>6</b> | <b>7</b> | <b>8</b> |
|------------------|----------|----------|----------|----------|----------|----------|----------|----------|
| Uncoated plates  | 5        | 3        | 4        | 6        | 3        | 3        | 4        | 5        |
| Coated plates    | 4        | 4        | 3        | 5        | 3        | 4        | 4        | 5        |

Reading <10 indicates negative phosphatase test.

As evident from the data in the Table, all the samples treated using the PHEs with and without PTFE-TiO<sub>2</sub> coated plates showed negative phosphatase test. This indicated that intensity of the heating was not affected by the PTFE-TiO<sub>2</sub> coating application and hence the plates of HTST milk pasteurizer could be coated without any adverse effect on the efficiency of pasteurization.

#### 4.11 Optimized design conditions

Table 4.10 depicts the summary of the optimized design conditions for the PHE with coated plates.

**Table 4.10 Summary of design parameters of the PHE with coated plates**

| <b>Particulars</b>              | <b>Specifications</b> |
|---------------------------------|-----------------------|
| <b>Material of construction</b> |                       |
| Plates                          | SS 316                |
| End plates                      | SS 304                |
| <b>Plate dimensions</b>         |                       |
| Height (L <sub>T</sub> )        | 430 mm                |
| Width (L <sub>w</sub> )         | 120 mm                |

|                                                 |                       |
|-------------------------------------------------|-----------------------|
| Thickness                                       | 0.5 mm                |
| Port diameter ( $D_p$ )                         | 29 mm                 |
| Vertical distance between the ports ( $L_v$ )   | 360 mm                |
| Horizontal distance between the ports ( $L_H$ ) | 60 mm                 |
| Chevron angle ( $\beta$ )                       | 30°                   |
| Heat transfer area per plate                    | 0.1 m <sup>2</sup>    |
| <b>PHE specifications</b>                       |                       |
| Total number of plates (N)                      | 5                     |
| Number of effective plates                      | 3                     |
| Number of passes                                | Two pass / Two pass   |
| Effective channel width                         | 10 mm                 |
| Thermal conductivity of the plate material      | 16.5 W/mK             |
| Gasket material                                 | Nitrile Rubber (NBR)  |
| Design pressure                                 | 6 bar                 |
| Design temperature                              | 110°C                 |
| Relative direction of flow                      | Counter flow          |
| <b>Coating specifications</b>                   |                       |
| Material                                        | PTFE:TiO <sub>2</sub> |
| Optimized ratio                                 | 84:16                 |
| Optimized coating thickness                     | 20 µm                 |
| Thermal conductivity of coated plate            | 0.281 W/mK            |
| <b>Performance parameters</b>                   |                       |
| Capacity (feed flowrate)                        | 25 L/h                |
| Product : Hot water ratio (approximate)         | 1:3                   |
| Inlet temperature of product                    | ~30°C                 |
| Outlet temperature of product                   | ~76°C                 |

|                                           |             |
|-------------------------------------------|-------------|
| Inlet temperature of hot water            | ~80°C       |
| Outlet temperature of hot water           | ~78°C       |
| Run period / duration                     | 8h          |
| Maximum overall heat transfer coefficient | 593.9 W/mK  |
| Minimum overall heat transfer coefficient | 468.53 W/mK |



# CHAPTER-5

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## SUMMARY AND ONCLUSION

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## 5. SUMMARY AND CONCLUSIONS

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The plate heat exchanger is an essential equipment used for thermal processing of milk and other products such as cream, skim milk, whey, etc. The PHE possesses the design features like thin heat transfer barrier, high surface area, high heat transfer coefficient and operational advantages like low floor-space requirement, energy efficiency, heat regeneration and flexibility of capacity expansion. By virtue of these, the PHE is most preferred heat exchanger in dairy and food processing plants. However, fouling is a severe problem encountered with PHE. It reduces thermal efficiency and increases pumping power requirement that impose costly and time-consuming de-fouling techniques to avoid consequential qualitative, technological and economic losses. Coating the plates of PHE with non-sticky materials along with nanoparticles has been reported to be effective to reduce fouling and improve the cleanability. Therefore, an attempt was made to design and develop nanoparticles coated PHE for fouling mitigation. The widely used coating polymer PTFE and nanoparticles of  $\text{TiO}_2$  were selected as the coating composite for coating the plates of PHE to be used for processing of milk and paneer whey. Following objectives were identified for the study.

- ❖ Optimization of composition and coating thickness of select nanoparticles for development of anti-fouling plate heat exchanger.
- ❖ Design and fabrication of nanoparticles coated plate heat exchanger module.
- ❖ Evaluation of the developed nanoparticles coated plate heat exchanger module for anti-fouling and heat exchange performance.

A skid mounted module having two PHE units, balance tank, PID-controlled hot water generator, piping and pumping systems for milk and hot water was developed and evaluated. The ratio of coating materials (PTFE: $\text{TiO}_2$ ) and the coating thickness was selected based on the change in thermal conductivity of SS 316 discs after coating. The coating was done by spraying method on the plates of one PHE unit and the other PHE was left uncoated (control). The coating was tested for its adhesion strength using the cross-cut tape test. Characterization of the coated surfaces was done by SEM-EDS, XRD, water contact angle, AFM and profilometer. Experimental trials were conducted for heat treatment of milk and paneer whey independently for 8 h using hot water as heating medium. Performance of the developed unit was evaluated

in terms of overall heat transfer coefficients, foulants deposition and fouling resistance as direct and indirect measure of fouling, respectively. The salient findings of the study are:

- ❖ The highest thermal conductivity (0.281 W/mK) was observed for 20  $\mu\text{m}$  coating thickness with the PTFE:TiO<sub>2</sub> ratio of 84:16. This combination of coating thickness and coating ratio was selected for the final coating over the SS 316 PHE plate surfaces.
- ❖ Based on the adhesion strength, the (PTFE-TiO<sub>2</sub>) coating was found to confirm with 5B rating. Therefore, spray coating was a suitable technique for coating SS 316 with PTFE-TiO<sub>2</sub> nanocomposite.
- ❖ The measurements with optical profilometer revealed that the average roughness values ( $R_a$ ) for SS 316 uncoated and PTFE-TiO<sub>2</sub> coated surfaces (1.67 $\times$ 1.67 mm<sup>2</sup>) were 0.20 $\pm$ 0.02  $\mu\text{m}$  and 0.74 $\pm$ 0.09  $\mu\text{m}$ , respectively.
- ❖ The measured contact angle values for uncoated and PTFE-TiO<sub>2</sub> coated surfaces for distilled water were 66.8 $\pm$ 6.3° and 112.8 $\pm$ 0.8°, whereas, for milk the values were 61 $\pm$ 6.1° and 97.5 $\pm$ 1.1°, respectively. The contact angles larger than 150° indicated successful induction of hydrophobicity on the plate surface because of PTFE-TiO<sub>2</sub> coating application. The contact angles for milk were less than for water for both the surfaces, which was attributed to the lower surface tensions of milk (51.19 $\pm$ 0.34 mN/m) and whey (49.45 $\pm$ 1.78 mN/m) as compared to water (72 mN/m).
- ❖ X-ray diffraction (XRD) analysis indicated that the crystallite size ranged from 56.25 to 135.51 nm with mean size of 82.35 nm on the SS 316 surface and from 4.19 to 173.10 nm with mean size of 49.62 nm for the coated surface. The energy dispersive spectroscopy (EDS) analyses revealed that the coated composite was distributed over entire surface of the substrate (SS 316) with 65.42% fluorine and 6.31% titanium by weight of the surface constituents, which had come from the PTFE and TiO<sub>2</sub> nanoparticles, respectively.
- ❖ Atomic force microscopic (AFM) analysis for uncoated SS 316 surface showed an average surface roughness of 65.5 nm, owing to clearly visible micro cracks on the surface as were supported by the SEM images. The surface roughness of the PTFE-TiO<sub>2</sub> coated surface was found to be 33.9 nm indicating smoothness of the surface on coating.

- ❖ Under SEM, the uncoated SS 316 plate surface showed heterogeneous surface with uneven cracks, which indicated higher degree of roughness at micro level. On the contrary, the images of the surface coated with composite (PTFE-TiO<sub>2</sub>) on the SS 316 surface were free from cracks.
- ❖ The SEM-EDS analysis indicated titanium, carbon, fluorine, iron and oxygen as major elements on the coated surface. The EDS analyses revealed that the coated composite was distributed over entire surface of the substrate (SS 316) as observed in SEM images also. It was observed that 65.42% and 6.31% by weight of the surface constituent in the coated surface is fluorine and titanium which had come from PTFE and TiO<sub>2</sub> nanoparticles, respectively.
- ❖ The X-ray photo electron spectroscopy (XPS) analysis confirmed the absence of PTFE, TiO<sub>2</sub>, fluorine and titanium in the foulant samples. It suggested no leaching or migration of PTFE or TiO<sub>2</sub> from the coating on the plates into the product for 8 h processing cycle. As the maximum duration of continuous operation for PHE in dairy industry is 8 h only, the use of coated plates could be concluded safe from migration related issues.
- ❖ Mean overall heat transfer coefficients during thermal processing of milk @ 25L/h for PTFE-TiO<sub>2</sub> coated surfaces (468.53 to 593.9 W/m<sup>2</sup>K) were less than the uncoated SS 316 surfaces (361.36 to 969.26 W/m<sup>2</sup>K) because the coating layer acted as thermal barrier for heat transfer. However, the heat transfer coefficients for uncoated surface decreased continuously with the processing time, after an initial induction period; whereas, that on the coated surface were almost constant throughout the trial period of 480 min. The decrease in the overall heat transfer coefficient over processing time could be mainly due to the fouling deposition over the plates that hindered the heat transfer.
- ❖ The uncoated SS 316 plates realized significantly more ( $P < 0.05$ ) foulant deposition (1.14 to 1.39 mg/cm<sup>2</sup>) than PTFE-TiO<sub>2</sub> coated plates (26.07 to 27.77 mg/cm<sup>2</sup>) after processing milk for 480 min. The presence of PTFE-TiO<sub>2</sub> layer on the surface prevented the adherence of constituents in milk that reflected in lesser deposition on the coated surfaces. Similar to milk processing, the SS 316 (uncoated) surface realized significantly lesser ( $P < 0.05$ ) foulant deposition (8.37 to 10.22 mg/cm<sup>2</sup>) than PTFE-TiO<sub>2</sub> coated surfaces (73.76 to 77.63 mg/cm<sup>2</sup>) after processing whey for 8 h. The foulant deposition in case of whey were quite higher than that of milk.

- ❖ The fouling resistance encountered over the coated and uncoated surfaces during the heat treatment of milk was negligible for initial 60-80 min and showed slightly upward trend thereafter with drifting pattern with clear separation at 210 min. The fouling resistance on coated surface was remarkably lesser than uncoated surface after 210 min. Similar trends were observed for whey with higher magnitudes as compared to milk.
- ❖ The mean overall heat transfer coefficients and foulant deposition during thermal processing of whey @ 25L/h for PTFE-TiO<sub>2</sub> coated surfaces were found to range from 259.77 to 326.55 W/m<sup>2</sup>K and 8.37 to 10.22 mg/cm<sup>2</sup>. The corresponding values in case of uncoated SS 316 surfaces were found to range from 274.91 to 666.99 W/m<sup>2</sup>K and 73.76 to 77.63 mg/cm<sup>2</sup>.
- ❖ The comparison of the thermal energy consumption for processing milk for 8 h in close loop using PHEs fitted with PTFE-TiO<sub>2</sub> coated and uncoated SS 316 plates revealed that the PHE fitted with PTFE-TiO<sub>2</sub> coated plates consumed on an average 9.56 % more thermal energy as compared to that with uncoated plates.
- ❖ The measurement total energy i.e. sum of the electrical energy consumed by the hot water generator to produce thermal energy and the electrical energy consumed by the pumps and other components revealed that the PHE fitted with PTFE-TiO<sub>2</sub> coated plates consumed 15.58±0.58 kWh against that of 14.62±0.59 kWh consumed by the PHE with uncoated plates for processing same quantity of milk.

Thus, it could be concluded that coating the plates of PHE with PTFE-TiO<sub>2</sub> using spray coating technique produced relatively smoother surface with good coating adhesion confirming to 5B grade as per ASTM, D-3359. The coating also improved the hydrophobicity of the SS 316 that eventually resulted in the lower fouling during thermal processing of the milk and whey. It could be concluded that the lower foulant deposition would make it possible to run the PHE for longer duration without CIP as compared to the present protocol. This will increase the productive hour per day resulting in more product throughput. The increased energy consumption due to the use of coated surface can be expected to be compensated by these extra productive hours.

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## 6. BIBLIOGRAPHY

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| <b>Education</b> | <b>Ph.D. (Dairy Engineering)</b> National Dairy Research Institute, SRS, Bengaluru – 560030<br>Year of passing :2019<br>C. G. P. A: 7.78 / 10.00<br><b>Research:</b> Design and development anti-fouling heat exchanger for milk processing                                          |
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| <b>Professional Experience</b> | 1. <b>Industrial Experience (2007 to 2012):</b> Sr. Process and proposals engineer, GEA Process Engineering India Pvt.Ltd, Vadodara/Baroda, India. Designed and commissioned about 14 Projects for dairy and food industries in India and overseas |
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- Namaste India, Kanpur, UP.
  - Ngon coffee, Vietnam
  - Egg way international, Hyderabad, Andhrapradesh.
  - Anik industries, Dewas, Madhya pradesh
  - Amul whey powder plant, Khatrej, Gujarat.
  - Mother dairy, Junagadh, Gujarat.
  - Chitawon Milk Limited, Nepal.
  - Prisha Dairy, Ahemadabad, Gujrat.
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1. **Teaching Experience (2012, July onwards):** Asst.Professor,  
College of Dairy Technology, SVVU Tirupathi-517502

**Consultant:** Designed, installed and commissioned milk products plant at College of Agricultural Engineering, Madakasira, SV Agricultural University, Tirupati.

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**Awards and Achievements**

**1<sup>st</sup> Prize** in National Seminar TNUAS, Coimbatore

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