Treatment for COD reduction of process wastewater: washing material removal with physicochemical tools

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Abstract
Fine chemical industry produces various types of wastes. Part of these wastes are already treated but certain process wastewaters (PWWs) are still to be recycled or reused following the principle of circular economy. In most cases the treatment method must be developed individually respectively to the waste composition.
Special treatment/cleaning of chemical equipment must be completed regularly in the fine chemical factory, therefore large amount of process cleaning wastewater is generated. A usual example of this water is the high content of organic compounds, in most cases with surfactant materials.
Before such wastewater can be discharged to sewage plants, it must be treated in some ways to decrease its organic content under the discharge limit. Among the possible treatment concepts, physicochemical approaches have become in the focus of interest lately. Such approaches offer relatively small environmental impact and the polluting organic substances can be recycled and/or reused.
Our method focuses on special wastewaters of high chemical oxygen demand (COD). It treats such kind of PWWs of fine chemical industry so that they meet environmental regulations. The two-stage treatment method, that is, vacuum evaporator and membrane filtration can reduce the COD of the process wastewaters under the discharge limit.

Keywords
Process wastewater, COD reduction, Vacuum evaporation, Reverse osmosis

INTRODUCTION

The high contaminant saturated wash waters are collected in containers in a fine chemical company. The lower pollutant flush water goes into pH neutralizer and then let into public sewer. The higher washing material contained liquid waste mean serious environmental problem for the companies, because its COD value is usually high above the sewer limit, that is 1000 mgO_2/L (28/2004. (XII. 25.) Ministry of Environment Regulation).

More methods can be reached in the literature to reduce the washing material concentration of process wastewater and treatment the liquid waste of fine chemical industry (Kowalska *et al.* 2005; Wang *et al.* 2009; Abdelmoez *et al.* 2013; Moreira *et al.* 2017). The aim of this study is to develop a method for reduce the COD value of PWW under 1000 mgO_2/L.

A number of physicochemical methods are suitable for treating PWW, which primarily remove the organic solvents, washing materials and reduce the chemical oxygen demand (Koczka & Mizsey 2010). The selection of these methods depend on many factors, such as: local conditions, economic parameters, environmental laws, composition of the process wastewater and the pollutant(s) (Toth

2015). The main physicochemical methods are: stripping, absorption, adsorption, ion exchange, extraction, wet oxidation, distillation, evaporation and membrane processes. In this study the last three method are examined.

The distillation of (volatile) organic compounds reduce significantly the COD of process wastewater. The distillation can be performed in discontinuous and continuous mode. There are two factors to consider: the quantity of the material and the need for a stripping column section. A batch distillation is suitable for the separation of small amounts and in the case of feed with frequently changing characteristics. Batch distillation can be realized so that total column is rectified or stripped (Toth 2015).

Nowadays volatilizing large part of water with evaporation is a realistic option, therefore only small amount of waste needs to be treated, for example incinerated. The increased costs and penalties made this method competitive (Koczka & Mizsey 2010).

The advantages of membrane processes are the high separation efficiency, the flexibility and the energy-efficient operation (Mulder 1996). The application of membrane technology is a realistic option for the treatment of PWWs, because it is suitable for reducing the COD value of PWW (Cséfalvay *et al.* 2008), reducing PWW quantity by using hybrid separation technology (Toth *et al.* 2011), cleaning heavy metals from PWWs (Koczka 2009). Reverse osmosis (RO) belong to the group of pressure-driven membrane processes, where the driving force is the transmembrane pressure between the two sides of the membrane.

MATERIAL AND METHODS

The average COD value of the waste sample is 8400 mgO_2/L. **Table 1** shows the pollutant concentration of PWW.

Table 1 Qualitative and quantitative measurement of initial process wastewater

	wt%	Compound name	CAS
1	1.31	1,2-Propandiol	57-55-6
2	3.27	Tetrahydrofurfuryl alcohol	97-99-4
4	0.23	1-Butoxy-2-Propanol	5131-66-8
5	7.22	2-(2-Aminoethoxy)ethanol	929-06-6
6	2.83	1-Ethyl-2-pyrrolidone	2687-91-4
7	32.20	Dipropylene glycol	25265-71-8
8	32.31	Dipropylene glycol monomethyl ether	34590-94-8
9	17.42	1-Methoxy-2-methyl-2-propanol	3587-64-2
10	2.72	2,4,7,9-Tetramethyl-5-decyne-4,7-diol	126-86-3
11	0.49	Tetraethylene glycol dimethyl ether	143-24-8

It can be determined, the aqueous sample contains substantially non-ionic washing material. The chemical formula of significant compounds can be seen in **Figure 1**.

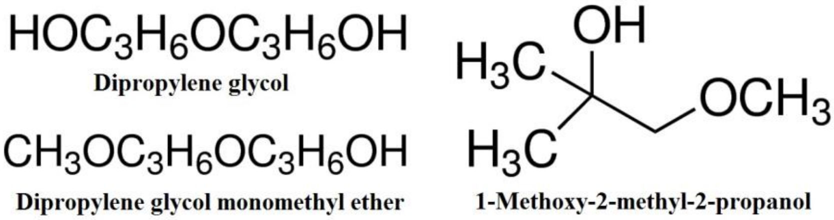

Figure 1 Main washing material molecules in process wastewater sample

The pollutant content is measured with Shimadzu GCMSQP-2010 gas chromatograph with a ZB-5 (30 m x 0.25 mm, 0.25 μm) column. The column temperature is kept at constant 100°C while the detector and injector are thermostated to 250°C. Pressure of carrier helium gas is kept at 133 kPa. COD is measured by ISO 6060:1991 (Toth 2015).

In such cases the batch distillation can be used more effectively than the continuous distillation. The main parameters of the laboratory distillation column are the following: Sulzer EX structured packing, internal diameters of 25 mm, 50 cm high. The column has 20 theoretical plates according to a measurement carried out by n-heptane–methylcyclohexane mixture. The column heating is controlled with a 350 W efficiency heating plate (see **Figure 2**).

Figure 2 Laboratory column for COD-reduction of PWW

Figure 3 shows the laboratory vacuum evaporator. 90°C water bath and 70 kPa are applied during the experiments.

Figure 3 Vacuum evaporator apparatus

Membrane filtration with CM-CELFA Membrantechnik AG P-28 apparatus is applied to further reduce the COD of the distillate of vacuum evaporation with reverse osmosis (RO). The membrane in the appliance is a circular plate of 75 mm diameter with an active surface area is 28 cm^2 placed on a porous sintered disc. In the device the liquid moves in winding canals creating cross-flow filtration. The volume of the tank is 500 cm^3. A gear pump circulates the water between the membrane surface and the tank. The constant temperature is maintained by an ultra thermostat. The tank of the apparatus is hermetically sealed and pressurized: inside the pressure is constant and higher than the atmospheric. The pressure difference between the feed and the permeate sides in the range of 30 bars is created by nitrogen gas. GE-SE-RO and TriSep-X201-RO membranes are applied. **Figure 4** and **Figure 5** show the test membrane apparatus (Toth 2015).

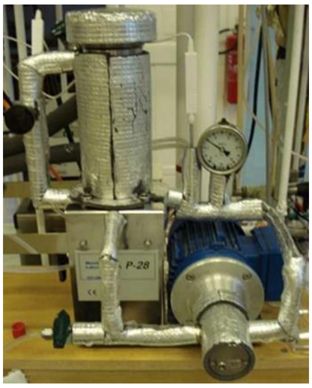

Figure 4 Photo of CM-Celfa Membrantechnik AG P-28 universal test membrane apparatus (Toth 2015)

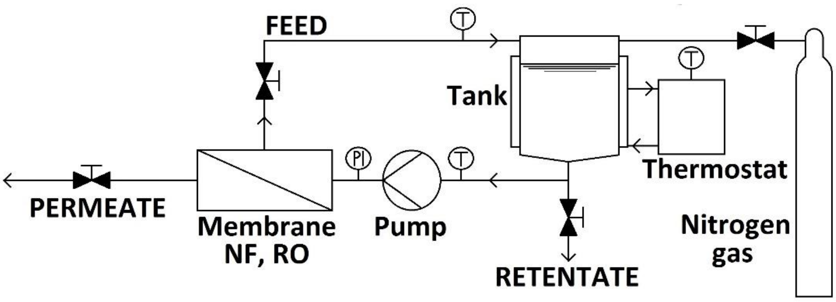

Figure 5 Schematic drawing of the experimental apparatus (filtration mode) (Toth 2015)

RESULTS

First of all, batch distillation is achieved for COD reduction. Despite, in every cases the distillate temperature is between 99.9–100°C, just 6000 mgO_2/L is reached in distillate, that is low reduction, only 29%.
Then laboratory vacuum evaporation experiments are examined to reduce the COD of PWW. **Table 2** shows that, 82–88% reduction can be realized with vacuum evaporator beside 20% material losses.

Table 2 Results of vacuum evaporator for COD reduction

COD in dist. [mgO_2/L]	Distillate/Feed [%]
1000–1500	80.0

Membrane filtration with CM-CELFA Membrantechnik AG P-28 apparatus is applied to further reduce the COD of the distillate of vacuum evaporation with reverse osmosis (RO). **Table 3** shows the results of examined membranes.

Table 3 Results of membrane separation for COD reduction

Membrane type	Flux [kg/m^2h]	COD in permeate [mgO_2/L]	Permeate/Feed [%]
GE-SE-RO	44.48	700–1000	86.1
TriSep-X201-RO	35.71	100–500	89.4

It can be seen, using TriSep-X201-RO membrane the COD value can be reduced under the emission limit. The material losses of vacuum evaporator and reverse osmosis processes can be established between 28.5–31.1%.

SUMMARY

According to our research, the suggested treatment for process wastewater containing washing material is the following: first of all stripping in vacuum evaporator and then reverse osmosis. In this case, the COD value can be reduced close to 100 mgO_2/L, so the treated process wastewater can be reused at the beginning of the cleaning method or if it is not possible, PWW can be discharged.

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