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Study of PVDF Tubular Ultrafiltration Membrane for Separating Oil/water Emulsion and Effect of Cleaning Method on Membrane

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Abstract

Oil/water emulsion is treated with polyvinylidenefluoride(PVDF) tubular ultrafiltration membrane. The flux of PVDF tubular ultrafiltration membrane is tested by varying the operation pressure(from 0.06Mpa to 0.25Mpa), membrane surface velocity of flow(from 1.47m/s to 3.69m/s) and system running time (from 1h to 20h). The average membrane flux is up to 108.2 L/(m^2.h) in proper experiment conditions. Then some cleaning methods are studied and the chemical cleaning has the best effect, the flux restoration rate is more than 92%. Oil concentration in permeate water was less than 10 mg/L. The rejection rate of oil was more than 90%, The cleaning periods were 24h. Using PVDF tubular ultrafiltration membrane to treat oil/water emulsion is a feasible and economical method.

Keywords: PVDF, Tubular ultrafiltration membrane, Oil/water emulsion, Separating, Membrane cleaning

1. Introduction

Oil/water emulsion are common by-products of manufacturing operations, such as the machining and washing of metal parts. Usually, over 90% of these solutions is water. The oil is chemically emulsified into the water phase because of the presence of surfactants. The entire mixture, even though it contains less than 10% total oil, can not be discharged, because the COD is up to 11000 - 37000 mg/L (Gao, 1989, pp.32-45 and Jiang,1986,pp.13-16). In addition, metals may be in it. So in most localities, these wastewater must be shipped off-site as hazardous waste which cost too much. Using traditional technology, such as chemical coagulation,to treat the oil/water emulsion is the commen method .Howere,the amount of sludge production is huge, which is likely to cause the secondary pollution. What’s more, the wastewater couldn’t be reuse after the treatment, which may cause the great waste of water .One the other hands,since there are high dense oil and organic substances in oil/water emulsion, large quantities coagulant as well as the high operating costs are needed (Jiang,1986,pp.13-16).Membrane filtration can be used to remove most of the water from the emulsion therefore reduce the volume of oil-containing solution.

Use ultrafiltration process to treat the oil/water emulsion not only can achieve the reuse of wastewater but also solve the secondary pollution problem (Lipp,1988,pp.161-177 and Bilstad,2001,pp.23-24). At present, there are many treatments with oil/water emulsion by using ultrafiltration or microfiltration membrane, such as flat membrane, hollow fiber membrane, ceramic tubular membrane. But the flux of flat membrane and hollow fiber membrane are too low and the ceramic tubular membrane is too expensive, which prevent from using of these membranes (Shao,1992). Because its low costs and high separating efficiency, the PVDF tubular ultrafiltration membrane show a bright prospect in separating oil/water emulsion.

2. Experimental

2.1 Materials and equipment

The oil/water emulsion was prepared with emulsified oil (No.1 machine factory in TianJin) and tap water. The sodium hydroxide, sulfuric acid, sodium hypochlorite (FuChen Chemical Ltd. Tianjin). Spongy rubber ball membrane cleaning system and evaluation system of membrane were equipped by lab. The oil concentration in the waste water is attainable by testing its absorbency with UV spectrophoto- meter (2450, SHIMADZU). PVDF tubular ultrafiltration membrane which rejection molecular weight were 100,000 (Tianjin Motian Membrane Eng&Tech Company).

2.2 Experimental methods

2.2.1 Membrane performance

This research used internal pressure PVDF tubular ultrafiltration membrane to treat oil/water emulsion. Under different running conditions, the flux and rejection rate to oil of membrane were investegated. The distilled water was used to determinate the pure water flux of membrane. First, the membrane filtrated distilled water under certain operation pressure for about 2h to stabilize the flux of distilled water. Then oil/water emulsion were instead , then the membrane flux was recorded in certain running time.

2.2.2 Cleaning methods

Using different cleaning membrane methods to compare their effects of cleaning (flux restoration rate). The flux restoration rate was determined as follows: First, the membrane filtrated distilled water under certain operation pressure for about 2h to stabilize the flux1 of distilled water. Then oil/water emulsion were instead and the flux was test after certain running time. Third, one of the cleaning method was used to clean the membrane. Last, the membrane filtrated distilled water again and flux2 value was test. The ratio between flux2 and flux1 was the flux restoration rate. The higher it was, the better the clean effect was .Scanning electron microscopy (SEM) to observe the surface of fouling and cleaning membrane. All the experiments were carried out under room temperature(20℃).

The cleaning methods include: washed by water, washed by alkaline solution (1.5%)and washed by spongy rubber balls. The spongy rubber ball cleaning system was shown in Fig.1, the spongy rubber balls were added into the system from ball circulator and circulated together with water. Thus turbulence were formed by these balls, with the balls colliding the interface of tubular ultrafiltration membrane, cleaning was achieved (Hao,2005,pp.75-80).

3. Results and Discussions

3.1 Effect on operation pressure

Fig.2. shows the flux of different oil concentration in oil/water emulsion change with operation pressure. Regardless of different oil concentration, all the flux increase with operation pressure increasing, and reached to maximum at 0.20Mpa. This maily because when the system runs, the membrane is compressed by the liquid, so the thickness of membrane decreased slightly which strengthen the liquid permeate resistance. When the operation pressure is beyond 0.20Mpa, the increase of flux caused by pressure increase is overcome by flux reduce caused by permeate resistance which increase with pressure increasing. So the flux decrease with pressure increasing when running pressure is beyond 0.20MPa.

3.2 Effect on membrane surface flow velocity

Fig.3 describes the membrane flux of different membrane surface flow velocity change with operation time. The flux increase significantly with the increase of membrane surface flow velocity, but the increase rate reduce. In addition, the flux decrease with the increase of running time under low flow velocity, while it is beyond 2.46 m/s, the flux almost unchange with the increase of running time. This is mainly because under high membrane surface flow velocity, the shear stress between flow and the membrane surface is large, which make it difficult for the oil drops in the water to adsorb membrane surface and reduce the fouling of membrane surface. When surface flow velocity is up to a certain level, this effect decreases, so the increase rate of flux decrease(Ma,2000,pp.191-200).

3.3 Effect on running time

Fig.4 shows the relationship between flux and system running time, the flux is gradually decrease with the increase of running time, after running 20h, the flux approximately reduce 30%. Obviously that is because of fouling of membrane. Therefore in the practical application, the membrane should be cleaned after the system running certain time in order to keep the steady flux.

3.4 The comparison of different membrane cleaning methods

In the treatment of oil/water emulsion using tubular ultrafiltration membrane, the flux was gradually decrease with the increase of running time, consequently different cleaning methods for the restoration of flux are studied. There were three cleaning methods in this research: chemistry cleaning, water cleaning and the spongy rubber ball cleaning, the effects of these methods had been compared in Fig.5.

It can be easily seen from Fig.5 that all of three methods can make the flux of membrane restore. But the effect of chemistry cleaning is better than the others. After the use of chemical cleaning, the flux almost fully restored to the intial value. The flux restoration rate is 95.7% while the values of water cleaning and spongy rubber ball cleaning are

40.2% and 75.6% respectively. From Fig.6 the flux was observed remained steadily in the following process. In the constantly running, membrane needs cleaning once a day.

Compared to the chemical cleaning and spongy rubber ball cleaning, water cleaning had the worst results, spongy rubber ball cleaning was slightly better than it, but still could not make the flux restore to the original value (Hao,2005,pp.75-80). The main reason is that the fouling (oil drops) attached on the membrane surface can be completely cleaned up by chemical cleaning, but not by the others. The water cleaning method could only partially remove the fouling on the membrane surface and spongy rubber balls which cycled in tubular ultrafiltration membrane system with cleaning fluid can most removed the fouling on the surface of membrane, so the flux can not fully restored.

In Fig.7 (a),the SEM micrograph shows that there are great mass of emulsified oil on membrane surface and well-distributed over the surface, thus the through resistance of water increased and the flux reduced. Fig.7 (b) shows the partial fouling still adhere to the membrane surface after the water cleaning. Fig.7 (c) and Fig.7 (d) show the membrane surface cleaned by spongy rubber ball and chemical solution, there are little emulsified oil on the membrane surface, so these two methods are feasible for the membrane cleaning.

3.5The rejection rate to oil of tubular ultrafiltration membrane

In this experiment, the oil retention rate of PVDF tubular ultrafiltration membrane are shown in Table 1. The rejection rate constantly increased with the increase of oil concentration of raw water. The PVDF tubular ultrafiltration membrane have the great rejection to oil in emulsion, the filtrate can meet the need of treatment to oil/water emulsion.

4. Conclusions

In the process treatment oil/water emulsion with the PVDF tubular ultrafiltration membrane, the flux of PVDF tubular ultrafiltration membrane is greatly influenced by the running pressure, membrane surface velocity of flow and the running time. Flux reached max value when the operation pressure is 0.20Mpa. It increased with membrane surface flow velocity increase, but the increase rate gradully reduced. It also decreased lentamente with the increase of running time. The average flux is 108.2L/(m2.h) when the running pressure is 0.20Mpa, membrane surface flow rate is 3.44m/s, the concentration of oil/water emulsion is 0.2g/L and the running time is 3 h.

The water cleaning method, the chemical cleansing and spongy rubber ball cleaning can make the flux restored after treatment of oil/water emulsion. The chemical cleaning methods was better and the flux can completely restore. The cleaning period is 24 h.

PVDF tubular ultrafiltration membranes have the great rejection rate to oil and the filtrate can meet the need of discharge or reuse. Using PVDF tubular ultrafiltration membrane to treat oil/water emulsion is a feasible approach.

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Table1.The Retention Rate to Oil of Membrane. Operation pressure was 0.20Mpa, running time was 6h, membrane surface flow rate was 3.44m/s

Concentration of raw water (g/L)	Concentration of filtrate (mg/L)	Retention rate (%)
0.2	6.5	96.8
0.6	9.6	98.4
1.0	9.5	99.0

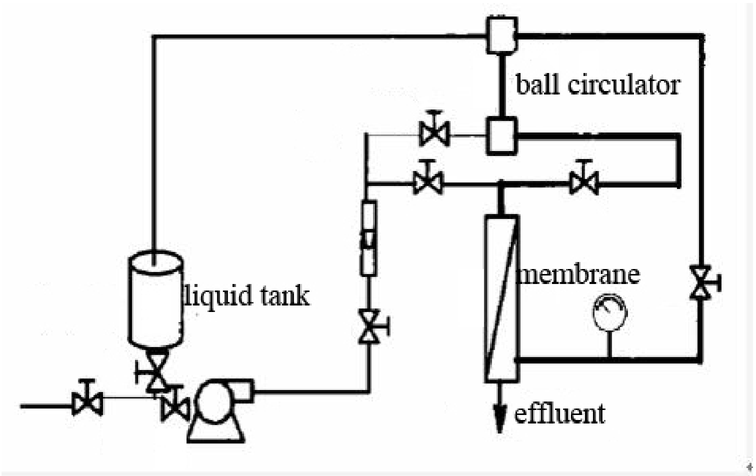

Figure 1. SchematicFlow-Sheet of Sponge Rubber Ball Cleaning System

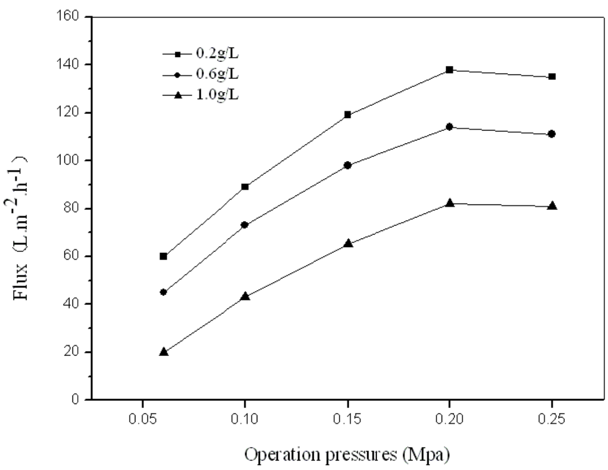

Figure 2. Flux Change with Operation Pressure. (Running time was 3h, membrane surface flow rate was 3.44m/s)

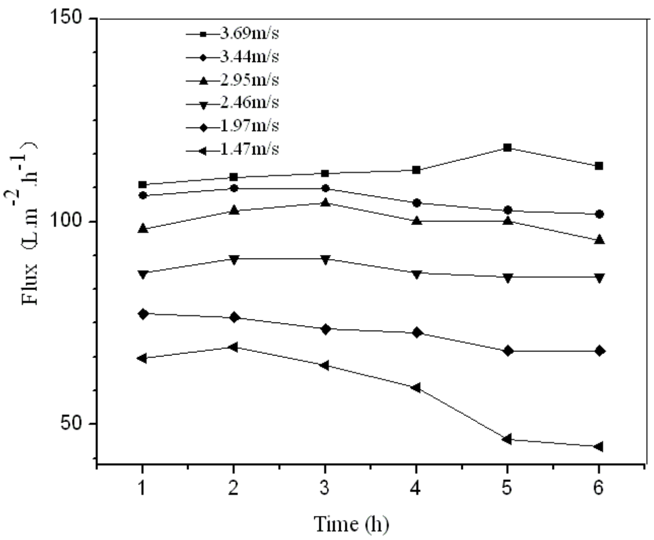

Figure 3. Flux Change with Membrane Surface Flow Velocity. (The concentration of oil/water emulsion was 0.2g/L, operation pressure was 0.20Mpa,)

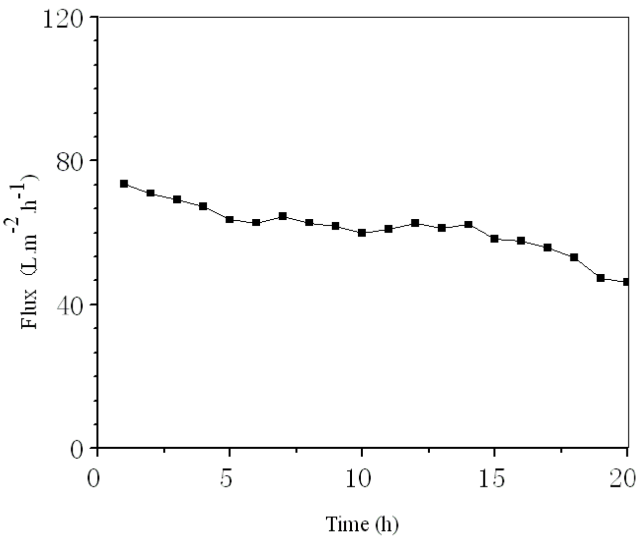

Figure 4. Flux Change with Running Time (The concentration of oil/water emulsion was 0.2g/L, operation pressure was 0.20Mpa, membrane surface flow rate was 3.44m/s)

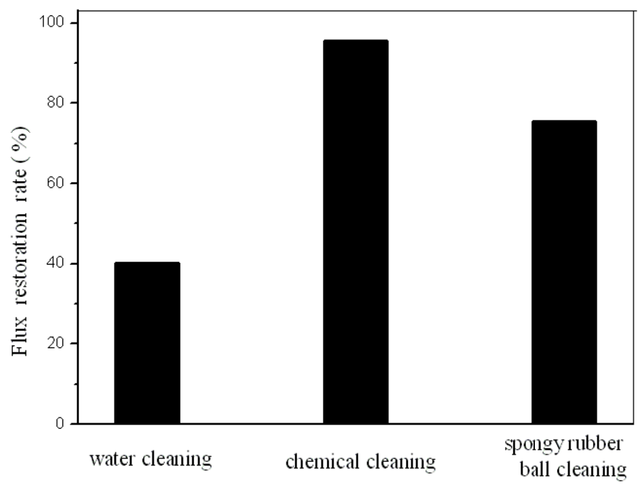

Figure 5. The Flux Restoration Rate of Three Cleaning Methods. (The concentration of oil/water emulsion was 1.0g/L, operation pressure was 0.20Mpa, operation, Running time was 20h, membrane surface flow rate was 3.44m/s)

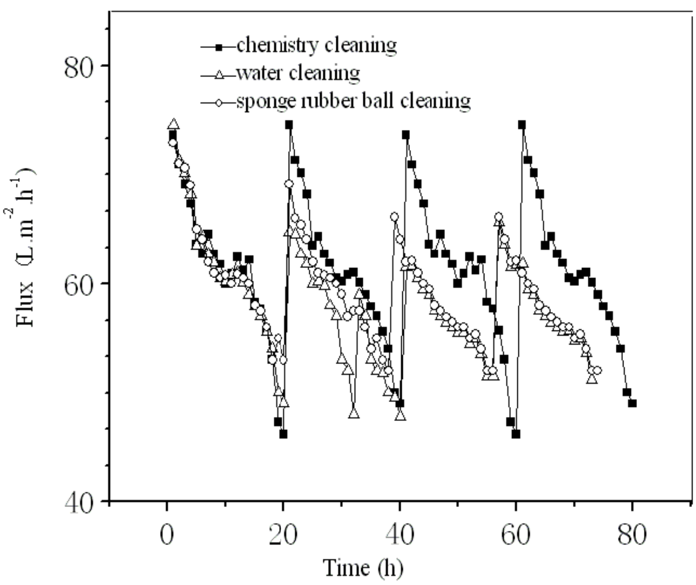

Figure 6. The Comparison of Different Membrane Cleaning Effects. (The concentration of oil/water emulsion was 1.0g/L, operation pressure was 0.20Mpa, membrane surface flow rate was 3.44m/s)

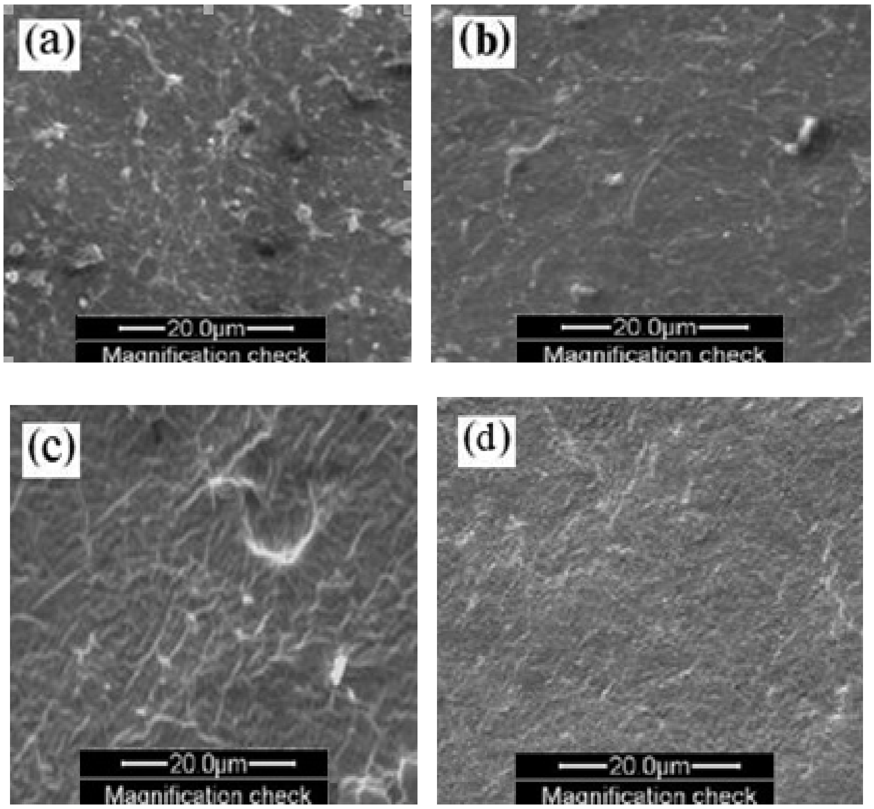

Figure 7. SEM Micrographs of PVDF Membrane Surface (a: fouled membrane; b: membrane after water cleaning; c: membrane after spongy rubber ball cleaning; d: membrane after chemical cleaning)