Ph.D. Thesis

Effect of pre-treatment on the membrane filtration parameters in oily wastewater and thermal waters purification

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1. BACKGROUND

One of the greatest challenges of our time, mainly due to the increase in population growth, is to maintain the quality of life, which is achievable by ensuring the adequate quantity and quality of healthy food, good quality of water and providing a pleasant environment. These factors are influenced by the management of natural resources, rational land use, and conservation of the landscape value and protection of the water reserve quality. Qualitative and quantitative protection of water resources can be realized by optimizing the consumption and by reducing the pollutant emission. Different industrial wastewaters are produced in large quantities with a very different composition and their integrated management is a big problem. Industries install their own wastewater treatment plants as a result of stricter environmental regulations, and therefore wastewater treatment technologies are constantly evolving.

Oil-containing industrial wastewaters especially emulsions can cause serious harm to the environment if they are inappropriately treated.

In recent years, membrane separation processes -with a pressure gradient as a driving force- are increasingly used in the treatment of oil emulsions. The advantages of these processes are their high separation efficiency, a low requirement of chemicals, they are relatively easy to maintain and in many cases they can be mobilised. The main disadvantage of the process is the membrane fouling which decreases the filtration efficiency, shortens the membranes life time which results in increased operating expenses (due to the membrane cleaning or change). For the purification of o/w emulsions ultrafiltration and micro-filtration proved to be efficient due to the membranes pore size. Ultrafiltration has a high separation efficiency (up to 99%), but a high transmembrane pressure is required; due to decreased fouling and lower membrane cleaning costs microfiltration membranes are more cost-effective, with less oil retention.

2. AIMS

My goal was to examine whether microfiltration of oily emulsions is an effective cleaning process by itself or in a combination with different pre-treatment methods. Reducing the membrane fouling is a top priority in membrane separation processes, and in their development and use, so pre-treatment methods that could be used to reduce membrane fouling were investigated.

My objective was to examine the purification of oil-in-water emulsions (emulsion forming motor oil, petroleum and crude oil), phenol-containing as well as oil-containing model thermal waters.

My goal was to examine the different treatment methods for increasing the efficiency of the membrane filtration (a) by changing the membrane properties with preconditioning or (b) by changing the properties of the solution with ozone pre-treatment.

3. EXPERIMENTAL

During my PhD research work the membrane filtration and its combinations with pre-treatment methods of oil-in-water emulsion, model thermal water solutions containing oil and phenol were studied. For the microfiltration experiments a laboratory scale MEUF (Millipore) membrane filtration unit was used.

In the experiments when the changing of the membrane properties were examined the following emulsions were used: MOL Makromil 200 and crude oil emulsions. The PTFE membrane was conditioned in acetone and in NLR-202 VSEP membrane cleaning fluid. The PTFE membranes pore size was 0.1 microns. A series of parallel experiments were performed with hydrophilic polyethersulfone (PES, pore size 0.1 microns) membrane.

The membrane filtration experiments combined with the ozone pre-treatment were carried out treating low concentration (0.01 w/w%) petroleum and crude oil emulsions as well as petroleum and oil emulsions (model thermal waters) with an identical high salt content (2500 mg/dm^3), using microfiltration PES membrane (pore size 0.1 microns). The ozone pre-treated model thermal water was filtered through a thin film composite nanofiltration membrane (200 Da molecular weight cut-off) in 3DTA (Uwatech, Germany) membrane filtration unit.

For the ozone pre-treatment the ozone was produced from oxygen (Linde 3.0 grade) by ozone generators based on a corona discharge principle (BMT (Germany) 802X ozone generator and an Ozomatic Modular 4 generator). The ozone flow was monitored at the generator outlet and at the reactor outlet with a flow-through cuvette and Biowave II diode array spectrophotometer (WPA, UK) (λ= 255 nm).

The membranes retention was characterised with retention of chemical oxygen demand (Lovibond COD Digestion Analyzer, Germany), Total Organic Carbon (TOC Analyzer, Teledyne Tekmar, USA) and oil content (INFRACOM TOG / TPH Analyzer, Wilks, USA). Phenol (BS 1484-1: 1992) was determined by spectrophotometric method. Ozone treatment induced changes in o/w emulsions droplet size was monitored (Mastersizer 2000, Malvern Instruments, Germany) as well. The membrane wettability was measured with contact angle measurements (OCA 15EC, Dataphysics, Germany).

4. NEW SCIENTIFIC RESULTS

Pre-treatment methods to change the membrane properties

1. New scientific results based on the filtration of oil-in-water emulsions by teflon membrane (I., V.):

It has been proven that a hydrophobic teflon membrane can be made suitable for filtering oil-in-water emulsion by conditioning pre-treatment agent (e.g. Acetone or VSEP wash solution). It was found that in the case of hydrophilic PES membrane the filtration mechanism can be described with the coalescence phenomenon, but in case of the hydrophilic (as a result of the pretreatment) PTFE membrane there is an emulsifier-containing oil film on the walls of the pores, which reduces membrane fouling, thereby increasing the flux. As a result of using various conditioning agents it was found that the water flux of the PTFE membranes increased because the conditioning allowed the water molecules to enter the pores of the PTFE membrane. Using acetone and VSEP membrane cleaning liquid solution as conditioning agents resulted in the highest water fluxes. Contact angle measurements proved that the PTFE membranes water wettability can be significantly increased, thus the o/w emulsions can be separated more efficiently.

The separation mechanism can be described as follows: As a result of increasing concentration of oil the hydrophilic PTFE membranes fouling decreases, but the hydrophilic PES membranes fouling increases with the oil concentration. Contact angle measurements show that the high emulsifier containing oil forms a thin film coat on the hydrophilic PTFE membrane pore walls which causes a decreased fouling resistance compared to the hydrophilic PES membranes coalescence phenomenon in its pores. Filtering the same high emulsifier containing emulsion through both membranes the fluxes were nearly identical and regardless to the membranes material the COD retention increased with the oil concentration.

Pre-treatment methods to change the solution properties

2. New scientific results obtained during the investigation of the oil-containing wastewater by combined treatment methods (ozone treatment and microfiltration) (II.)

It was proven that in the o/w emulsions ozone pre-treatment causes chemical changes which allow the formation of larger droplets. This reduces the membrane fouling during filtration and increases the COD retention. The ozone pre-treatment of 0.01 w/w% oil emulsions caused a COD retention increase from 70.4% to 91.6% in case of PES membrane microfiltration. The results showed that the effect of ozone pre-treatment reduced the membrane fouling. Model calculations also proved that in case of o/w emulsion and ozone pre-treated o/w emulsions filtration cake filtration occurs. The ozone pre-treatment changes the content of the compounds by breaking them down in to polar hydrocarbons which results in the increase in the membranes wettability.

During the ozone treatment the pH of the emulsion decreases, which can be explained with the appearance of acidic and ion components. The increasing ion content reduces the repulsive force between the emulsion droplets, promoting their aggregation. Based on the droplet size analysis ozone pre-treatment can increase the emulsions droplet size, which has a significant effect on the microfiltration retention.

3. New scientific results obtained during oil containing model thermal water purification (ozone treatment and microfiltration) (VIII.)

It was proven that the model thermal waters (with oil and high salt content) ozone pre-treatment decreases the membrane fouling during the microfiltration. It was concluded that oil and high salt-containing waste water treated by ozone combined with microfiltration causes a higher separation efficiency compared to the non-ozone-treated experiments with same flux.

In ozone pre-treated model thermal waters the high COD caused by the aliphatic hydrocarbons was reduced. After a longer period of ozone treatment of the emulsions, which do not contain salts, the pH of the emulsion decreased which is a result of the organic acid formation. The high-

salt-containing model thermal waters pH tends to stagnate due to the buffering capacity, but the inorganic ions may form precipitate with the organic acids -which form during the ozone treatment- which can diminish the membrane fouling and increase the COD retention (from 54.4% to 87.4%).

4. New scientific results obtained during phenol containing model thermal water treatment with combined processes (ozone treatment and nanofiltration) (III., VI.)

It has been proven that ozone pre-treatment combined with nanofiltration is a beneficial purification process, because ozone pre-treatment completely eliminates phenol from the model phenol containing thermal water, however with nanofiltration ion content, which increased during the ozone treatment, can be significantly reduced.

Due to the ozone treatment acids with low molecular weight are produced, which may form a precipitate with inorganic ions. This precipitate is more easily removed by nanofiltration, thus a more effective phenol and COD removal can be obtained compared to the nanofiltration alone.

5. ARTICLES RELATED TO THE SUBJECT OF THE THESIS

I. Treatment of model oily waste water by microfiltration
Zsolt László Kiss, László Talpas, Zita Seres, Sándor Beszédes, Cecilia Hodúr, Zsuzsanna László
Periodica Polytechnica-Chemical Engineering 57:(1-2.) (2013) 21-24. IF: 0,130

II. Treatment of oily wastewater by combining ozonation and microfiltration
Zsolt László Kiss, Lajos Kocsis, Gábor Keszthelyi-Szabó, Cecilia Hodúr, Zsuzsanna László
Desalination and Water Treatment (doi:10.1080/19443994.2014.939877)(2014) 1-8. IF: 0,988

III. Treatment of waste thermal waters by ozonation and nanofiltraton
Zsolt László Kiss, Angéla Szép, Szabolcs Kertész, Cecilia Hodúr, Zsuzsanna László
Water Science and Technology 67:(6) (2013) 1272-1279. IF: 1,212

IV. Economic Evaluation Combined Membrane and AOPs Wastewater Treatment Methods
Zsolt László Kiss, Gábor Keszthelyi-Szabó, Cecilia Hodúr, Zsuzsanna László
Annals of Faculty of Engineering Hunedora – International Journal of Engineering XII:(4) (2014) 79-82.

V. Effect of Conditioning Methods of PTFE Membranes on microfiltration of oil-in-water emulsions
Zsolt Kiss, László Talpas, Sándor Beszédes, Cecilia Hodúr, Gábor Keszthelyi-Szabó, Zsuzsanna László
Proceedings: The 6th Membrane Conference of Visegrad Countries, Warsaw: Polish Acad. Sci., (ISBN:978-83-7789-227-5) (2013) 139-147.

VI. Waste thermal waters purification by ozonation and nanofiltration
Zsolt László Kiss, Angéla Szép, Sándor Beszédes, Cecília Hodúr, Zsuzsanna László
Review of Faculty of Engineering Analecta Technica Szegedinensia 3-4 (2012) 1-8.

VII. Investigation of parameters affecting the ultrafiltration of oil-in-water emulsion wastewater
Zsolt László Kiss, Szabolcs Kertész, Sándor Beszédes, Cecilia Hodúr, Zsuzsanna László
Desalination and Water Treatment 51:(25-27) (2013) 4914-4920. IF: 0,988

VIII. Előkezelések hatása olajtartalmú szennyvizek membránszűrésére
Zsolt László Kiss, Zsuzsanna László
Expected publication: Membrántechnika és Ipari Biotechnológia (ISSN 2061-6392) VI. (2.) (2015)

LECTURES AND POSTER PRESENTATIONS

1. Treatment of waste thermal waters by ozonation and nanofiltration
A. Szép, Zs. L. Kiss, Sz. Kertész, Zs. László
IWA Regional Conference on Wastewater Purification & Reuse
Heraklion, Crete, 2012, (ISBN:978-960-99889-2-6)

2. Treatment of model oily waste water by microfiltration
Zs L Kiss, S Beszédes, C Hodúr, Zs László
Conference of Chemical Engineering
Veszprém, Hungary, 2012, (ISBN:978-615-5044-54-0)

3. Waste thermal waters purification by ozonation and nanofiltration
Zsolt László Kiss, Angéla Szép, Sándor Beszédes, Cecília Hodúr, Zsuzsanna László
International Conference on Science and Technique in the Agri- food Business –ICoSTAF
Szeged, Hungary, 2012.

4. Nagyhatékonyságú oxidációs eljárások és membránszeparáció kombinációjának alkalmazása a víz- és szennyvíztisztításban
Zsolt László Kiss, Zsuzsanna László
Környezettudományi Doktori Iskolák Konferenciája,
Budapest, Hungary, 2012 (ISBN:978-963-284-242-4)

5. Investigation of parameters affecting ultrafiltration of oil-in-water emulsion waste water
Zsolt László Kiss, Szabolcs Kertész, Sándor Beszédes, Cecilia Hodúr, Zsuzsanna László
Leeuwarden, Netherlands, 2012.

6. Combination of Advanced Oxidation Processes and ultrafiltration – comparison of the pretreatment by ozone and Fenton-reaction of model dairy wastewater
Zsolt László Kiss, Nándor Csorba, Cecilia Hodúr, Gábor Keszthelyi Szabó, Zsuzsanna László
Conference of Chemical Engineering
Veszprém, Hungary, 2013, (ISBN:978-615-5044-79-3)

7. Ultrasonically assisted ultrafiltration of whey solution
Zsolt László Kiss, Sándor Beszédes, Cecilia Hodúr, Gábor Keszthelyi Szabó, Zsuzsanna László
40th International Conference of SSCHE
Tatranske Matliare, Slovakia, 2013, (ISBN:978-80-89475-09-4)

8. Effect of Conditioning Methods of PTFE Membranes on microfiltration of oil-in-water emulsions
Zsolt Kiss, László Talpas, Sándor Beszédes, Cecilia Hodúr, Gábor Keszthelyi-Szabó, Zsuzsanna László
The 6th Membrane Conference of Visegrad Countries, Permea 2013
Varsaw, Poland, 2013, (ISBN:978-83-7789-227-5)

9. The effect of TiO2 for ultrafiltration parameters by whey separation
Zsolt László Kiss, Szabolcs Kertész, Cecilia Hodúr, Gábor Keszthelyi Szabó, Zsuzsanna László
Food Science Conference 2013
Budapest, Hungary, 2013, (ISBN:9789635035502)

10. Olaj a vízben, emulziók membránszeparációja
Zsolt Kiss, Gábor Keszthelyi-Szabó, Cecília Hodúr, Zsuzsanna László
Tavaszi szél 2014 konferencia
Debrecen, Hungary, 2014.

11. Economic evaluation for combined membrane and AOPs wastewater treatment methods
Zsolt László Kiss, Gábor Keszthelyi-Szabó, Cecilia Hodúr, Zsuzsanna László
ICoSTAF'14: International Conference on Science and Technique Based on Applied and Fundamental Research
Szeged, Hungary, 2014. (ISBN:978-963-306-276-0)

12. Treatment of oily wastewater by combining ozonation and microfiltration
Zsolt László Kiss, Lajos Kocsis, Gábor Keszthelyi-Szabó, Cecilia Hodúr, Zsuzsanna László
Conference and Exhibition on Desalination for the Environment Clean Water and Energy Limassol, Ciprus, 2014.

13. Effect of pre-flotation by oily waste water combined treatment
Zsolt László Kiss, Gábor Keszthelyi-Szabó, Cecilia Hodúr, Zsuzsanna László
XXXV. Óvári Tudományos Nap
Mosonmagyaróvár, Hungary, 2014

14. Előkezelések hatása olajtartalmú szennyvizek membránszeparációs tisztításában
Zsolt László Kiss, Zsuzsanna László
Soós Ernő Tudományos Konferencia
Nagykanizsa, Hungary, 2014

ARTICLES NOT RELATED TO THE SUBJECT OF THE THESIS

1. Investigation of AOPs and membrane filtration combination for wastewater treatment
Zsolt László Kiss, Nándor Csorba, Cecilia Hodúr, Gábor Keszthelyi - Szabó, Zsuzsanna László
Review of Faculty of Engineering Analecta Technica Szegedinensia 3. (2013) 22-26.

2. Whey separation using TiO2-modified utrafiltration membrane
Zs L Kiss, Sz Kertész, C Hodúr, G Keszthelyi-Szabó, Zs László
Acta Alimentaria 43:(Suppl. 1) (2014) 78-84. IF: 0,427

3. Ultrasonically assisted ultrafiltration of whey solution
Marietta Ábel, Zsolt László Kiss, Sándor Beszédes, Cecilia Hodúr, Gábor Keszthelyi-Szabó, Zsuzsanna László
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