Novel method for reuse of process wastewater based on distillation

A. J. Toth*, E. Haaz*, J. Manczinger*† and P. Mizsey*,**

* Department of Chemical and Environmental Process Engineering, Budapest University of Technology and Economics, H-1111, Hungary, Budapest, Műegyetem rkp. 3. (E-mail: *andras86@kkft.bme.hu; haaz.e@kkft.bme.hu; mizsey@mail.bme.hu*)
** Department of Fine Chemicals and Environmental Technology, University of Miskolc, H-3515, Hungary, Miskolc, Egyetemváros C/1 108. (E-mail: *kemizsey@uni-miskolc.hu*)

Abstract
The industrial production unavoidably generates waste in many cases and that should be recycled and reused following the principle of circular economy. New method or process should be developed usually for solving this problem. Pharmaceutical industry has a typical example, since these plants generate wastewaters with high organic content in significant quantities, so-called process wastewater. These waters should be treated definitely before discharge, so that the organic content must be removed and then the process wastewater may be allowed into the sewer. Nowadays, the physicochemical methods are used increasingly, which are unlike the biological treatments, they have a smaller footprint and the polluting organic substances can be recycled and/or reused.
In our case distillation is applied, that is based on relative volatility of the individual components. During this method, the volatile organic polluters of treated process wastewaters are obtained as the top product of distillation, in reusable form. The bottom product of distillation, namely the process wastewater can satisfy the sewer regulations.
Our innovative method is made to remove and reuse organically bound halogens (AOX) from process wastewaters and it provides its task precisely until today. This planned industrial apparatus is served the Sustainable Water Solutions and Circular Economy, in fact it should be highlighted separately the payback time of the investment is less than two years.

Keywords
Process wastewater, AOX removal, Dichloromethane, Distillation

INTRODUCTION

The treatment of process wastewaters (PWWs) are difficult, because there are other problems besides the large quantity of by-products (Mizsey 1994; Toth *et al.* 2011): in many cases the chemical PWWs 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 and the biological treatment is often not officially authorized (Bhakta 2017). In many cases the PWW fees are very significant and the incineration is also expensive because the samples have high water content. So other, cheaper alternative methods must be sought to solve the problem (Getzner 2002; Belis-Bergouignan *et al.* 2004; Toth *et al.* 2011).

The large amount of process wastewater with organically bound halogens (AOX) content means serious problem in pharmaceutical industry. The chemical sector of EU countries generated 353 ton AOX waste in 2010. Within this sector, the production of basic organic chemicals was responsible for almost 90% of all AOX emissions (Brinkmann *et al.* 2016). AOX is a sum parameter which indicates the overall level of organic halogen compounds (chlorine, bromine and iodine) in water samples. It is important as many organic halogen compounds are persistent and/or toxic. The AOX method has the advantage that it is quite a simple measurement if it is compared with the alternative methods of measuring levels of individual compounds which are complex and require costly equipment (Brinkmann *et al.* 2016).

The respective treatment techniques of AOX removal methods from PWWs: chemical oxidation (pretreatment), wet oxidation (pretreatment), chemical hydrolysis, nanofiltration/reverse osmosis, adsorption, extraction, evaporation, pervaporation, stripping, incineration and distillation (Shestakova & Sillanpää 2013; Brinkmann *et al.* 2016).

The distillation of VOCs significantly reduces the chemical oxygen demand (COD) of process wastewater. The volatile chemical oxygen demand (VOC-COD) can be enriched in the distillate (Koczka & Mizsey 2010; Tóth *et al.* 2011). The AOX could be removed with distillation too, but the process should be carried out carefully (Levec & Pintar 2007). This study investigates a physicochemical approach for recycling wastewaters by applying distillation. The concept of this method is that there is a difference of the relative volatility of individual components in the wastewater. **Figure 1** introduces a distillation schema for treatment of PWW with AOX and/or VOC content.

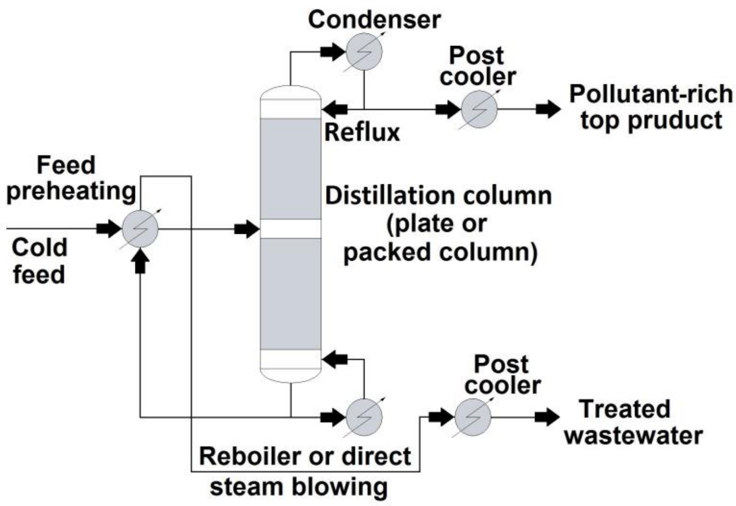

Figure 1 General schema for process wastewater distillation (Toth 2015)

The energy requirements of distillation can be reduced significantly if the feed of the bottom product is preheated (Tóth *et al.* 2011).

The aim of this study is to introduce a method for treatment of PWW with ~6000 ppm AOX concentration. Laboratory, pilot experiments and industrial application are also demonstrated. The target of the treatment is to reduce the AOX below 8 ppm and COD below 1000 mgO_2/L in order to channeling the PWW. These emission values are the regulation limit, as it can be found in 28/2004. (XII. 25.) Ministry of Environment Regulation. According to literature study, the largest phase of PWW can be recycled/reused as far as possible using our elected method, that is distillation (McCabe & Vivona 1999; Mizsey *et al.* 2008; Koczka & Mizsey 2010; Tóth *et al.* 2011). So it can be determined, it follows the principles of circular economy (see **Figure 2**).

Figure 2 Flowsheet of circular economy
(http://epnetwork.tumblr.com/post/123113312207/circular-economy-the-importance-of-re-using)

Material and methods

Table 1 contains the pollution compounds of real industrial PWW samples. The distillation of process wastewaters containing organic solvents, especially halogenated organic compounds behaves like the distillation of mixtures with limited solubility. 99.8% of AOX is dichloromethane, further halogen compounds in the water are carbon tetrachloride, chloroform, 1,2-dichroethane, tetrachloroethylene and trichloroethylene. They are minimum boiling heterogeneous azeotropic (Marsden 1954; Gmehling & Onken 1977). It can be determined, every pollution compounds are belong to the group of VOC.

With other words, steam distillation is taking place where the Raoult's law is not applicable, however, the sum of the partial pressure of the compounds determines the circumstances. It results in that the temperatures in the process wastewater distillation is always below 100°C.

The dry substance is not significant, but the COD-values are so far from the emission limit. Furthermore the average density is 1.02 g/cm^3 and pH is 6.7. Continuous operations are examined, because the large amount of PWW, that is 570 ton/year.

Table 1 Mean parameters of process wastewater samples

Sample	Feed composition [ppm] AOX	Methanol	Acetone	Dry subs. [%]	COD [mgO$_2$/L]
1	5720	2330	3530	1.02	15200
2	6630	2110	3580	0.59	14800
3	5390	1980	2940	1.10	17300
4	5530	1990	3450	0.33	15300
5	6570	2050	2760	0.51	16400
Average	5968	2092	3252	0.71	15800
Deviation	589	143	375	0.33	1027

Before the experiments, flowsheet simulations are carried out with flowsheet simulator (ChemCAD) to minimize the solution space, the required number of experiments and to find the proper parameters of the unit operations. The optimal mass flow rates, reflux ratio, heating and cooling requirements can also be determined (Toth *et al.* 2016). Rectifying (upper) section is required for enrichment of AOX and other VOC-COD in PWW. The pollutant compounds must be also reduced with stripping (lower) section of column, so the PWW have to be fed at the middle of the column.

Laboratory and then pilot columns are built in order to develop the treatment method (see **Figure 3**). The main parameters of the laboratory experimental column are the following: random packing, internal diameters of 40 mm, 1.5 m high. The column has 10 theoretical plates according to a measurement carried out by methanol-water mixture. The PWW feed is not preheated and the column heating is controlled with a 300 W efficiency heating basket.

After the laboratory experiments pilot distillation have to be carried out to determine whether industrial equipment can be designed (Tóth *et al.* 2011). The pilot column has 70 mm internal diameter, 3 m high with Sulzer Mellapak 750 type structured packing, which is equivalent to 14 theoretical plates in our case (see **Figure 3**). Direct injection of the steam with 2 bar is applied for the heating of the kettle. The feed is preheated with ultra thermostat.

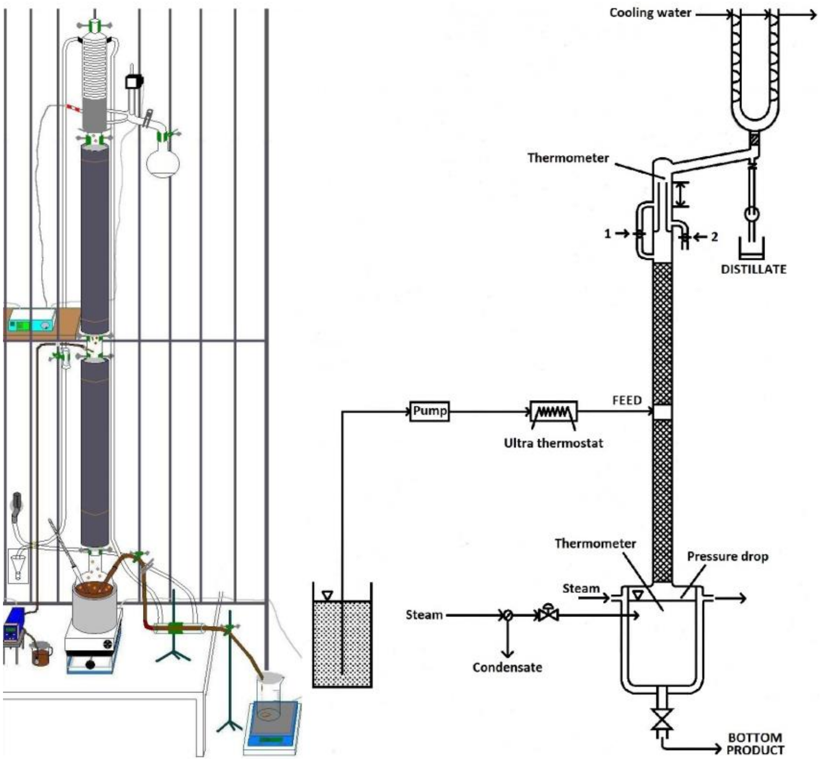

Figure 3 Laboratory and pilot columns (Toth 2015)

The pollutant content of the feed (F), distillate (D) and bottom product (W) are measured with Shimadzu GC2010Plus+AOC-20 autosampler gas chromatograph with a CP-SIL-5CB column connected to a flame ionization detector, EGB HS 600. Headspace apparatus is used for sample preparation. The AOX is determined with Mitsubishi TOX-100 apparatus and the COD is measured by ISO 6060:1991 (Toth 2015).

RESULTS AND DISCUSSION

Experimental evaluation

Table 2 represents the measured results of laboratory and pilot experiments too.

Table 2 Results of laboratory and pilot experiments

Experiment	Stream			R	PWW composition (W)			
	F [kg/h]	D [kg/h]	W [kg/h]	[-]	AOX [ppm]	Methanol [ppm]	Acetone [ppm]	COD [mgO$_2$/L]
Laboratory	1.03	0.015	1.004	20	6	380	430	5810
Pilot	5.00	0.16	4.75	10	2	120	150	1640

It can be seen, the AOX concentration of the PWW can be reduced below 8 ppm with applying continuous distillation experiments. 63% reduction in COD-value can be reached with laboratory experiment and 90% applying pilot column, but the value is above the emission limit (1000 mgO$_2$/L) yet. The results of pilot experiment in the case of pollutant compositions and COD of process wastewater are more favourable, because the condensation steam can dilutes the bottom product and it can reduces further the COD and AOX (Tóth *et al.* 2011). The reflux ratio can be kept between 10–20 and low distillate flow (1.5% and 3% of the feed) is necessary for this. Examining the streams, it can be determined the mass balance error can be kept under 2% in both cases.

Industrial implementation of AOX and VOC-COD removal column

Using our experimental results observations an industrial distillation column is designed with 17 theoretical plates and structured packing. The main parameters of the column can be seen on **Figure 4**. The feed tray location is located at the middle of the column and even 500 L/h PWW can be treated.

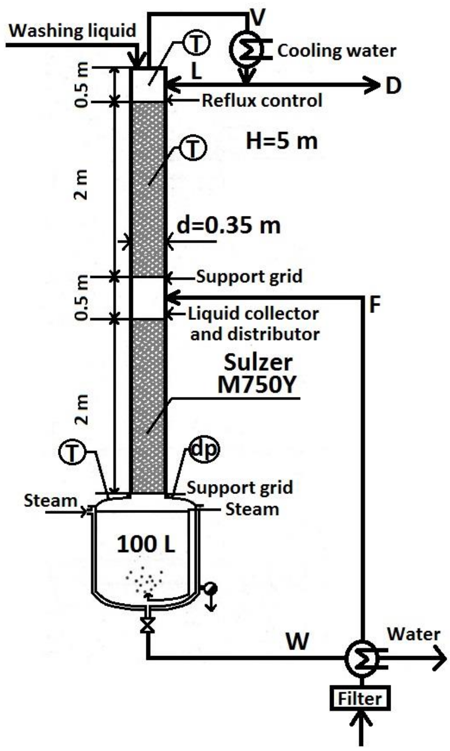

Figure 4 Schematic figure of the industrial column (Toth 2015)

Key points of efficiency and economic aspects of our industrial process are highlighted, as follows.

Novelty, innovative engineering solutions of the method and apparatus:

- The condensing steam dilutes the bottom product and reduces the AOX and also COD below the emission limit. The halogen compounds are below the detection limit and COD is measured ~500 mgO_2/L in PWW, that is, the sewer requirements of water are satisfied. Another unique feature of this method is that there is no need for designing a kettle/reboiler separate from the column, since direct steam injection can be applied for the heating of the kettle (Tóth *et al.* 2011).
- On the other hand, the heat integration can reduces the energy demands, only 25 kg/h steam is required for the process. The hot effluent wastewater is used for feed preheating, thus this separation process involves 90% energy savings.
- Last, but not least, the distillate can be utilized in other plant after a simple phase separation, as dichloromethane solvent, because the column has rectifying section. So it can be seen that the process can fit into the main concept of circular economy.

Economic and social benefits of the method and apparatus:

- Very high wastewater fee must be paid, if this PWW is channelled without any treatment by pharmaceutical company, so there is essential for the manufacturer to develop waste treatment method in order to just the maintenance of its industrial production.
- The process of calculating of the wastewater fee can be found in 220/2004. (VII. 21) Government Regulation, Annex 2. It can be red that the specific penalty factor of AOX is an outstanding value, that is 250 $/kg to comparison, there is 0.25 $/kg in the case of COD emission.
- The economic benefits of the apparatus is supported by concrete data (Réti 2014). The above mentioned heat integration and lower steam consumption result favourable operating cost. **Table 3** shows that, the column's payback time is only less than 2 years.

Table 3 Cost parameters of the apparatus

Investment cost	355 000 $
Operating cost/year	73 000 $
Savings/year	267 000 $
Payback time	1 year 10 month

- The real benefit of the pharmaceutical company is even greater, because more different PWWs can be treated as well with this apparatus, especially it is suitable for alcohols (meanly methanol and ethanol) removal and recycling from water based mixtures.
- After installation process, another 4 columns were built according to this method, which indicate the success of the procedure. These columns operate successfully and economically in the chemical industry still today. We have 3 pharmaceutical and 1 petrochemical references, the presented one in this text can be only our public tender, which can demonstrates the technology. According to our estimation, the benefit of current method exceeds 3 million $ per year.

SUMMARY

The column is currently performing far above the expectations. More practical engineering consideration have resulted in the success of the developed method. The dichloromethane and AOX concentration of bottom product is below the detection limit, because the direct steam blowing of reboiler dilutes the PWW. The distillate, after a simple phase separation, can be utilized in other plant, as dichloromethane solvent. On the other hand heat integration reduces the energy demands and operating cost. The hot effluent wastewater is used for feed preheating, thus this separation process enables 90% energy savings. The column’s payback time is less than 2 years.

The waste treatment can be achieved locally in the factory and we can drive the chemical sector towards the circular economy, because through the reuse of materials the cycle of manufacturing processes can be closed. The featured method reflects to the popular "think globally, act locally" concept.

ACKNOWLEDGEMENT

The authors would like to acknowledge the financial support of Swiss-Hungarian Cooperation Programme – SH 7/2/14 and OTKA 112699 project.

REFERENCES

28/2004. (XII. 25.) Ministry of Environment Regulation.

220/2004. (VII. 21) Government Regulation.

http://epnetwork.tumblr.com/post/123113312207/circular-economy-the-importance-of-re-using.

Belis-Bergouignan M. C., Oltra V. and Saint Jean M. (2004). Trajectories towards clean technology: Example of volatile organic compound emission reductions. *Ecological Economics* **48**(2), 201-20.

Bhakta J. N. (2017). *Handbook of Research on Inventive Bioremediation Techniques*. IGI Global.

Brinkmann T., Santonja G. G., Yükseler H., Roudier S. and Sancho L. D. (2016). *Best Available Techniques (BAT) Reference Document for Common Waste water and Waste Gas Treatment/Management Systems in the Chemical Sector*, Union POotE.

Getzner M. (2002). The quantitative and qualitative impacts of clean technologies on employment. *Journal of Cleaner Production* **10**(4), 305-19.

Gmehling J. and Onken U. (1977). *Vapor-Liquid Equilibrium Data Collection: Aqueous-Organic Systems*. DECHEMA.

Koczka K. and Mizsey P. (2010). New area for distillation: Wastewater treatment. *Periodica Polytechnica: Chemical Engineering* **54**(1), 41-5.

Levec J. and Pintar A. (2007). Catalytic wet-air oxidation processes: A review. *Catalysis Today* **124**(3-4), 172-84.

Marsden C. (1954). *Solvents And Allied Substances Manual With Solubility Chart*. Cleaver-Hume and Elsevier, London.

McCabe D. L. and Vivona M. A. (1999). Treating process wastewater employing vacuum distillation using mechanical vapor recompression. *Environmental Progress* **18**(1), 30-3.

Mizsey P. (1994). Waste reduction in the chemical industry: a two level problem. *Journal of Hazardous Materials* **37**(1), 1-13.

Mizsey P., Koczka K. and Tungler A. (2008). Treatment of process wastewaters with physicochemical tools. *Hungarian Journal of Chemistry* **114**, 107-13.

Réti G. (2014). Globális célok - helyi megoldások az Egis környezetvédelmében. *Ablakon Bedobott Pénz, KÖVET Egyesület* **12**(1), 12–3.

Shestakova M. and Sillanpää M. (2013). Removal of dichloromethane from ground and wastewater: A review. *Chemosphere* **93**(7), 1258-67.
Toth A. J. (2015). *Liquid Waste Treatment with Physicochemical Tools for Environmental Protection*. PhD Thesis, BME, Budapest.
Toth A. J., Gergely F. and Mizsey P. (2011). Physicochemical treatment of pharmaceutical wastewater: distillation and membrane processes. *Periodica Polytechnica: Chemical Engineering* **55**(2), 59–67.
Toth A. J., Szanyi A., Angyal-Koczka K. and Mizsey P. (2016). Enhanced Separation of Highly Non-ideal Mixtures with Extractive Heterogeneous-azeotropic Distillation. *Separation Science and Technology* **51**(7), 1238–47.