Ph.D. thesis

IMPROVEMENT OF THE MEMBRANE FILTRATION'S EFFICIENCY WITH THE APPLICATION OF COMBINED METHODS BY PURIFICATION OF INDUSTRIAL WASTEWATERS

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2013

INTRODUCTION

Water pollution is a major global problem which requires ongoing evaluation and revision of water resource policy at all levels. The principal objective of wastewater treatment is generally to allow human and industrial effluents to be disposed of without danger to human health or unacceptable damage to the natural environment. Industrial waste often contains many toxic compounds that damage the health of aquatic animals and those who eat them. The treatments of wastewater require sufficient removal pollutants and enable the wastewater to be discharged into receiving water or to be reused for industrial purposes.

Pressure-driven membrane separation processes (microfiltration, ultrafiltration, nanofiltration and reverse osmosis) are important and attractive alternatives to conventional treatments for the purification of wastewater. They display high removal efficiencies and also allow reuse of the treated water. These membrane techniques present a number of advantages: the purified permeate usually exhibits high quality, the processes are easy to operate at moderate temperatures and with low energy requirements in general, no chemicals are needed, and combination with other separation processes is easy because of the modular construction.

In my dissertation, the objective was the reduction of the pollutions presents in the industrial wastewater by complex technology: the combination of the membrane process with another technology.

The industrial applications of the membrane filtration encounter two main problems. The permeate flux in the processes decreases with time as the retained particles accumulate on the membrane. The particles being filtered often foul the membrane by blocking the membrane pores

and by forming a cake-layer on the membrane surface. Membrane fouling leads to a decrease in filtration productivity, resulting in a decrease in flux with time under operation at constant trans-membrane pressure, decreases the lifetime of the membrane modules, increases the cost of production and limits further industrial applications of membrane technology. Pretreatment before the membrane filtration leads to decrease the membrane fouling, resulting improving efficiency of the membrane filtration. In my research work I investigated 3 combined technologies for the purifications of industrial wastewaters:

- application of microparticles for the reduction of membrane fouling
- combination of ozonation and membrane filtration
- combined membrane system

MATERIALS AND METHODS

In my experiments, I clarified the chalk model suspension, pharmaceutical-, meat industry wastewater and produced water with combined methods. My objective was the reduction of the pollutions presents in the industrial wastewater, and improving of the membrane filtration's efficiency.

I investigated the following combined methods:

1. <u>The first alternative approach for the reduction of fouling is the microparticles.</u>

   Fine bakelite particles were suspended in the chalk-dust solution. I investigated the effect of bakelite particles on the fouling of the microfiltration membrane.

2. The combination of ozonation and membrane filtration:

   2.1. I investigated the applicability of the nanofiltration and the effect of preozonation in the pharmaceutical wastewater. The primary aim of this was to assess the potential use of an integrated ozone and NF process for improving the NF performance.

   2.2. I investigated the reduction of the organic matter presents in the meat industry wastewater by the combination of ozonation and ultrafiltration, by taking advantages of both systems. I started the treatment with an ozonation stage, and the effluent obtained was used as a feed for an UF process. Meat industrial wastewater was treated with ozone, and the effects of the ozonation time and flow rate of bubbling gas were measured on the membrane filtration parameter as well as the flux, fouling of the membrane and retention of chemical oxygen demand (COD).

3. Combined membrane system (ultrafiltration + reverse osmosis):

   I tested produced waters using a mobile station to design a plant to cost efficiently treat the produced water for agricultural irrigation.

   I devised a combined ultrafiltration and reverse osmosis technique to cost efficiently treats the wastewaters and can be discharged into value of receiving natural water.

NEW SCIENTIFIC RESULTS

1. New scientific results related to the examination of micropraticles

1.1. **I proved that during the microfiltration tests, the use of bakelite particles decreased the cake resistance and improved the flux of the membrane processes. A linear correlation was observed between the mass and the size of the dolly-particles and the permeate flux and the fouling of the membrane.**

The highest flux was achieved by using 40 g of 200–400 μm bakelite in the 20 L chalk suspension. The hydrodynamic shear force decays the fouling rate on the membrane and improves the efficiency of the cross-flow MF.

1.2. **I proved that the use of the bakelite particles improved the retention of the turbidity by microfiltration.**

I introduced a new formula to express the turbidity ratio (TR). This formula compare the turbidity of permeate without bakelite with the turbidity of permeate with bakelite.

I showed that using bakelite particles with the same parameters, results higher retention of the turbidity. The highest retention was achieved by using 40 g of 200–400 μm bakelite.

2. New scientific results related to the examination of ozone combination with membrane filtration by the purification of pharmaceutical wastewater

2.1. I created a combined treatment with the combination of ozone and nanofiltration for the purification of pharmaceutical wastewater. This combined technology decreased the COD value of treated wastewater under the value of receiving natural water.

In the first step I tested different membranes. I compared the efficiency of the ultrafiltration and nanofiltration membranes by the purification of pharmaceutical wastewater.

I proved that during my experiments the AFC30 nanofiltration membrane is the most effective with the combination of ozone for the pharmaceutical wastewater filtration. In the case of AFC30, the ozone decreased with 49% the fouling of the membrane and with 60 % the flux values.

2.2. I showed the effect of the ozone treatment on the nanofiltration's parameters: the flux of the nanofiltration, the fouling of the membrane and the retention of the organic matter. I proved that the lower dissolved ozone caused lower fouling on the membrane, higher flux and higher COD retention by the nanofiltration of pharmaceutical wastewater.

The lower ozone dosage enhanced better the flux and decreased the fouling during membrane filtration. This phenomenon can be explained by microflocculation effect

of ozone treatment. The highest, two times higher flux increase was achieved by using 4,85 mg/L ozone dosage.

The highest COD retention was achieved with the lowest (4,85 mg/L) ozone dosage. The microflocculation effect of ozone caused a looser structure on the surface of the membrane, which increases retention values.

3. New scientific results related to the examination of ozone combination with ultrafiltration by the purification of meat industry wastewater.

3.1. I created a combined treatment with the combination of ozone and ultrafiltration for the purification of meat industry wastewater. This combined technology decreased the COD value of treated wastewater under the value of receiving natural water.

The limit value of the COD was achieved by using minimum 10 min ozone pretreatment before the 5 kDa ultrafiltration membrane by the meat industry wastewater.

3.2. I showed the effect of the ozone treatment on the meat industry wastewater's COD value. I proved that the highest effect on the decrease of COD value was the ozone gas flow rate.

I showed that using ozone treatment with lower ozone gas flow rate, resulting in lower COD values. The lower ozone gas flow rate decreased the COD values the half of the original values. The COD decrease with a lower gas flow rate, because more ozone can dissolve into the sample.

3.3. **I showed the effect of the ozone treatment on the fouling of the ultrafiltration membrane and the retention of the organic matter. I proved that the effect of ozone gas flow rate on the fouling of the membrane and COD retention was significant by the ultrafiltration of meat industry wastewater.**

During my experiments I investigated the effect of ozone parameters (flow rate, treatment time) on the measurement values of the ultrafiltration membrane (flux, fouling, retention). The lower ozone gas flow rate (1 L/min) caused 75% reduction by the fouling resistance, and 73% improving by the COD retention.

This phenomenon can be explained by microflocculation effect of ozone treatment. Using lower gas flow rate, the flocculated molecules cannot go into the membrane porous resulting lower porous membrane fouling.

4. <u>New scientific results related to the examination of combined membrane technology by the purification of produced water.</u>

4.1. **I created an economical treatment for the purification of produced water. I proved that this technology is more economical than to dispose of the produce water by injection.**

I used combined physical and chemical treatments of produced water (MDU-Mobil Design Unit) in order that to comply with the discharge limits. This mobile station consists of three stages: pretreatments (primary oil/water separator, degasser, electrocoagulation, bagfilter), combined membrane filtration (ultrafiltration, revers osmosis) and

post treatment. I calculated that the treatment cost of produced water with MDU is less expensive than to dispose of it by injection and this treated water may be of great value in water-poor regions.

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