Template Preparation and Experimental Study on Superhydrophilic-Superoleophobic Nano-structures Surfaces Based on Titanium Mesh Membrane

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Abstract. With the development of industrial process, the crude oil leakage of industrial oil wastewater is increasingly serious. The development of efficient and environmentally friendly separation mesh membrane technology is the best way to solve the water pollution problem. With the rapid development of micro-nanotechnology, the wetting change caused by surface structure (micro-nano scale) that can solve the problem of fabrication for oil-water separation mesh. If the liquid contact angle at the surface is less than 10\degree, the surfaces are called superhydrophilic surfaces. Meanwhile, the liquid contact angle is greater than 150\degree, the surfaces are called superhydrophobic surface. Surface with superhydrophilic/superhydrophobic is also known as special wetting surfaces. The special wetting surface is fabricated by coating / spraying. The process is simple and easy to operate. By constructing the multi-stage surface roughness and reducing the surface energy, the titanium mesh with different orders are used as the base, the mesh membrane with special superhydrophilic-superoleophobic properties is constructed. Comparing the influence of titanium mesh with different molybdenum numbers (mesh size) on hydrophilic/hydrophobicity, the mechanism of the macroscopic size of the pore spacing substrate on the special surface wetting is analyzed. The preparation of ultrahydrophobic multi-stage surface roughness titanium mesh is realized. The experimental analysis of oil and water separation effect is carried out. For the preparation of high-efficiency oil-water separation mesh film that can be used in industrial production. The oil and water separation mesh membrane was prepared by the titanium mesh substrate to achieve effective oil and water separation.

1. Introduction

With the development of economy, it is increasingly prominent that the environmental pollution problems of oil wastewater and crude oil exploitation leakage in industrial production. The separation of oil wastewater mainly includes gravity separation, centrifugal separation, ultrasonic separation, gas float method, electric field method, condensation method, adsorption method, biological method and membrane separation method \cite{1,2}. By comparing the above methods, the most popular method is the membrane separation method. The mesh membranes commonly used for oil-water separation include: superhydrophobic/super-oleophilicity type and superhydrophilic/superoleophobic type. The preparation process of superhydrophobic/super-oleophilicity is relatively simple and the preparation materials are...
easy to obtain. But there are many shortcomings in the practical engineering application process[3,4]. For the oil-water separation by filtration method, the oil droplets are easy to attach or blocked in the filter mesh hole. The oil-water separation mesh film is easy to suffer pollution and cause failure. And it needs high requirements for the viscosity of oil in the oil-water mixture[5]. Due to the different proportion of water and oil, the small proportion of oil is layered above the mixture, resulting in the inability to use gravity driving method for separation of oil and water. Requiring special processes for auxiliary driving and increasing the cost of separation. Relatively by contrast, the superhydrophilic/superoleophobic type can realize the adsorption and filtration of water. The mesh material is not easy to pollution. The use and circulation performance is good. The service life is greatly extended. Since the density of water is generally larger than oil, gravity driving can be used as the power of oil and water separation, energy saving, consumption reduction and simple operation. Therefore, superhydrophilic/superhydrophobic material mesh membrane is one of the directions of research. However, the surface energy of water can be larger than that of oil. The surface of hydrobic material is also hydrophobic. So the preparation of hydrobic material is difficult[6].

Current reliable methods to constructing such mesh membranes include two methods: One is to modify the surface properties, reducing the surface energy to simultaneously construct the hydrophobic surface simultaneously; The second is to establish graded micro-nanostructures on the surface to increase the surface roughness. The study of membrane surface wetting begins with bionics, self-cleaning of the surface of lotus leaves in nature. Fish remain clean and unpolluted in oil-polluted rivers, and the special phenomenon that water striders can walk freely on the water surface. The above are superhydrophobic to water. it provides design ideas for special wetting surface[7]. Scholars from various countries have conducted extensive theoretical and experimental research on superhydrophobic/superhydrophilic oil separation mesh membrane. However, the preparation of superhydrophilic/superhydrophobic mesh membrane is still being explored. A variety of superhydrophobic/hyperhydrophobic mesh separation media with different preparation methods, different substrates and different properties are explored for the research[8].

In this paper, a metallic titanium mesh is used as a substrate, by using titanium mesh number with 40/100/200 items as mesh infrastructure. The surface of the titanium mesh is modified by constructing a hydrophilic group of multi-stage nanostructures by using spraying/immersion. Three different numbers of titanium mesh are obtained. Comparative analysis of oil and water contact angle of metal titanium mesh with different numbers. Making a simple device for oil and water separation for oil and water separation test that provide technical feasibility for the next engineering application.

2. Fabrication of microstructures on titanium mesh

2.1. Materials
Titanium with mesh number40/100/200 (purchased from Rui Metal Store), TiO₂ Nanoparticles (P5~10)(Aladdin, 99.8%), Hexadecane(Sigma Aldrich, 99%), Ethanol absolute(Aladdin, 99.5%), FS-50(Capstone), Ultra-pure water was used in all experiments.

2.2. Laboratory apparatus

| Table 1. Laboratory apparatus. |
|--------------------------------|
| **Model / Features** | **Manufacturer** |
| Spray gun | 116BK | Hangzhou Shenchao Co., Ltd. |
| Magnetic stirrer | 85-2 | Droide Co., Ltd. |
| Ultrasonic cleaner | PS-20 | Whale Control instruments Co., Ltd |
| Contact angle measuring meter | DropMeter A-60 | Haishu Mai Testing Co., Ltd |
| Vacuum drying oven | DZF | Shanghai Yiheng Co., Ltd. |
2.3. Methods
Cut and sample the titanium mesh with different numbers of 40/100/200 respectively, then polished with sandpaper to remove impurities such as oxides on the titanium mesh surface. The polished titanium mesh was cleaned with acetone, anhydrous ethanol and deionized water ultrasound for 20 minutes. The cleaned titanium mesh passes 60 ℃ for constant temperature drying for 1 hour. Next, a hydrophilic TiO₂ nano-solution is prepared. 50ml anhydrous ethanol is taken aside. 2g FS-50 added to ethanol solution, mixing for 2 hours with a magnetic mixer. then add 1g TiO₂ nanoparticles to the stirred solution. Continue stirring fully for 2 hours. Finally, the prepared solution is sprayed to the titanium mesh surface, keeping spray nozzle 15cm from titanium mesh substrate. The spraying uniform spraying time is not limited in the spraying process. Or that an immersion method may be used, diaching the titanium mesh substrate in the prepared solution. Metal mesh is need to soak in solution by 60s-120s. Finally, sprayed / dipped titanium mesh is placed in vacuum drying oven for 4 hours at temperature:60℃. A titanium mesh with different mesh numbers for 40/100/200 with superhydrophilic/superhydrophobic characteristics is obtained after cooling.

2.4. Characterization
The TiO₂ nanoparticles selected in the experiment were 50nm diameter particles. It can increase the surface roughness by preparing a nanoparticle suspension solution for surface modification with spraying/infiltration to make it attach to the metal titanium mesh substrate. The construction of surface multi-scale micronano roughness is realized by increasing the surface roughness structure of the metal mesh. According to the influence of infiltration characteristics of contact surface, the constructed multi-stage roughness structure can realize the liquid drainage characteristics of the surface interface. Also its surface energy is reduced by FS-50 fluoride. Both ways have achieved improving the characteristics of network drainage. Surfaces with hydrophobic properties can be made hydrophilic by grafting of hydrophilic substances. Ethanol solution containing FS-50/TiO₂ include fluoride reduced surface energy and mass material with hydrophilic characteristics. By attaching it to the titanium substrate network with a different number of entries later. A titanium base filter mesh membrane with hydrophilic/hydrophobic can be constructed. The comparison of different number of titanium mesh substrate is made. Its hydrophobic characteristics of titanium mesh base were obtained by experimental analysis.

3. Hydrophilic-hyperhydrophobic of titanium mesh substrate

3.1. Contact angle measurement
According to the special wetting interface theory, when the water/oil contact angle at the contact surface is less than 10°, such surfaces are called superhydrophilic / liquid surfaces; when the contact angle of the water/oil on the contact surface is greater than 150, such surfaces become hyper-hydrophilic/oil surfaces. For a titanium mesh of three orders prepared in this paper, the oil-water contact angle was measured on the three titanium mesh 40 / 100 / 200 respectively by using contact angle meters. Using pure water and positive-hexane on the base of three orders to get contact angle measurement using a contact angle tester. According to the results, three kinds of titanium mesh substrate mesh membrane have a certain oil thinning. Drop orthohexane on a titanium net of 40/100/200, oil droplets gather into spherical. As shown in Figure 1. oil and water separation mesh membrane with 200 mesh number has the hydrophilic and oleophobic properties: contact angle of the oil and titanium mesh is 152.4°, contact angle of water and titanium mesh is 0°. As shown in Figure 2.oil and water separation mesh membrane with 100 mesh number has the hydrophilic and oleophobic properties: contact angle of the oil and titanium mesh is 110.1°, contact angle of water and titanium mesh is 0°. As shown in Figure 3. oil and water separation mesh membrane with 200 mesh number has the hydrophilic and oleophobic properties: contact angle of the oil and titanium mesh is 152°, contact angle of water and titanium mesh is 0°.
According to hydrophilic test, water droplets are observed to fully infiltrate the titanium mesh after placing water droplets on the net base of three counts. Comparison of titanium mesh substrate with hydrophilic/oil thinning effect with three mesh numbers. Titanium mesh substrate is better hydrophilic to water with fully spread. Oil-water separation mesh film prepared by titanium mesh base of 200 objective has super oil thinning characteristics.

3.2. Oil and water separation experiment

By measuring the contact angle of three order titanium mesh, the 200 mesh film is super hydrophilic/superhydrophobic in three orders. Therefore, 200 mesh number is selected as the mesh film of the oil-water separation experiment. First, the oil-water mixture is prepared by mixing 30ml orthohexane with 30ml purified water stained with methyl blue. The oil-water mixture is placed in the beaker for reserve. Oil and water separation device using double pass barrel/test bench/200 titanium mesh film. Process steps are: Cutting the 200-eye titanium mesh into a round with same-section diameter as the cylindrical section. Attaching it to the double cylinder side, securing the cylinder to the metal stand and keep the open portion upward. It is placed that a 100ml empty beaker directly below the titanium mesh. Then the oil-water mixture is slowly poured from the opening into the cylinder. The process of separation of oil and water separation device is shown in Figure 4. After the oil-water mixture is completely poured into the cylinder. The stained blue water flows through the titanium mesh into the lower beaker. Orthohexane is blocked by the titanium mesh in the upper cylinder. Reliable oil and water separation is achieved.
4. Conclusion
This research object is titanium mesh metal as the base. A layer of multistage roughness structure with nanostructure with three different orders. The surface energy of structure is reduced by the surface modified by fluoride. Multi-stage nanostructure also improves the surface roughness. Thus hydrohydroproperties is produced. Since the presence of a hydrophilic group material is achieved as hydrophilic by constructing the titanium mesh surface modified by fluoride and titanium dioxide. The hydrophilic and oily mesh membrane is realized. According to the experimental results: titanium mesh with 200 mesh number can realize the functional characteristics of Superhydrophilic/Superoleophobic nanostructures surfaces. The titanium mesh in the remaining two orders also exhibit superhydrophilic / hydrophobic properties. It shows that the base order number of metallic titanium mesh has a great influence on superhydrophilicity. It is also proved that the superhydrophilic/superhydrophobic mesh membrane is achieved by the oil-water separation test. Superhydrophilic/Superoleophobic nanostructures surfaces play an important role in pollution control of industrial crude oil wastewater. Further study is necessary on the mesh membrane service life and separation efficiency of oil and water.

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Figure 4. The separation process of oil and water.