

Sticky Business: A review on Surface Aspects of Fouling Mitigation

Phanida Saikhwan

Department of Chemical Engineering, Faculty of Engineering, Thammasat University,
Khlong Luang, Pathumthani, Thailand, 12120
E-mail: psaikhwan@engr.tu.ac.th

Abstract

There have been a number of recent studies searching for ways to avoid or reduce fouling. One modern strategy is the development of surface treatment technology that produces less sticky or less fouling-prone surfaces. Various surface treatments involve modifying surface energy or surface roughness or both in some cases. The generated surfaces are also known as modified surfaces. This work summarizes a general overview of surface modification and provides practical aspects in using modified surfaces in order for the purpose of fouling mitigation.

Keywords: fouling, surface treatment, modified surface

1. Introduction

The accumulation of deposits on process surfaces, or fouling, is a major problem in food processing [1]. There is an important product contamination issue since there exists a risk of micro-organisms growing at enhanced rate within the fouling layers. As a result, higher investment, production and maintenance costs are involved.

There have been a number of recent studies investigating different strategies to avoid or reduce fouling *e.g.* [2, 3]. One of these is the use of surface treatment technology that aims to produce tailored surfaces that are less sticky or less prone to fouling. This idea has attracted considerable attention, particularly in the food industry. This is partly because the use of treated or modified surfaces does not involve the alteration of process fluids (*e.g.* by adding chemicals) and operating conditions, which would affect product quality. Moreover, cleaning of equipment in food processing plants is performed regularly, and hence is expensive and time consuming. Therefore,

surfaces that promote cleaning thus shortening cleaning time and avoiding the use of strong chemicals appear attractive.

In order to engineer any surfaces to have anti-fouling properties, the interaction between these modified surfaces and the foulant must be understood. As the foulant molecule adheres to the surface, adhesion forces play a role. This interaction is dependent on the type and size of the foulant molecules as well as the surface properties of the substrate. Once the first layer is formed, the second layer and later layers develop into structured deposits. Surface properties also play a role here. This is because the structure of the first layer, which is dependent on the surface properties, may determine the structure and the strength of final deposits.

2. Understanding Adhesion

2.1 Adhesion forces

Adhesion of particles is an important step in the formation of fouling. Fouling occurs when gravitational forces are negligible; therefore only particulate

materials of colloidal size (within dimensions $< 1 \mu\text{m}$) will adsorb onto solid surfaces immersed in flowing fluids [4]. Accordingly, the net force of interactions between foulants and the surface has been described in terms of DLVO theory. Figure 1 gives an overview of the interactions involved in adhesion. The **DLVO theory** (named after Derjaguin, Landau, Verwey and Overbeek) introduced the fundamental idea that the complex colloidal phenomenon could be understood using the concept of long-range forces, both attractive (van der Waals) and repulsive (electrostatic double layer), which act between assemblies of atoms or molecules.

Van der Waals (LW) forces arise from intermolecular dipole-dipole and dipole-induced dipoles. These forces are also dependent on the geometry and on the physical and chemical properties of the interacting bodies. When a surface is immersed in an aqueous medium, it shows a tendency to acquire an electrical surface charge. As a result a redistribution of the ions in solution occurs: the ions of opposite charge will be attracted to the surface, whereas the ions of the same type of charge will be repelled. This effect creates an **electrical double layer** adjacent to the surface. Repulsion arises if these double layers are interpenetrated when like-charged solid bodies approach each other. Other forces to be considered in adhesion are hydrophobic interactions, steric interactions and ion bridging. These are described in [4].

2.2 Surface energy

Researchers have attempted to explain adhesion behaviour of fouling deposits in terms of interfacial free energies. According to equation (1) the interfacial free energy, or surface tension, is defined as the total work to create an interfacial area at the interface of the phases i and j [4]:

$$\gamma_{ij} = \left(\frac{\partial G}{\partial A} \right)_{T,P} \quad (1)$$

where G represents the Gibbs free energy of the system, A the interfacial area, T the temperature and P the pressure.

Various approaches to determine the interfacial free energy of solid substrates submerged in liquid, γ_{sl} , are available and these are listed in Table 1. The geometric mean and harmonic mean methods (see Table 1 equations (2) and (3)) are based on a macroscopic approach followed by Lifshitz [6] with respect to van der Waals forces: (i) dipole-dipole interactions; (ii) dipole-induced dipole; (iii) fluctuating nonpolar forces; and (iv) hydrogen bonding forces. The resulting surface energies are called Lifshitz-van der Waals (LW). Assuming van der Waals forces are predominant, the interfacial energy is divided into a dispersive (index “dis”) and a polar (index “pol”) component [6].

In contrast to the geometric mean and harmonic mean techniques, van Oss [7] accounts for polar interactions due to the presence of polar media (equation (5)). These interactions are divided into an electron acceptor fraction corresponding to a Lewis acid (electron receiving fraction) γ^+ and electron donor corresponding to a Lewis base (electron donor fraction) γ^- (equation (6)). The net surface energy is calculated using equation (4) in Table 1 so that γ_{ij} can have a negative value representing repulsive interactions between two phases immersed in polar media.

$$\gamma_{ij} = \gamma_{ij}^{LW} + \gamma_{ij}^{AB} \quad (5)$$

$$\gamma_{ij}^{AB} = 2\sqrt{\gamma^+ \gamma^-} \quad (6)$$

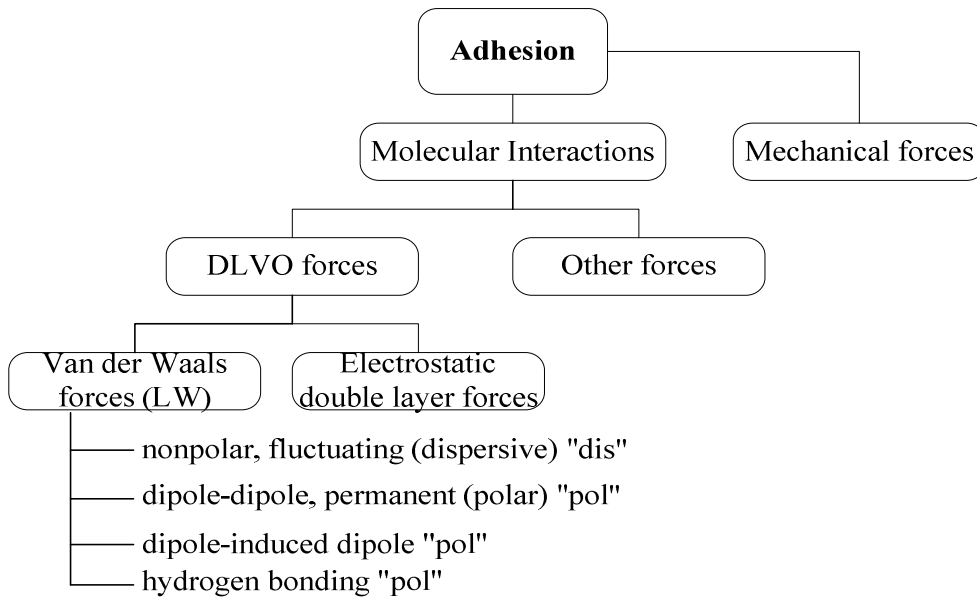


Figure 1 Interfacial interactions influencing adhesion (adapted from [3]).

Table 1 Calculation of the interfacial energy γ_{sl}

Approach		Application
Owens and Wendt (1969):		Geometric mean method for non-polar systems
$\gamma_{sl} = \gamma_{lg}^{LW} + \gamma_{sg}^{LW} - 2 \left(\sqrt{\gamma_{lg}^{dis} \gamma_{sg}^{dis}} + \sqrt{\gamma_{lg}^{pol} \gamma_{sg}^{pol}} \right)$	(2)	
Wu (1982):		Harmonic mean for low energy systems such as polymer or organic liquids (≤ 35 mN/m)
$\gamma_{sl} = \gamma_{lg}^{LW} + \gamma_{sg}^{LW} - 4 \left(\frac{\gamma_{lg}^{dis} \gamma_{sg}^{dis}}{\gamma_{lg}^{dis} + \gamma_{sg}^{dis}} + \frac{\gamma_{lg}^{pol} \gamma_{sg}^{pol}}{\gamma_{lg}^{pol} + \gamma_{sg}^{pol}} \right)$	(3)	
van Oss <i>et al.</i> (1994):		Lewis-acid (A)-base (B) method for polar systems.
$\gamma_{sl} = \gamma_{sl}^{LW} + \gamma_{sl}^{AB}$ $= \left(\sqrt{\gamma_{sg}^{LW}} - \sqrt{\gamma_{lg}^{LW}} \right)^2 + 2 \left(\sqrt{\gamma_{lg}^{+} \gamma_{lg}^{-}} + \sqrt{\gamma_{sg}^{+} \gamma_{sg}^{-}} - \sqrt{\gamma_{lg}^{+} \gamma_{sg}^{-}} - \sqrt{\gamma_{lg}^{-} \gamma_{sg}^{+}} \right)$	(4)	

2.3 Surface roughness

In addition to molecular interactions illustrated by the DLVO theory, the JKR theory proposed by Johnson, Kendall and Roberts [8] showed other factors that influence adhesion forces. The JKR theory states that two beads of the same size and geometry adhere onto a given surface with different forces if they are made of different materials. This is because adhesion forces

are not only dependent on the distance between the two objects but also the **nature of the contact**, *e.g.* roughness.

Greenwood and Williamson [9] proposed that where more complex surface roughness exists at the particle contact, three parameters are needed to describe the contact adequately: σ , the standard deviation of the height distribution, β , the radius of each asperity, and N , the number

of asperities per unit area. σ is defined in the same way as the root mean square roughness used by most researchers for the purpose of surface characterization.

3. Modified Surfaces

Generally, the process of modifying surfaces involves applying coatings to the original surface. In the food sector, the base material is usually a stainless steel.

Initial attempts to produce anti-fouling or less sticky surfaces was by coating surfaces with polytetrafluoroethylene (PTFE) or other polymer layers [2]. However, these low surface energy coatings exhibit low thermal conductivity, unsatisfactory abrasion resistance and poor adhesion to the metal substrate. Hence, one solution to this problem is the use of electroless (or auto-catalytic) nickel-phosphorus and PTFE composite coatings (Ni-P-PTFE). More recently, a polymer containing fluorine, developed by NASA, has shown comparable friction to Teflon while offering greater scratch resistance and toughness. Work is ongoing to reduce the cost of such coatings [11].

Another surface coating involves the use of diamond-like carbon (DLC), which has the unique combination of excellent tribological properties and low surface energies [12, 13]. Advances in surface technology also lead to other surface treatments, such as ion-implanted surfaces [14] and silica surfaces [15, 16]. Recently, such tailored coatings have become more affordable and can be applied to items of equipment on the process scale and ships.

Detailed explanations of techniques used to modify surfaces are given by Zhao *et al.* [2] (Ni-P-PTFE) and Santos *et al.* [17] (other coatings). Descriptions of some common coatings are:

(i). *Diamond-like carbon (DLC)-based coatings*: a thin film of amorphous carbon containing both diamond and graphite bonding. The former creates

hardness whilst the latter gives the surface a low coefficient of friction. It is possible to control the surface energy, as well as wetting properties of DLC coatings, by embedding non-metallic elements (*e.g.* F, Si, O, N) in the DLC matrix. *SiCAN*, for example, contains embedded Si; the coating has a unique combination of a Teflon-like surface with high wear resistance. Another example is Si and O doped DLC, *SICON*[®], which has a hard glass-like silica surface. DLC-based coatings are achieved by either sputtering (physical vapour deposition: PVD) or plasma-enhanced chemical vapour deposition (PECVD); both methods involve depositing atoms of coating material on a substrate. The latter provides the possibility of having additional atoms in the coatings (*e.g.* *SICON*[®]).

(ii) *Silica coatings*: Silica, SiO_x, is well-known for its hardness, which provides resistance to abrasion. Organic substances can be incorporated in silica coatings to obtain unique chemical and physical properties depending on the properties of the added substances. For instance, 'sol-gel' which is produced by applying an organic solvent in the sol-gel process, is a hydrophilic and hydrated anionic surface. The sol-gel process involves dipping or spinning solvent onto a surface, which is later annealed to oxidise or remove the residual organic molecules.

(iii) *Teflon surface*: The base Teflon (poly-tetrafluoroethylene: PTFE) material is relatively soft, so a composite of PTFE and Ni has been developed to give wear resistance, PTFE particles are co-deposited with nickel phosphorus alloy. A comprehensive review of this type of coating is given by Kerr *et al.* [19].

(iv) *Ion-implanted coatings*: Ions are implanted directly onto a substrate by sputtering to create an alloy at the surface. The ions used include SiF⁺³, MoS₂⁺² and TiC (hard coating, low friction) (*e.g.* [15, 20]).

4. Fouling mitigation by modified surface

Various coatings are available for tribological applications and those that are smooth, with low surface energies and friction, have been studied for their anti-fouling properties. Recently, there have been many studies on the efficacy of surface coatings in preventing fouling and/or promoting cleaning. For instance, the EU-funded MODSTEEL project studied a range of coated stainless steels for use in dairy plate heat exchangers. Santos *et al.* [16] conducted part of the project, focusing on the adsorption of β -Lactoglobulin (β -Lg) from whey protein solutions and found that SiF^{+3} -implanted and DLC surfaces were promising mitigators of β -Lg adsorption. These two modified surfaces have been previously reported to be efficient in reducing formation of calcium sulphate scale and attachment of bacteria [2, 22]

Bornhorst *et al.* [21] reported that deposit layers formed on these two surfaces were thinner and easier to remove compared to uncoated stainless steel. They reported that surface modification had a stronger effect on cleaning than on deposition, *i.e.* although surface energies changed, the food material was still able to foul the surface. Significant reduction in mineral scale formation was observed on heat exchanger surfaces using graded Ni-P-PTFE surfaces [19]. In addition, Beuf *et al.* [15] reported that the Ni-P-PTFE surfaces fouled with milk proteins were the easiest to clean compared with DLC, silica, ion implantation coatings and two commercial surfaces, Excalibur® and Xylan®. Ni-P-PTFE was also recommended by Rosmaninho *et al.* [19] as an ideal heating surface for milk pasteurisation.

The effect of surface coating combined with smoothing the surface (electro-polishing) was investigated by Augustin *et al.* [22]; electropolishing the surface before applying coating was found to increase performance in reducing the

thickness of whey protein foulants. Other than milk and scale fouling, recent studies of surface coatings for fouling mitigation include those involving food soil [23], fruit juice [24], biofilm [25] and marine [26].

It is seen from several literature examples that the effectiveness of coatings varies with the foulants involved. Nonetheless, the work done mostly focused on specific types of deposits and the guidelines for selecting coatings for a given process have not yet been established. One challenge is therefore to establish some relation between the fouling problems caused by different components of deposits and the surface properties of the substrates. Another point to take is that the modified surfaces used are not for the purpose of anti-fouling originally. Hence, another challenge is to engineer anti-fouling surfaces specifically for a given process, for example, roughness is smaller than cell sizes to prevent cells adhesion.

5. Effects of surface properties

Adhesion or adsorption of fouling precursors is the result of several interactions occurring between the deposit, surface, and process fluid. These interactions are significantly influenced by the surface properties, particularly its surface energy, γ_{sg} [19]. This is confirmed by experimental work. For instance, Förster and Bohnet [27] reported that surface energy and a lag time before fouling can be observed (induction period), are related. Their work reports the advantage of using low energy surfaces for heating equipment. Moreover, there exist surface energies which minimise adhesion by deposits; the values of optimum surface energies have been determined experimentally. For example, bacterial attachment [28] and milk proteins [29] exhibit reduced adhesion on surfaces with energies around 25 mN m^{-1} . Recently, it has been found that the optimum surface energies (minimal fouling) could be estimated by extended DVLO

theory, which includes Lifshitz-van der Waals, Lewis acid-base, and electrostatic double layer interactions (*e.g.* [27, 28, 30]). However, the work based on a theoretical approach does not include some observations made from experimental works. For example, Zhao and Müller-Steinhagen [30] proposed an equation to find optimum surface energy based on total surface energy. However, experimental work by Liu *et al.* [31] and Wu *et al.* [32], reported that at a fixed total surface energy, more nucleation of calcium phosphate is observed with increasing Lewis base component of the surface energy.

Apart from surface energy, it has been suggested that the hydrophobicity of a surface influences fouling or cleaning rates (*e.g.* [19]). The general concept is that a surface that is hydrophilic should prevent fouling by hydrophobic deposits. Several articles also look into the effect of surface roughness on fouling or cleaning (*e.g.* [22, 27]).

Santos *et al.* [29] found that DLC sputtered surfaces were the most promising of their selections tested, in terms of reducing protein adsorption, but found that surface properties (*e.g.* surface energy) changed after cleaning. [33] and Jullien *et al.* [34] also reported that contact between stainless steel and food or detergents altered the surface energy of stainless steel. Therefore the study of modified surfaces should include stability testing.

6. Conclusion

The effectiveness of surface treatment needs to be considered holistically, as the prime benefit may be in cleaning rather than anti-attachment. Information on deposit structure, strength, and fouling or cleaning mechanisms and rates, is required for this. Selection of surface coatings for a particular process is currently done by trial and error and there is a need to establish a more systematic approach to the selection. Moreover, the stability of surface coatings

to mitigate fouling must be investigated and improved as the ideal surface coatings should remain stable over repeated fouling and cleaning cycles.

7. Acknowledgement

Helpful discussions with Dr. Bill Paterson, Dr. Ian Wilson, and Dr. John Chew are gratefully acknowledged.

8. References

- [1] Chew J. Y. M., Paterson W. R. and Wilson D. I., Fluid Dynamic Gauging for Measuring the Strength of Soft Deposits *J. Food Eng.*, Vol. 65, pp. 175-187, 2004.
- [2] Zhao Q., Liu Y., Müller-Steinhagen, H. and Liu G., Graded Ni-P-PTFE Coatings and Their Potential Applications, *Surface & Coatings Technology*, Vol. 155, pp. 279-284, 2002.
- [3] Förster M. and Bohnet M., Modification of Molecular Interactions at the Interface Crystal/Heat Transfer Surface to Minimize Heat Exchanger Fouling, *J. Therm. Sci.*, Vol. 39, p. 699, 2000.
- [4] Oliveira R., Understanding Adhesion: A Means for Preventing Fouling. *Exp. Therm. Fluid. Sci.*, Vol. 14, pp. 316-322, 1997.
- [5] Wu S., *Polymer Interface and Adhesion*, Marcel Dekker Inc., New York, 1982.
- [6] Chaudhury M. K., Good R. J. and Van Oss, C. J., Interfacial Lifshitz-Van Der Waals and Polar Interaction in Macroscopic Systems, *Chem. Rev.*, Vol. 88, pp. 927-941, 1988.
- [7] Fowkes F. M., Dispersion force Contribution to Surface and Interfacial Tensions, Contact Angles and Heats of Immersion, in: *Advances in Chemistry Series 43*, pp. 99-111. Am. Chem. Soc., Washington, 1964.

- [8] Van Oss, C.J., Good R. J. and Chaudhury M. K., The Role of Van Der Waals Forces and Hydrogen Bonds in Hydrophobic Interactions between Biopolymers and Low Energy Surfaces. *J. Colloid Interf. Sci.*, Vol. 111, pp. 376-390, 1986.
- [9] Johnson K. L., Kendall K. and Roberts A. D., Surface Energy and Contact of Elastic Solids, *P. Roy. Soc. Lon. A. Mat.*, Vol. 301, No.13, 1971.
- [10] Greenwood J. A. and Williamson J. B. P., Contact of Nominally Flat Surfaces. *Proc. R. Soc. Lond. A*, Vol. 295, p. 315, 1966.
- [11] King A., Teflon Replacement Up to Scratch, but at a Price, *Chemical & Industry*, Vol. 59, pp. 3381-3398, 2007.
- [12] Donnet C., Recent Progress on the Tribology of Doped Diamond-Like and Carbon Alloy Coatings: A review, *Surf. Coat. Technol.*, Vol. 100-101, p. 180, 1998.
- [13] Grill A., Tribology of Diamond-Like Carbon and Related Materials: An updated Review. *Surf. Coat. Technol.*, Vol. 94-95, p. 507, 1997.
- [14] Müller-Steinhagen H. and Zhao Q. Investigation of Low Fouling Surface Alloys Made by Ion Implantation Technology, *Chem. Eng. Sci.*, Vol. 52, pp. 3321-3332, 1997.
- [15] Beuf M., Rizzo G., Leuliet J. C., Müller-Steinhagen H., Yiantsios S., Karabelas A. and Bénézech T., Fouling and Cleaning of Modified Stainless Steel Plate Heat Exchangers Processing Milk Products, In *Proceedings of Heat Exchanger Fouling and Cleaning: Fundamentals and Applications*, (Watkinson P., Müller-Steinhagen H. and Malayeri M. R., eds), Vol. RP1, pp. 99-106, 2003.
- [16] Santos O., Nylander T., Rizzo G., Müller-Steinhagen H., Trägårdh C. and Paulsson M., Study of Whey Protein Adsorption Under Turbulent Flow, In *Proceedings of Heat Exchanger Fouling and Cleaning: Fundamentals and Applications*, (Watkinson P., Müller-Steinhagen H. and Malayeri M. R., eds), Vol. RP1, pp. 175-183, 2003.
- [17] Santos O., Nylander T., Rosmaninho R., Rizzo G., Yiantsios S., Andritsos N., Karabelas A., Müller-Steinhagen H., Melo L., Boulangé-Petermann L., Gabet C., Braem A., Trägårdh C. and Paulsson M., Modified Stainless Steel Surfaces Targeted to Reduce Fouling-Surface Characterization., *J. Food Eng.*, Vol. 64, pp. 63-79, 2004.
- [18] Kerr C., Barker D., Walsh F. and Archer J., Fouling of Heat-Transfer Surfaces by Crystallization and Sedimentation, *Trans. Inst. Metal Fin.*, Vol. 78, p. 171, 2000.
- [19] Rosmaninho R., Santos O., Nylander T., Paulsson M., Beuf M., Benezech T. B., Yiantsios S., Andritsos N., Karabelas A., Rizzo G., Müller-Steinhagen H. and Melo L. F., Modified Stainless Steel Surfaces Targeted to Reduce Fouling: Evaluation of Fouling by Milk Components. *J. Food Eng.* Vol. 80, pp. 1176-1187, 2007.
- [20] Bornhorst A., Müller-Steinhagen H. and Zhao Q., Reduction of Scale Formation under Pool Boiling Conditions by Ion Implantation and Magnetron Sputtering on Heat Transfer Surfaces, *Heat Transfer Eng.*, Vol. 20, No. 2, pp. 6-14, 1999.
- [21] Zhao Q., Liu Y. and Müller-Steinhagen H., Effects of Interaction Energy on Biofouling Adhesion, In *Proceedings of Fouling Cleaning and Disinfection in Food Processing*, (Wilson D. I., Fryer P. J. and Hasting A. P. M., eds), UK, 2002.
- [22] Augustin W., Geddert T. and Scholl S., Surface Treatment for the

- Mitigation of Whey Protein Fouling, in Proceedings of 7th International Conference on Heat Exchanger Fouling and Cleaning: Challenges and Opportunities, (Müller-Steinhagen H., Malayeri M. R., and Watkinson P., eds), Tomar, Portugal, 2007.
- [23] Saikhwan P., Geddert T., Augustin W., Scholl S., Paterson W. R. and Wilson D. I., Effect of Surface Treatment on Cleaning of a Model Food Soil. *Surf. & Coat. Tech.*, Vol. 201, pp. 943-951, 2006.
- [24] Balasubramanian S. and Puri V. M., Fouling Mitigation during Product Processing Using a Modified Plate Heat Exchanger Surface, *Trans. Of ASAB*, Vol. 51, pp. 629-639, 2008.
- [25] Dong B. Y., Manolache S., Somers E. B., Wong, A. C. L. and Denes F. S., Generation of Antifouling Layers on Stainless Steel Surfaces by Plasma-Enhanced Crosslinking of Polyethylene Glycol. *J. App. Pol. Sci.*, Vol. 97, pp. 485-497, 2005.
- [26] Youngblood J. P., Andruzzi L., Ober, C. K., Hexemer A., Kramer E. J., Callow J. A. Finlay J.A. and Callow, M.E., Coatings based on Side-Chain Ether-Linked Poly (Ethylene Glycol) and Fluorocarbon Polymers for the Control of Marine Biofouling. *Biofouling*, Vol. 19, pp. 91-98, 2003.
- [27] Förster M. and Bohnet M., Influence of the Interfacial Free Energy Crystal/ Heat Transfer Surface on the Induction Period During Fouling, *J. Therm. Sci.*, Vol. 38, pp. 944-954, 1999.
- [28] Zhao Q. and Wang S. Tailored Surface Free Energy of Membrane Diffusers to Minimize Microbial Adhesions, *App. Surf. Sci.*, Vol. 230, pp. 371-378, 2004.
- [29] Santos O., Nylander T., Schillén K., Paulsson M. and Trägårdh C., Effect of Surface and Bulk Solution Properties on the Adsorption of Whey Protein onto Steel Surfaces at High Temperature, *J. Food. Eng.*, Vol. 73, p. 174, 2006.
- [30] Zhao Q. and Müller-Steinhagen H., Intermolecular and Adhesion Forces of Deposits on Modified Heat Transfer Surfaces, In Proceedings International Conference on Heat Exchanger Fouling, Fundamental Applications and Technical Solutions, (Müller-Steinhagen H., Reza Malayeri M. and Watkinson A. P., eds), Germany, 2001.
- [31] Liu Y., Wu W., Sethuraman G. and Nancollas G. H., Intergrowth of Calcium Phosphates: An Interfacial Energy Approach. *J. Cryst. Growth*, Vol. 174, pp. 386-392, 1997.
- [32] Wu W.J ., Zhuang H. Z. and Nancollas G. H., Heterogeneous Nucleation of Calcium Phosphates on Solid Surfaces in Aqueous Solution, *J. Biomed. Mat. Res.*, Vol. 35, pp. 93-99, 1997.
- [33] Boulangé-Petermann L., Process of Bioadhesion on Stainless Steel Surfaces and Cleanability: A review with Special Reference to the Food Industry, *Biofouling*, Vol. 10, pp. 275-300, 1996.
- [34] Jullien C., Benezech T., Carpentier B., Lebret V. and Faille C., Identification of Surface Characteristics Relevant to the Hygienic Status of Stainless Steel for the Food Industry, *J. Food Eng.*, Vol. 56, pp. 77-87, 2003.