Proceedings of the 3rd International Conference on Materials Chemistry and Environmental Engineering (CONF-MCEE 2023), Part II
DOI: 10.54254/2755-2721/7/20230483

Review: Bio-inspired surfaces for fouling resistance

Shengjun Niu[1+], Surui Tang[2+], Lezhi Wang[3+], Jiayan Zhou[4+*], Ningfeng Zheng[5+]

[1]Beijing National Day School, Beijing, 100039, China
[2]The Eberly College of Science, The Department of Chemistry, The Pennsylvania State University, State College, 16802, United States
[3]Beijing No.2 Middle school international department, Beijing, 100010, China
[4]Material Science and Engineering, City University of Hong Kong, Hong Kong, 999077, China
[5]Hongling High School, Shenzhen, 518043, China
+These authors contributed equally to this work and should be considered co-first authors

*2656897376@qq.com

Abstract. This paper discusses the anti-fouling principle of lotus surfaces in nature and applies it to the production of anti-fouling surfaces, providing information and ideas for the research and application of anti-fouling. We discuss various fouling (Biofouling, Icefouling, Precipitation Fouling, Dust fouling, and Chemical Reaction Fouling) and their anti-fouling solution. Currently, no single engineered surface can solve the solid fouling problem extensively, so this paper mainly reviews various complex micro or macro structures and coatings that play a role in different fouling.

Keywords: bio-inspired surfaces, anti-fouling, contact angle, self-cleaning.

1. Introduction

Fouling occurs all around us at all times. It is the accumulation of unwanted material on solid surfaces. It can be either living organisms or non-living substances. Fouling has many classifications, including biofouling, ice fouling, precipitation fouling, dust fouling, and chemical reaction fouling. Fouling may or may not be conspicuous, but it can generate tremendous losses. For example, in 2006, China lost 4.68 billion dollars, 0.169% of the country's GDP, because of boiler and turbine fouling. As a result, people have been trying to develop methods to control and clean fouling from the ancient world to modern society.

Some terms are required to know to understand fouling. First, surface energy is the energy difference between particles at the surface and in the bulk of one object. The inner particles' movement requires energy, which results in the energy difference. Second, surface tension is the trend of the rest liquid surfaces shrinking into the surface with the minimum area possible. The attraction difference between air and the bulk of the liquid causes it. Third, contact angle. This is an essential concept in fouling. As figure 1 shows below, it is an angle at which liquid-vapor interface contact with a solid surface and is measured conventionally through the liquid. A high contact angle with water means the object is hydrophobic, and a low contact angle means the object is easily wet by the water.

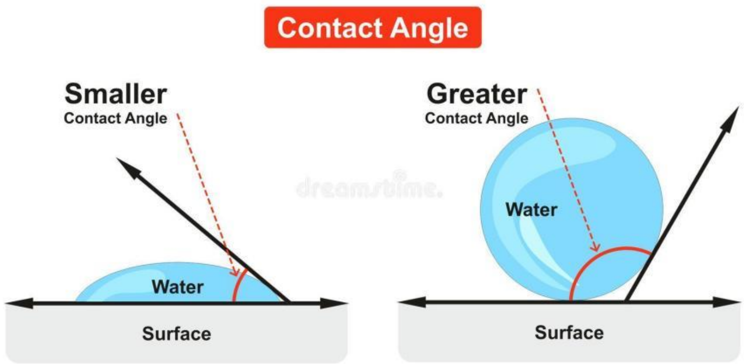

Figure 1. Contact Angle Diagram of water meeting solid surface.
(Source: https://www.dreamstime.com/stock-illustration-contact-angle-diagram-example-water-bubble-greater-splash-smaller-where-meet-solid-surface-image92206329)

Another essential concept is contact angle hysteresis. Contact angle hysteresis (CAH) is the difference between advancing and receding angles. Figure 1 shows the contact angle of water meeting the solid surface. For example, on rainy days, some raindrops on the window seem to stick to the window, although gravity is pulling them down. The CAH causes this. Next, the Wenzel model describes a situation when fluid meets both the concave and the convex surfaces. In this situation, increasing the surface roughness improves the wettability caused by the performance of chemical properties. For example, when surfaces are chemically hydrophobic, it becomes more hydrophobic as the surface roughness increases. Finally, the Cassie -Baxter Model describes a rough surface that only meets fluid by its convex surface.

Through the long history of anti-fouling, we can tell that there is no universal way to solve all the fouling problems. Antifouling history began with the Phoenicians, who are believed with the first group of people to prevent marine biofouling on their wood ships by making sheets of lead and copper. They also created coatings containing copper, arsenic, and mercury covering boat shells.

Nowadays, along with industry development, fouling in industries has given its appearance. For heat exchange, fouling occurs since unwanted materials such as scale, dry solids, insoluble salts, and algae accumulate and deposit on the internal surfaces of the heat exchanger. Scientists have developed several ways, including using tributyltin, copper, and some other biocides, to deal with the problem. Although from these two examples of antifouling, we can see that there is no universal way to solve all the fouling problems, we still need to develop methods for antifouling in each area. In this passage, we will talk about different anti-fouling techniques for different fouling problems.

2. Lotus effect

2.1. Introduction of the lotus effect

The Lotus effect refers to objects' superhydrophobic and self-cleaning characteristics, just like lotus leaves. From a macro perspective, since the contact angle between the water drop and the lotus leaf is more significant than 150 degrees, the lotus leaf's surface is hydrophobic. When the water drops fall on the lotus leaf, it will form a water drop, which will roll down if it is slightly tilted. Therefore, the lotus leaf can quickly resume drying after heavy rain. It can be found under the microscope that there is a layer of fluff and some nanoparticles on the surface of the lotus leaf. Water will form spheres on these particles, removing the dust when they roll off so that the lotus leaf has a self-cleaning effect.

Figure 2 shows the structure of the leaves of nelumbo Nucifera, which is the scientific name for lotus, on micrometer scales. As this figure shows, the surface of the lotus leaves is full of papillose epidermal cells. Therefore, when the water droplets contact the leaves, the water easily sits on the apex of the papillae because the air bubbles fill the trench between the papillae. That is the reason the leaves of lotus are superhydrophobicity.

DOI: 10.54254/2755-2721/7/20230483

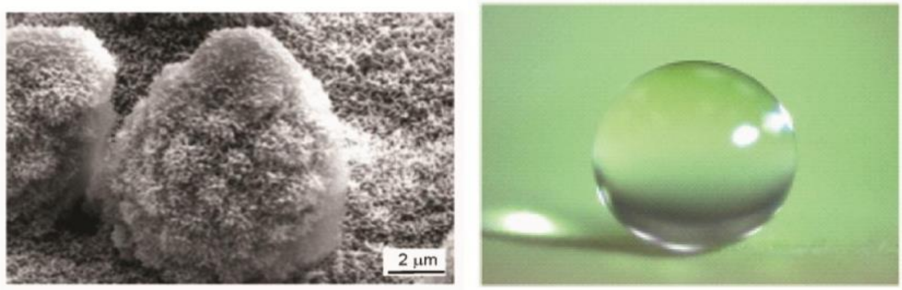

Figure 2. Lotus Effect.

2.2. Anti-fouling methods related to lotus effect

Drawing on the lotus effect, we must have three characteristics to prepare anti-fouling coatings or surface materials: hydrophobic surfaces with low surface energy, appropriate surface roughness, and low sliding angle. To realize the lotus effect, we can adopt two methods. One is to add super hydrophobic agents, such as fluorosilicone surfactants. In this way, the coating surface can have ultra-low surface energy, so dust is not easy to adhere to. The other is to simulate the concave-convex microstructure of the lotus leaf surface to design the coating surface to reduce the contact area between pollutants and the coating. This way, the pollutants cannot adhere to the film's surface.

2.3. Potential applications of similar surface

Nature gave birth to the lotus, a super capable plant, and humans can also follow nature and use bionics to prepare bionic "artifacts" to serve our daily life. First, we can use the lotus effect to make many kinds of paints. In the process of producing emulsion paint, we use some particular substances such as silicone lotion, a little emulsifier with long-lasting hydrophobicity, and form a nano-microstructure, so that the film has a surface structure similar to lotus leaves and achieves the function of water repellent and cleaning. Moreover, we can use the lotus effect to produce waterproof and moisture-permeable fabrics, such as tents and food preservation bags, which have a wide range of applications. This fabric has a soft feel, good drapability, and a bright luster. Therefore, it is a perfect choice for home and travel.

3. Different kinds of fouling and artificial Antifouling Surfaces

3.1. Introduction

To begin with, we need to classify the main ways of anti-fouling. We can sort it into different types ways based on the method they used to anti-fouling. First is Self-Cleaning. Second is Anti-fouling coatings The modern self-cleaning coating is based on the unique structure discovered on lotus leaves. That specific structure significantly improved the contact angle of water drops among the lotus leaves, causing the drop to roll down from the surface quickly. This discovery was based on a mechanism to let water drops take those fouling away with them while dropping down from surfaces. Until now, the main application of self-cleaning coatings has surfaced, often having fouling contact with a high possibility of meeting water flowing upon them, such as glass windows, culverts, or heat exchangers.

Anti-fouling coatings have the same feature as self-cleaning coating: they are both a solution through changing the contact surface to fouling but achieve their goal through different principles. Anti-fouling coating focus on stopping fouling from remaining on the surface or letting them be easy to get clean instead of letting nature element cleans them away. In addition, anti-fouling coating uses a specific solution to deal with different types of fouling, like using a special response polymer to kill biofouling or degrade oily staining.

3.2. Bio-fouling

Bio-fouling refers to the unexpected accumulation of microorganisms, plants, algae, or small animals on artificial or natural surfaces with mechanical function, causing surface functional deficiencies. In this review, we divide biological fouling into microfouling and macrofouling. Microfouling refers to the formation of biofilms attached to surfaces. Macrofouling refers to attached organisms such as barnacles, soft corals, and seaweed. Whether a surface is micro or macro-fouling, the degree of fouling is influenced by several different factors. The temperature, which profoundly influences the growth rate and breeding period of Marine animals, plays a role in the settlement of microorganisms. Geographical Location, species diversity, and the amount of solar radiation also play a role.

According to figure 3, biofouling steps can be separated into four stages: First, the settlement of a layer of organic carbon called the conditioning layer. Second, the bacteria spore colonizes this conditioning layer. After that, this substrate enables the growth of some larger organisms, such as protozoa and macroalgae. And then, the surface experiences fouling from increasingly complex organisms, like mussels and barnacles. Figure 3 shows each stage of fouling accumulation.

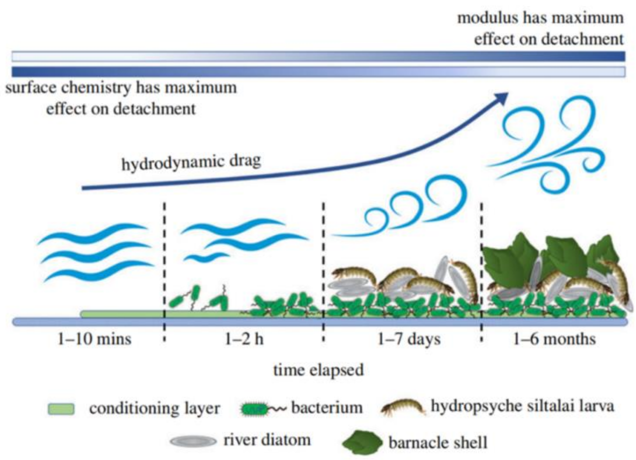

Figure 3. Stages of bio-fouling accumulation.

Biofouling causes significant health risks, environmental impacts, and economic losses in the medical, Marine, and industrial fields. For example, in the medical field, microorganisms foul medical apparatus and instruments, like orthopedic implants, catheters, and hemodialysis equipment, causing expensive maintenance costs and risk of infection. In addition, the study has shown that more than 45% of biofilm infections can be traced to medical recommendations for biofilm infections. For example, in 1998, United States hospitals count that 9 percent of 9000 patients using a ventilator acquired ventilator-associated pneumonia, which increased the average hospital stay costs by $40000 making ventilator.

For the Marine field, biofouling can lead to increased instrument costs, reduced speed, environmental problems, corrosion, and safety hazards. For buoys like Sofar Oceans Spotter, microfouling like algae and other organisms' adhesion on the solar panels impeded the buoy's power production. In addition, micro-biofouling can directly influence the weight and size of the spotter's buoy and drag the buoy under the surface, causing a severe impact on observation data.

Over the past centuries, toxic chemicals have been the fundamental solution to Biofouling. However, their use is now under strict control, sometimes even banned from application due to the various damage they cause to the natural environment. For example, Tributyltin-Oxide has been used against Bio-fouling as an additive to chemical coating for more than 40 years. However, because of their various harmful effects on the environment, including their toxicity to a variety of substances, including Marine animals, and their high carcinogenicity to humans, the use of such chemicals have been banned in areas of almost all countries. On the other hand, physical methods like manual cleaning are not suitable for all circumstances, especially for some surfaces that humans can hardly reach, which limits the application to their use. Research on this difficulty over the last two decades is mainly focused on self-cleaning surfaces. Combining hydrophobic surfaces with chemically bound antimicrobial agents, these new strategies eliminate most of the environmental threats caused by unbound chemical biocides.

The latest studies show that the main ways against biofouling can be divided into five main directions: Chemical Control, Physical Control, Limiting Nutrients, Biological Control, and Electrokinetic control.

Chemical Control refers to using chemicals or biocides to control microbial activities. Using biocide, oxidizing or non-oxidizing, to kill microbial can be separated into three stages: First, uptake at the target cell wall. Second, the fungicide penetration into the cell eventually leads to the death of the target cell due to the loss of the coherent structure and function of the cell. Until now, the primary oxidizing biocide in use is called Chlorine. On the other hand, the main non-oxidizing includes Aldehyde, quaternary ammonium compounds, isothiazolinone, organosulphur compounds, and detachment-promoting agents like surfactants.

Physical Control is to control surface biofouling without the use of chemicals so it could avoid potential problems associated with those chemicals and their targets, like antimicrobial resistance and environmental hazard. The technique of Physical Control includes backflushing, backwashing, pulsed flow, and cross flushing, and a new way discovered recently by using ultrasonic waves to increase and decrease flux rhythmically, which minimizes microbial attachment.

The nutrient restriction is another way to control biofouling by limiting the amount of biodegradable dissolved organic carbon and assimilable organic carbon. Limit phosphate in liquid media and reduce biofouling. The technology is highly efficient and environmentally friendly.

Biofouling by biological control uses microorganisms within the biofilm or internal mechanisms of other microorganisms or organisms to interfere with their presence. For example, disturbance mechanisms such as quorum sensing can interfere with or control biological contamination. The use of bacteriophages is another widely used method to control biological contamination, which has been widely used in agriculture, the food industry, the medical industry, and membrane filtration systems.

3.3. Ice fouling

Ice fouling is an unwanted accumulation of ice (ice, snow, frost, glaze, rime, or mixtures) on surfaces. This adhesion of ice on the surface creates many problems in different areas, including aviation, hydropower, telecommunications, navigation, electrical distribution, and all forms of transportation.

This review mainly covers the different approaches to anti-ice fouling surface design. Nowadays, in industry, the standard methods to deal with icing include 1) Freezing Point Depressants, engineers, developed porous leading edges that could anti-ice the wings during flight. The stainless-steel leading edges were provided with slots through which passed ethylene glycol. It is mainly used for deicing the wing, propeller, and fuselage of aircraft; 2) Thermal Melting is used to clean the ice off the aircraft's surface. The most prevalent thermal anti-icing technique is the use of hot bleed air from the engine's high-pressure compressor; 3) The surface deformation reduces the energy required for anti-icing. The ice cracks and anti-bonds from the surface, and aerodynamic forces carry the particles away.

To achieve anti-ice, this question addressed how to reduce the adhesion strength of ice and how to prevent the formation of condensation nuclei. Generally, superhydrophobic surfaces are first tried in studies on anti-ice surfaces. Under Cassie -- Baxter State, the air diaphragm at the contact surface can reduce heterogeneous ice nucleation by utilizing low surface energy and nanostructure. However, some studies point out that the anti-ice of superhydrophobic surfaces lacks efficiency at high humidity and low temperature. Some studies have shown that frost formation occurs quickly on rough superhydrophobic surfaces with relatively high humidity, and subsequent adhesion of ice to the surface is much higher than on smooth substrates. This indicates that this superhydrophobic surface is not suitable for anti-ice applications.

DOI: 10.54254/2755-2721/7/20230483

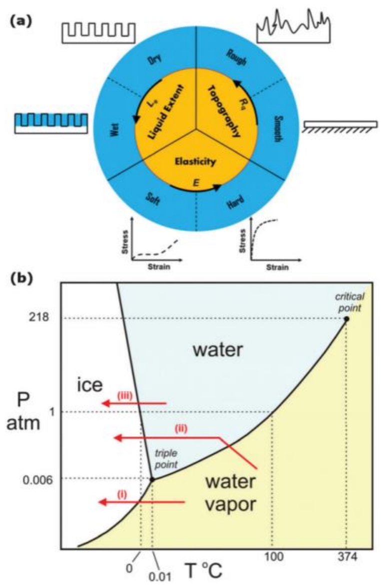

Figure 4. a) A framework for classifying recently developed ice-repellent coatings. B) Water phase diagram showing three different formation pathways for water-based solids formed by water temperature and pressure changes.

Multi-scale micro/nano hierarchies usually provide superior performance to solve this problem. Figure 2 shows an example of a recently developed coating. Barthwal et al. prepared hybrid structures on aluminum substrates using chemical etching and anodizing aluminum surfaces.

Liao et al. prepared aluminum-based superhydrophobic surfaces with micro/nanostructures in a similar way. These surfaces significantly delay ice nucleation and formation.

Wang and his team proposed a shift in ice-proof surface design principles from static properties, where changes in ice-base contact areas are never considered after ice formation, to a focus on achieving dynamic changes in the chemical/physical state of the ice/substrate/ice-substrate interface to enhance ice-proof performance. These anti-icing surfaces as called dynamic anti-icing surfaces (DAIS). DAIS integrates an active strategy into the evolution of the ice-base contact area to reduce the resistance to anti-icing. For example, the integration of dynamic antifreeze secretory capabilities into superhydrophobic surfaces can provide continuous assistance in anti-icing even after freezing. DAIS exhibit higher durability, wider temperature tolerance, and better environmental adaptability.

3.4. Precipitation fouling

The fouling commonly in hard water operating boilers and heat exchangers is called Precipitation fouling or Crystallization fouling. Most of the time, Precipitation fouling can be caused by Supersaturation, where the crystal structure of the fouling forms at the surfaces. The rate of Precipitation fouling directly refers to the crystallization rate. It is affected by multiple causes such as flow hydrodynamics, bulk, sub-stratum temperature, suspended particles, surface roughness, and water quality like pH and hardness[1]. The rise of temperature or the increase of surface roughness greatly enhances fouling. On the other hand, it affects the rate of fouling and decides the type of fouling forming on the surface, along with the water's hardness.

Usually, the primary type of precipitation fouling is Calcium Carbonate and Calcium Sulfate. Calcite is reported as the most thermodynamically stable form of $CaCO_3$, and Vaterite is the least stable. Mostly, Calcite forms at room temperature and has a hexagon crystal form. Calcium Sulfate, on the other hand, is one of the most commonly encountered scale-forming materials.

As figure 5 shows below, the type of Crystallized Calcium Sulfate can be subdivided into three forms based on the aqueous solution: Gypsum ($CaSO_4 \cdot 2H_2O$), Calcium Sulfate Hemihydrate ($CaSO_4 \cdot 0.5H_2O$) and Anhydrite ($CaSO_4$).

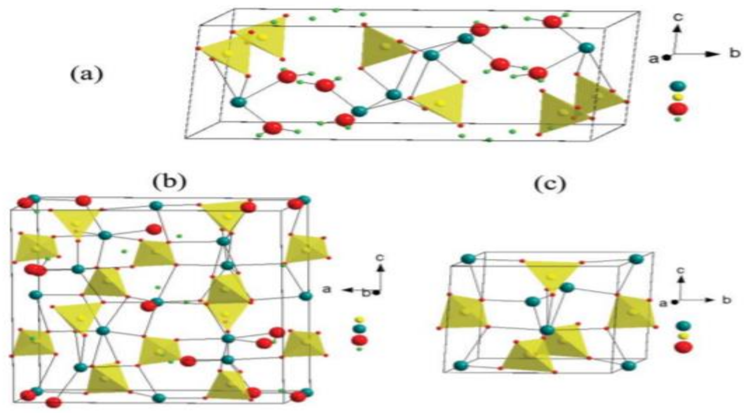

Figure 5. Crystal structure.

Gypsum is usually sediment between 40-98 degrees, while Anhydrite and Hemihydrate are usually sediments above 98 degrees. In addition, investigations show that the solubility of Calcium Sulfate is greatly affected by the presence and concentration of other ions in the systems, and the water quality, such as hardness, has a magnificent effect on the induction time and precipitation of Calcium Sulfate.

Until now, supersaturation's effect is widely considered the only important factor in solving precipitation fouling, which determines the intensity of scaling. It could be achieved when the solution concentration is beyond the solubility limits of its constituent. Reports show that increasing the initial solution concentration increases the fouling rate of $CaCO_3$ and $CaSO_4$ [2]. In general, the increase in pH value causes the precipitation fouling to decrease and vice versa. When only considering $CaCO_3$, pH is the most critical factor. However, pH seems not to be the main reason affecting $CaSO_4$. With a pH range of 10-12, Aragonite, which Calcite transforms, rises under these circumstances. Nearly pure Calcite was obtained at a pH lower than 11, while almost pure Aragonite resulted in a pH lower than 10.

Till now, there are two main types of ways to control Precipitation Fouling. The chemical control method mainly determines the type of ion causing precipitation fouling.

Table 1. Using acid to change pH value is an efficient way to control high-valence metallic ions formed by fouling.

Foulant	Cleaning solvent
Iron Oxides	Inhibited hydrofluoric acid, hydrochloric acid, sulfamic acid, EDTA, or mono-ammoniated citric acid
Calcium and magnesium scale; oils or light greases	Inhibited hydrochloric acid, citric acid, EDTA, sodium hydroxide, trisodium phosphate with or without detergents, water-oil emulsion

Solutions vary in physical ways due to the different targets they tend to use. One way is to use a unique surface structure to reduce the work of adhesion between the surface and deposit and increase the sheer wall stress. Another way through physical control is to treat hard water to prevent or mitigate fouling before using it [3]. This type of way includes using a magnetic field, electric field, vortex flows, and ultrasound. Surface charge alteration and sudden pressure change also work physically.

3.5. *Dust fouling*

Dust Fouling or Particulate Fouling, defined as the accumulation of particles on a heat transfer surface that forms an insulating layer, is a similar type of fouling compared to Precipitation Fouling when in water, judging by the crystal structure's forming position. Both are affected by Supersaturation; Dust Fouling is the diffusion of colloidal particulate matter to the surface. Unlike precipitation fouling, van der Waals Force and Born Energies control the attaching of particles, leading to particle Dust Fouling. Also, in a higher degree of supersaturation environment, Dust Fouling increases as there is a higher possibility for crystallization and immediate nucleation. However, the sediment in Dust Fouling is usually polypore and pliable for removal.

Due to Dust Fouling's unique characteristic in bulk, transport and capturing particles before nucleation becomes a possible and operational solution for Dust Fouling. Ignoring the same anti-fouling method, like Precipitation Fouling after nucleation happened, a unique way for minimizing Dust Fouling is to control the flow direction of bulk.

Figure 6 shows the mechanism of the experiment studying the connection between flow direction and dust fouling in bulk, and figure 7 shows the variable settled in the experiment.

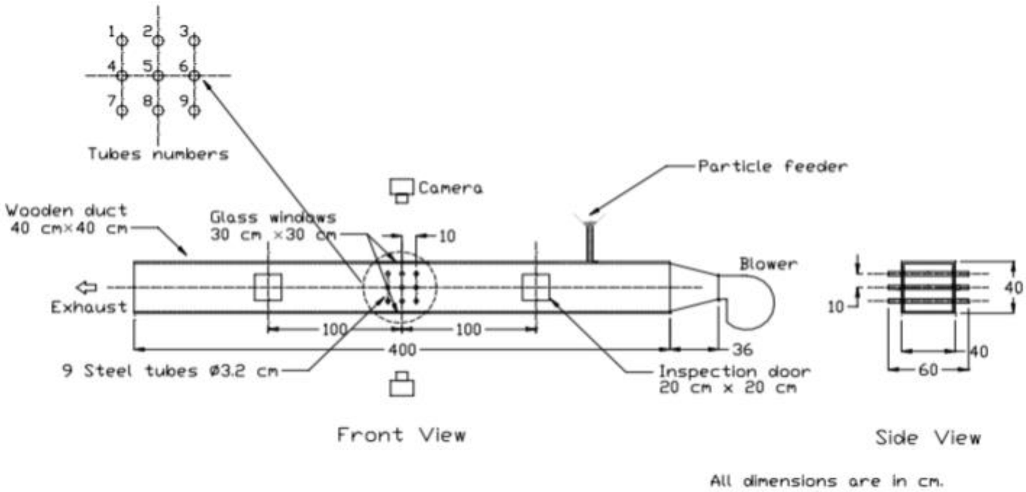

Figure 6. Experiment with how flow direction affects particulate fouling in heat exchangers.

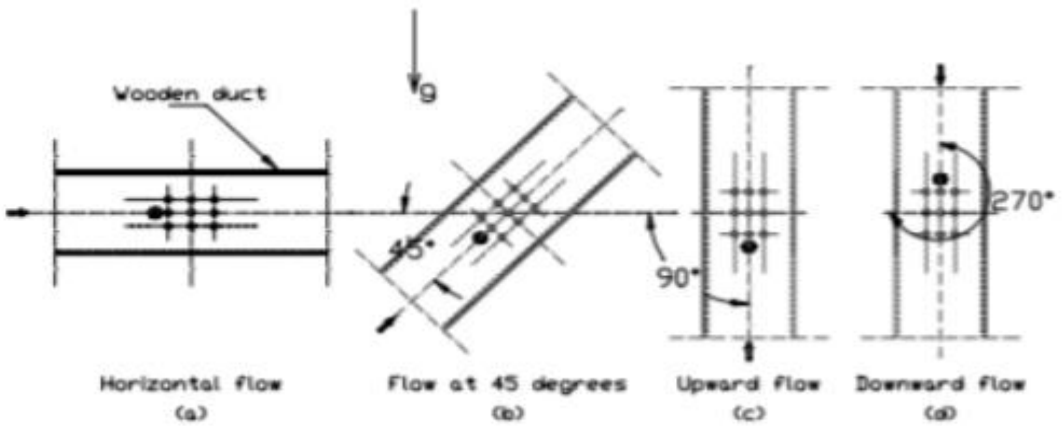

Figure 7. Three setups used to study different orientations of flows in the experiment. :(a) level flow, (b)flow at a 45-degree angle, (c)vertical flow.

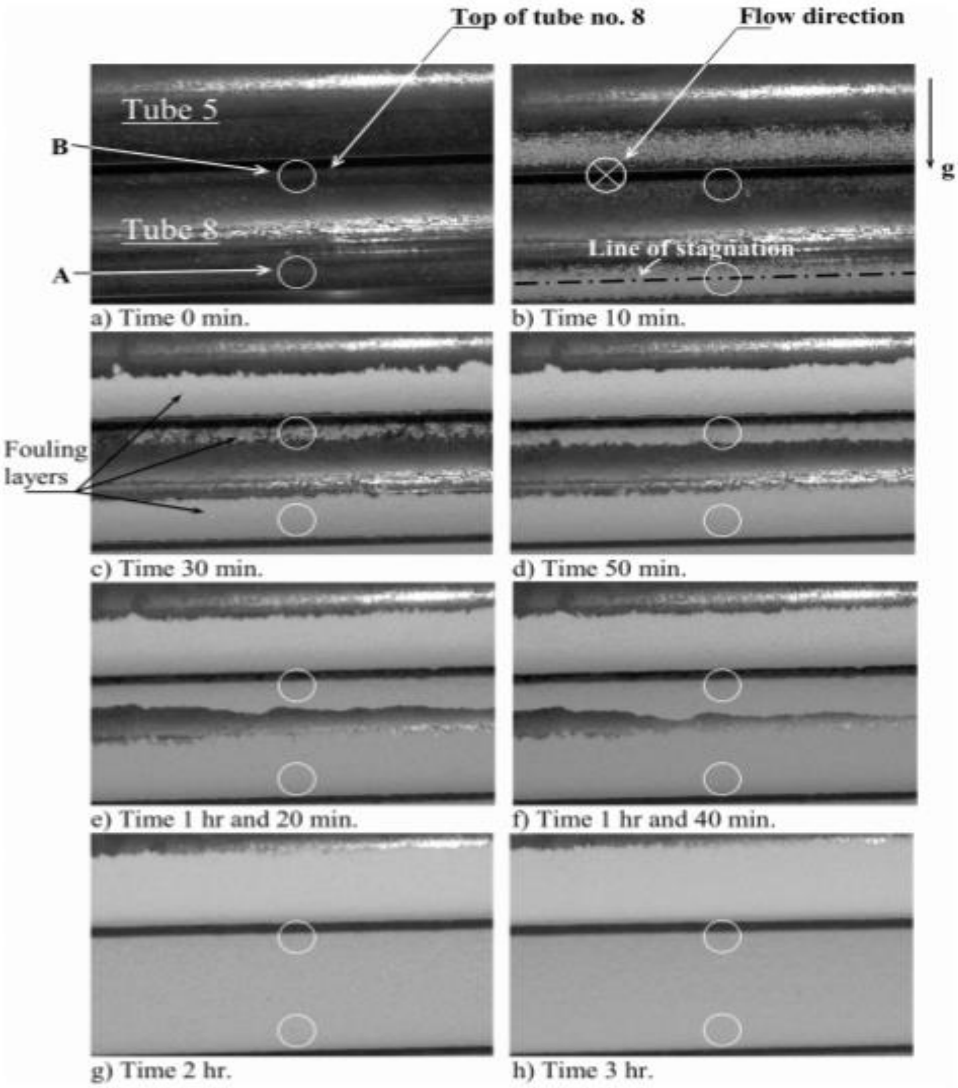

Figure 8. Tube.

In conclusion, according to the experiment result, figure 8 shows above, all orientation fouling starts precipitating from the tunnel's upper area, and the lower half sector fouls much slower than the upper half. On the other hand, the downward flow only starts fouling at one position while the horizontal, upward, and 45 degrees flows start at two positions, indicating that downward is the best flow direction to oppose particulate fouling.

3.6. Chemical reaction fouling

A chemical reaction on the heat transfer surface causes chemical reaction fouling. This kind of fouling includes organic and inorganic substances, most of which are artificially manufactured products and secondary pollutants. According to the damage caused, chemical reaction fouling can be divided into environmental hormone damage, carcinogenic, teratogenic, mutagenic damage, and sudden pollution of toxic chemicals.

Since chemical reactions will bring severe fouling to our production and life, we must take various measures to solve this fouling.

First, we can use chemical functionalization to deal with this fouling. This strategy includes selecting and creating a surface chemical that either reduces the substrate's surface energy or allows the surface

DOI: 10.54254/2755-2721/7/20230483

to interact with the fouling material in a specific way. Minimizing the energy of the surface can reduce the strength of any potential adhesion interaction between the surface and the dirt material. Surfaces designed with this approach commonly use silicones or fluorinated polymers, among the lowest surface energy materials.

The controlling surface micro-texture is also a good method if the reaction product is liquid. By designing the surface texture of objects, we can deal with liquid fouling in the way we want. However, in the case of solid fouling, this method is not feasible because it may increase the contact area between the adhesive and the interface and may also increase the potential interface, making the fouling treatment more difficult.

3.7. Additional challenge

However, despite already countless anti-fouling ways, there are a few challenges that cannot be avoided. First is the damage to the environment. To achieve the ability of anti-biofouling, most chemicals put in use are toxic, leading to environmental damage. For example, Tributyltin-Oxide was banned from use due to toxicity. Another problem is the difficulty of encountering compound fouling. The most common way for anti-fouling is to use a specific solution for a specific type of fouling. However, fouling is usually complex, which means multiple types of fouling exist simultaneously, and each of those fouling reacts together, causing a single measure even harder to take effect. The final problem is the cost problem. It could be revealed in a different area, such as the high cost of production of the anti-fouling coating or the high-power consumption in some electrical anti-fouling measures.

4. Conclusion

This review has discussed the super-hydrophobic and self-cleaning surfaces in nature, including lotus leaves. Their functional surface helps them adapt to their living environment. The artificial surface structure in this paper is mainly based on the bio-inspired structure inspired by the self-cleaning surface in nature.

Fouling is the adhesion or adsorption of solid contaminants to a given surface. We discussed various solid fouling, including biofouling, ice fouling, precipitation fouling, dust fouling, and chemical reaction fouling. Each form of solid fouling is problematic or dangerous for various applications and industrial processes. Currently, no single engineered surface can solve the solid fouling problem extensively, so this paper mainly reviews various complex micro or macro structures and coatings that play a role in different fouling.

Acknowledgment

Shengjun Niu, Surui Tang, Lezhi Wang, Jiayan Zhou, and Ningfeng Zheng contributed equally to this work and should be considered co-first authors.

References

[1] Composite Fouling of Heat Transfer Equipment in Aqueous Media - A Review, Heat Transfer Engineering, 21:3, 34-42, DOI: 10.1080/014576300270889, Inorganic Fouling, Paragraph 3, line 1, http://dx.doi.org/10.1080/014576300270889

[2] Sudmalis, M., and Sheikholeslami, R., Coprecipitation of $CaCO_3$ and $CaSO_4$, Canadian Journal of Chemical Engineering, vol. 78, no. 1, pp. 21–31, 2000//Kazi, S. N., Duffy, G. G., and Chen, X. D., Mineral Scale Formation and Mitigation on Metals and A Polymeric Heat Exchanger Surface, Applied Thermal Engineering, vol. 30, no. 14–15, pp. 2236–2242, 2010

[3] Zhao, X., & Chen, X. D. (2013) A Critical Review of Basic Crystallography to Salt Crystallization Fouling in Heat Exchangers, Heat Transfer Engineering, 34(8-9), 719–732. doi:10.1080/01457632.2012.739482,FOULING MITIGATION STRATEGY, Physical method, Physical Water Treatment