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Liquid waste treatment with physicochemical tools for environmental protection

Thesis leaflet

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Introduction

Nowadays waste management is one of the most important tasks to realize sustainable development. The treatment, recovery and/or disposal of hazardous liquid waste are necessary task according to the environmental laws and ideas. Furthermore the regeneration of hazardous materials is an important point in the waste hierarchy. Therefore the goal is to minimize the use of materials and energy so that the amount is waste is also minimized [1].

In the fine chemical industry, the process water represents one of the biggest environmental problems. Process waters can be divided into two groups: input waters and output waters that are the so-called process wastewaters (PWWs). This dissertation work is dealt with the latter.

According to the current praxis, the chemical industry requires a huge amount of organic solvents. This is most typical for the fine chemical industries, such as, the paint-, printing, and pharmaceutical industries. Especially in the latter sector it is also true that the applied solvents generate large amount of waste. This is explained by the nature of the technology, because typically the generated by-product's weight is very high compared to the main product.

The other problems besides the large quantity of by-products are that the chemical process wastewaters and used solvents form azeotropic mixtures. The microbes in the conventional activated sludge process wastewater treatment system are not able to convert the substances in the chemical process wastewaters into their own nutrition. So other alternative methods must be sought to solve the problem.

The preferred environmental option is the prevention of waste formation. However, this most preferred option cannot be followed in every case and therefore other environmental options should be followed, like waste minimization, reuse, recycling. The least preferred option is the end-of-pipe treatment. In spite, the end-of-pipe treatment methods are in use and their improvement has a paramount importance in the chemical industry.

A number of physicochemical methods are suitable for treating process wastewater, which primarily remove volatile organic compounds (VOC), absorbable organically halogen compounds (AOX) and reduce the chemical oxygen demand (COD) [2].

[1] National Waste Management Plan 2014-2020. http://nkfih.gov.hu/download.php?docID=28337
[2] Best Available Techniques (BAT) Reference Document for Common Waste water and Waste Gas Treatment/Management Systems in the Chemical Sector, 2014

Literature review and problem statement

The main physicochemical methods are: absorption, adsorption, ion exchange, extraction, evaporation, wet oxidation, stripping, distillation and membrane processes. This dissertation work is dealt with the last three treatments.

Stripping

In the engineering practice there are two basic alternatives of physicochemical treatment for the VOCs and AOX from PWWs: stripping with air or stripping with steam. In the case of air stripping, water is usually also transferred into the gas phase, which lowers the temperature of the hot air, and therefore lowers volatility of the impurities.

The process wastewater is fed at the top and the air or steam is fed at the bottom. The pollutants can be typically found in the top product, that can be also called distillate. The treated wastewater is removed at the bottom.

Air stripping must not be used alone because the output gases and possible vapors enter the atmosphere and as a consequence the pollution is just transformed from the liquid into the air. In order to avoid it, these gases and vapors have to be treated. These methods of treatment are often more complicated and more expensive than the stripping itself [3].

The steam stripping is an alternative of air/inert gas stripping, used for less volatile pollutants. If steam is applied, the volatile stripped compounds do not enter the atmosphere, and they can be condensed and treated, since this is the liquid distillate. The top product of the steam stripper is usually the pure VOC that can be reused and this option is an environmental friendly, green option that favors the steam stripping by far [2].

In this dissertation these alternatives are investigated and compared in the case of a real industrial problem, that is AOX removal from pharmaceutical wastewater. The two alternatives are modelled in the professional software environment of ASPEN Plus®.

[2] Best Available Techniques (BAT) Reference Document for Common Waste water and Waste Gas Treatment/Management Systems in the Chemical Sector, 2014.
[3] Driscoll, T. P.: Industrial wastewater management, treatment and disposal, 3rd edition, McGraw-Hill, 2008.

Distillation

Out of the various liquid waste treatment technologies the most widely used method is distillation. The reason for this is that the recycling of materials is feasible practically without waste. We can extract the organic impurities, reuse the distilled materials and dispose of the pollutants in concentrated form.

The distillation of VOCs significantly reduces the COD of process wastewater. The AOX could be removed with distillation but the process should be carried out carefully.

In this work the aim is to reduce the COD and AOX content of real pharmaceutical PWWs with distillation. Laboratory and scale-up experiments, charge cost calculations are carried out for verify VOC-COD and AOX removal of distillation [4].

Sometimes the bottom contains no more volatile organic material, but the COD value does not reach the emission limit. In such cases, additional procedures are necessary, e. g. membrane processes.

The disadvantage of distillation is that the separation of several solvents with similar boiling points is usually a very difficult task and the separation of azeotropic mixtures with simple distillation is not possible at all. To achieve this different hybrid separation operations, such as the extractive heterogeneous-azeotropic distillation (EHAD) were developed.

Szanyi [5] introduced a novel kind of distillation, EHAD that has been proved as a powerful and efficient separation method for the separation of highly non-ideal liquid mixtures. The EHAD combines the advantages of extractive and the heterogeneous-azeotropic distillations. Heteroazeotropic distillation exploits the differences in volatility and liquid-liquid phase split by linking a distillation column and a decanter. The EHAD differs from the heteroextractive distillation since no new azeotrope is formed, namely the extractive agent/entrainer is water and this component is already present in the mixtures to be separated. Moreover, the extractive and relative volatility changing effect of the extractive agent is fully utilized and therefore the extractive effect takes place in the whole column.

[4] Koczka, K.: Environmental conscious design and industrial application of separation processes, PhD Dissertation, BME, Budapest, 2009.

[5] Szanyi, Á.: Separation of non-ideal quaternary mixtures with novel hybrid processes based on extractive heterogeneous-azeotropic distillation, PhD Dissertation, BME, Budapest, 2005.

The aim is to compare the two separation structures, EHAD and two column distillation system (TCDS) [6], with modelling and experiments. The separation of ternary and quaternary mixtures (problem 1 and problem 2, that is, Methanol, Ethyl-acetate and Water; Ethanol, Ethyl-acetate, Methyl ethyl ketone and Water) are investigated. The feed concentration of mixtures are motivated by industrial separation problem. These mixtures are real used solvents from fine chemical companies.

Membrane processes

The advantages of membrane processes are the high separation efficiency, the flexibility and the energy-efficient operation. High-purity product could be produced in one step and the use of foreign organic compounds is not required to aid the process. During the operation scaling and fouling must be prevented. It is also important to emphasize that membrane process can separate materials that no other process could. It is also environmentally beneficial because no further waste is generated.
The application of membrane technology is a realistic option for the treatment of process wastewaters, because it is suitable for cleaning heavy metals from process wastewaters, reducing process wastewater quantity by using hybrid separation technology, reducing the COD value of process wastewater [7].

Ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) can be used for COD removal from different industrial wastewaters [8]. These membrane processes belong to the group of pressure-driven membrane processes, where the driving force is the transmembrane pressure between the two sides of the membrane [9]. More membrane experiments are carried out to further reduce the COD of the bottom product of pharmaceutical PWWs with ultrafiltration, nanofiltration and reverse osmosis.

[6] Mizsey, P.: A global approach to the synthesis of entire chemical processes, PhD Dissertation, ETH, Zurich, 1991.
[7] Baker, R. W.: Membrane Technology and Applications, Wiley, 3rd edition, 2012.
[8] Cséfalvay, E.: Membrane operation in the green technology: solvent recovery and process water treatment, PhD Dissertation, BME, Budapest, 2009.
[9] Bélafiné, Bakó, K.: Membrane processes, Veszprémi Egyetemi Kiadó, Veszprém, 2002.

Pervaporation is a chemical unit operation where the mixture to be separated is vaporized at low pressure on the downstream side of the membranes and the separation of the mixtures takes place by preferential sorption and diffusion of the desired component through the dense membranes. One way of achieving the difference in the partial pressures is to maintain a low vapor pressure using a vacuum pump on the permeate side. Depending on the permeating component two main areas of pervaporation can be identified: hydrophilic and organophilic (hydrophobic) pervaporation [7]. The process of separation by pervaporation originates in the solution–diffusion principle, since this resemble the most the real phenomenon recommended the "solution–diffusion" model for pervaporation which can be applied for two-layered composite membranes [8].

In the pharmaceutical industry it is an actual problem that the cooling water circle can be polluted with methanol because of malfunction. To remove methanol from aqueous mixture organophilic pervaporation is investigated with commercially available Sulzer PERVAP™ 4060 and 2211 membranes. Based on the measurement results, parameters are fitted to the improved Rautenbach transport model [9, 10]. Since the motivating example comes from the industry and therefore such methanol and water mixture is studied where the methanol composition is usually 0.5 m/m% but mixtures of higher methanol contents can arise and therefore such concentration range is also investigated.

The last chapter of this dissertation is motivated by another environmental problem originating from the industry, that is, isobutanol removal from aqueous mixture. To complete this goal organophilic and hydrophilic pervaporation of isobutanol–water mixture through commercially available Sulzer PERVAP™ 4060 and 1510 membranes are matched and investigated to obtain information about the removal of isobutanol. The experimental data are evaluated with the improved Rautenbach pervaporation model [10]. The hybrid organophilic-hydrophilic separation system is rigorously modelled with ChemCAD and optimized with the dynamic programming optimization method. The objective function is the total annual cost but the energy consumption is also investigated.

[7] Baker, R. W.: Membrane Technology and Applications, Wiley, 3rd edition, 2012.

[8] Wijmans, J. G., Baker, R. W.: The solution-diffusion model: a review, J. Membr. Sci., 107/1, pp. 1–21, 1995.

[9] Rautenbach, R., Herion, C., Meyer-Blumenroth, U.: Pervaporation Membrane Separation Processes, Elsevier, 1991.

[10] Valentínyi, N., Cséfalvay, E., Mizsey, P.: Modelling of pervaporation: Parameter estimation and model development, Chem. Eng. Res. Des., 91/1, pp. 174–183, 2013.

Experimental and calculation methods

The work in this dissertation is significantly based on laboratory experiments and computer simulations using ChemCAD 6.4.3 5595 and Aspen Plus V8.0 (27.0.0.36) software packages. The separation systems are rigorously modelled and optimized with dynamic programming optimization method.

The calculation results are verified with experiments. The experimental set up is CM-Celfa Membrantechnik AG P-28 for ultrafiltration, nanofiltration, reverse osmosis and pervaporation. The distillation experiments are carried out in laboratory and scale-up column.

STATISTICA® program is applied for parameter estimation and Douglas equations [11] are used for the cost calculation.

The analytical methods are as follows: gas chromatography with Shimadzu GC-14B, Karl Fischer titration with Hanna HI 904 coulometric titrator, COD measurement according to ISO 6060:1991 and AOX measurement with Mitsubishi TOX-100.

[11] Douglas, J. M.: Conceptual design of chemical processes, McGraw-Hill, 1988.

Results

1 Research in the area of physicochemical treatment methods

Process wastewater stripping

Both air stripping and steam stripping are suitable methods for removing volatile and AOX compounds. There is a dispute among the engineers which one should be preferred. The results show a clear decision: in spite that the steam stripping uses steam that is more expensive than the air, finally it comes out cheaper because the additional costs of the air stripping are too high.

Moreover, the operation of the steam stripping is much simpler and it can offer the option of reutilizing the removed organic compounds obtained in the distillate. Such an option contributes also to the sustainable production with the reduction of the organic solvent consumptions.

Process wastewater distillation

Distillation is examined as possible solutions for the treatment of process wastewaters. It is demonstrated through the examples of five industrial waste solvent mixtures of fine chemical industry that distillation is capable for the reduction of the volatile chemical oxygen demand (VOC-COD) and AOX. It is also calculated that the column construction is a more environmental friendly and cheaper solution than the waste disposal with paying penalty. As a consequence for the pharmaceutical companies such a physicochemical treatment might be a better solution for the treatment of PWW problem. Distillation is also found economical since the fines can be reduced significantly and the payback time of the industrial AOX removal column is 2 years.

Membrane filtration for COD-reduction of bottom product

Using membrane filtration process can be also a beneficial option for treating the bottom product of distillation to concentrate non-volatile pollutants. In shortly it can be said that in this case the membrane filtration of the bottom is rewarding when the COD is close to the limit value (1000 mgO_2/L) and that significant scaling and fouling are not experienced.

2 Application of a new tool for liquid mixture treatment: EHAD

The application of extractive heterogeneous-azeotropic distillation improves significantly the possibilities for the separation of highly non-ideal mixtures. It opens new areas for the design of distillation based systems.

The EHAD has been already introduced in the practice but its current experimental verification and cost analysis confirms its really attractive capabilities in the separation of extremely non-ideal mixtures containing water. The application of the EHAD allows also the simplification of the separation schemes and the separation reduces the energy requirements of the distillation and opens new horizons for the separation of non-ideal mixtures saving energy, money and natural resources. The total cost of the EHAD is only 6% of the two column distillation system showing the excellent features of EHAD.

3 Separation of liquid mixture with the combination of organophilic and hydrophilic pervaporation

Methanol removal from aqueous mixture with organophilic pervaporation

The investigated organophilic membranes show slightly different parameters but they are in agreement with the parameters of other membranes published in the literature, however, they cannot exceed the performance of the flash distillation. The long-time experiments suggests that the pervaporation is not able to remove the methanol from an aqueous mixture and other separation method should be used for the removal of the entire methanol from such mixtures. It is worth to note that the flash distillation would not also been able to remove the methanol form an aqueous mixture but rectification should be rather considered for this task. With other words, such a task gives also a challenge for the membrane developers to produce more selective membranes increasing their performance also for this kind of separation.

The results of parameter estimation and modelling of the pervaporation show that the new model that considers the concentration dependency of the transport coefficient is also capable for the modelling of organophilic pervaporation and results in a better fit to the experimental data.

Isobutanol dehydration with organophilic and hydrophilic pervaporations

The experiments, the other research works and simulation suggests that the pervaporation is able to remove isobutanol from an aqueous mixture. The separation capability of hydrophilic pervaporation is much better than that of the organophilic membranes.

The results of parameter estimation of the pervaporation show that the new model which considers the concentration dependency of the transport coefficient is also capable for the modelling of organophilic and hydrophilic pervaporation and results in a better fit to the experimental data.

The investigation of hybrid organophilic-hydrophilic process is carried out and the lowest total annual cost is determined with dynamic programming optimization method. The results show that the capital cost of the pervaporation unit is the highest part of the total annual cost.

Both pervaporations are modelled with verified and adequate model in professional flowsheeting environment that enables verified rigorous modelling, optimization with the dynamic modelling method and cost estimation. The simultaneous investigation and modelling of both organophilic and hydrophilic pervaporation shows that

- the limiting capital cost is determined by the organophilic and hydrophilic pervaporators' membrane areas,
- the membrane area of the organophilic pervaporation is determined by the fact that the retentate (water) should contain practically no organic material since it is discharged,
- the membrane area of the hydrophilic pervaporation is determined by the fact that the retentate should fulfil the purity prescriptions for the organic material,
- the hydrophilic membranes have much better selectivity features that calls the attention to the necessity of the organophilic membrane developments.

The results obtained in this work are unambiguous, the modelling proves that the combination of the organophilic and hydrophilic pervaporation results in a powerful hybrid separation technology that can be competitive with distillation and opens new horizons for the application and improvement of the pervaporation.

Theses

Thesis 1 [I, II, III]

I determined that the dichloromethane can be removed much simply for recycling purposes from pharmaceutical process wastewater with rectification, contrary to the air stripping treatment. I designed industrial rectification column for this process, where the feed is 400 L/h and AOX of the treated process wastewater is less than 8 ppm.

Thesis 2

I determined that the extractive heterogeneous-azeotropic distillation is applicable for separation of organic liquid mixtures an order of magnitude more cost-effective than other classical distillation based separation method. The total cost of the EHAD is only 6% of the two column distillation system.

Thesis 3 [IV]

I proved with measurements that methanol could be removed in a five times more concentrated form from methanol–water mixture with organophilic pervaporation. I determined also that the current organophilic pervaporation membranes are not capable to remove the methanol from aqueous mixture below 1.7 m/m% methanol concentration.

Thesis 4 [IV]

I determined the parameters of the improved Rautenbach model for the organophilic pervaporation of methanol–water and isobutanol–water mixtures. I also verified the applicability of the parameters of isobutanol–water mixtures in professional flowsheeting environment (ChemCAD), and the data obtained are in good agreement with measured data.

Thesis 5

I rigorously modelled and optimized the hybrid organophilic and hydrophilic pervaporation system for isobutanol removal from water in professional flowsheeting environment (ChemCAD). This method hasn't been published yet. As a result I obtained that the system is capable for the separation of isobutanol and water of 99.9 m/m% purity for both.

Fields of application

The distillation column I designed for the removal AOX from process wastewaters operates according to my plans in the pharmaceutical industry. This column won four scientific awards too.

Steam stripper for AOX removal from process wastewater can be offered for industrial application, because its operation is much simpler than air stripper.

It has been found, that the extractive heterogeneous-azeotropic distillation for liquid mixture treatment is much simpler and more economic than current distillation based solutions.

The hybrid organophilic-hydrophilic pervaporation process designed for the separation of the isobutanol–water system can be directly applied for industrial purposes.

The ChemCAD firm accepted the pervaporation model for separation of methanol–water and isobutanol–water mixtures with improvement of the Rautenbach-model and integrated in its software package. This enables the rigorous modelling of the pervaporation together with distillation or other unit operations.

These research results may assist engineers to choose physicochemical technology for treatment of process wastewater from fine chemistry industry.

Publications

Articles

I Andras Jozsef Toth, Felician Gergely, Peter Mizsey: **Physicochemical treatment of pharmaceutical wastewater: distillation and membrane processes**, Periodica Polytechnica Chemical Engineering, 55/2., (2011), pp. 59–67.
doi: 10.3311/pp.ch.2011-2.03
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II Peter Mizsey, Andras Jozsef Toth: **Application of the principles of industrial ecology for the treatment of process waste waters with physicochemical tools (in Hungarian)**, Industrial Ecology, 1/1., (2012), pp. 101–125.
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III Andras Jozsef Toth, Peter Mizsey: **Comparison of air and steam stripping: removal of organic halogen compounds from process wastewaters**, Int. J. Environ. Sci. Technol., 12/4., (2015), pp. 1321–1330.
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IV Andras Jozsef Toth, Peter Mizsey: **Methanol removal from aqueous mixture with organophilic pervaporation: Experiments and modelling**, Chem. Eng. Res. Des., 98/6., (2015), pp. 123–135.
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Presentations

V Andras Jozsef Toth (speaker), Felician Gergely, Peter Mizsey: **Physicochemical treatment of pharmaceutical wastewater (in Hungarian)**, *Conference of Chemical Engineering*, Veszprém, Hungary, 27–29 April 2011, pp. 112–113.

VI Andras Jozsef Toth (speaker), Peter Mizsey: **AOX- and COD reduction of process wastewater with physicochemical tools (in Hungarian)**, *Hungarian Hydrological Society – 29th National Symposium*, Eger, Hungary, 6–8 July 2011., 8 pages on internet

VII Andras Jozsef Toth (speaker), Peter Mizsey: **Physicochemical tools for treatment of wastewaters of fine chemical industry (in Hungarian)**, *1st Conference of Environmental Science Graduate Schools*, Budapest, Hungary, 30–31 August 2012, pp. 157–164.

VIII Andras Jozsef Toth (speaker), Peter Mizsey: **Physicochemical tools for treatment of pharmaceutical wastewaters (in Hungarian)**, *4th PhD Conference of Association of Professors for the European Hungary*, Budapest, Hungary, 15 November 2012, pp. 46–51.

IX Peter Mizsey (speaker), Tamas Benko, Edit Csefalvay, Mate Haragovics, Jozsef Manczinger, Tibor Nagy, Andras Jozsef Toth, Nora Valentinyi: **Physicochemical treatment of pharmaceutical wastewater (in Hungarian)**, *BME - Richter Gedeon 2rd Scientific Day*, Budapest, Hungary, 12 December 2012.

X Andras Jozsef Toth (speaker), Peter Mizsey: **Methanol removal from pharmaceutical wastewater (in Hungarian)**, *1st Economics and Management Sciences Conference*, Kecskemét, Hungary, 5 September 2013, pp. 381–385.

XI Andras Jozsef Toth (speaker), Peter Mizsey: **Methanol removal from process wastewater (in Hungarian),** *University of West Hungary, Faculty of Science Conference*, Sopron, Hungary, 10 December 2013, pp. 130–134.

XII Andras Jozsef Toth (speaker), Katalin Angyal-Koczka, Jozsef Manczinger, Peter Mizsey: **Method and apparatus for AOX and COD removal from pharmaceutical process wastewaters (in Hungarian),** *Hungarian Wastewater Association III. Junior Symposium*, Budapest, Hungary, 6 February 2014.

XIII Andras Jozsef Toth (speaker), Anita Andre, Tamas Benko, Peter Mizsey: **Isobutanol removal from process wastewater with organophilic pervaporation (in Hungarian),** *19th International Scientific Conference of*

Young Engineers, Cluj-Napoca, Romania, 20–21 March 2014, pp. 405–408.

XIV Anita Andre (speaker), Andras Jozsef Toth, Tamas Benko, Peter Mizsey: **Modelling of organophilic pervaporation: isobutanol removal from water (in Hungarian)**, *Conference of Chemical Engineering,* Veszprém, Hungary, 14–16 May 2014, pp. extra paper

XV Andras Jozsef Toth (speaker): **Organic solvents removal from water: distillation, pervaporation (in Hungarian)**, *Conference of Chemical Engineering,* Veszprém, Hungary, 21–23 April 2015, pp. 1

XVI Andras Jozsef Toth (speaker), Agnes Szanyi, Eniko Haaz, Peter Mizsey: **Treatment of complex non-ideal mixtures with extractive heterogeneous-azeotropic distillation (in Hungarian),** *2nd Economics and Management Sciences Conference*, Kecskemét, Hungary, 27–28. August 2015, accepted for presentation

XVII Andras Jozsef Toth (speaker), Anita Andre, Eniko Haaz, Peter Mizsey: **Isobutanol removal from water with hybrid organophilic-hydrophilic pervaporation system (in Hungarian),** *Innovation in Natural Science – PhD Conference,* Szeged, Hungary, 26. September 2015, accepted for presentation

Posters

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XIX Peter Mizsey, Tamas Benko, Edit Csefalvay, Mate Haragovics, Katalin Angyal-Koczka, Jozsef Manczinger, Tibor Nagy, Andras Jozsef Toth, Nora Valentinyi: **Green technologies in the service of sustainable development (in Hungarian),** *Bridge of Future*, Budapest, Hungary, 22 September 2012.

XX Andras Jozsef Toth, Agnes Szanyi, Peter Mizsey: **Complexities of design of distillation based separation: extractive heterogeneous-azeotropic distillation,** *10th International Conference on Distillation & Absorption*, Friedrichshafen, Germany, 14–17 September 2014, pp. 416–421.