COD reduction of process wastewater with vacuum evaporation

1 Introduction

Fine chemical process wastewaters (PWWs) contain a wide range of pollutants and their pH is usually not neutral, which is why such wastewaters must be treated. In many cases, the PWWs also contain catalyst materials, emulsifying materials and other components. It is already apparent that these process wastewaters are significantly different from the communal wastewaters and from other industrial wastewaters too, primarily because they contain more non-biodegradable components. The organic pollutants are often molecularly dispersed, which complicates the destabilization and flocculation [1].

The treatment of the PWWs has two main objectives. On one hand the amount of non-biodegradable pollutants entering into the process wastewaters must be minimized and these components must be removed with greater efficiency by physical or chemical treatment before the biological step. On the other hand greater the reduction in Chemical Oxygen Demand (COD) must be implemented with the biological treatment, even if there are quantitative and qualitative fluctuations in the composition of the process wastewater [1].

A number of physicochemical methods are suitable for treating PWWs and the primary focus of the treatment is to remove the organic solvents and reduce the COD [2]. Selection of the method to use depends on the composition of the PWW, the chemical nature of the pollutant present in the wastewater, environmental legislation in a country, economic parameters and local conditions [1]. The main physicochemical methods are: ion exchange, adsorption, absorption, stripping, extraction, wet oxidation, distillation, membrane processes and evaporation.

Some of the solvents that contaminate the PWWs can be regenerated by different procedures. However, these regenerated solvents often do not meet the relevant pharmacopoeial standards and so their reuse and recycling are limited in the production of fine chemicals. In some cases, the multi-regenerated solvent can be reused in other industries. Yet in practice solvent transfer
is not typical between industries. The reason for this is that the regenerated and/or recycled materials have variable quality, due to the contaminating chemical compounds which are present in the solvents [1].

The most widely current and applied form of disposal of pharmaceutical wastewater and PWWs is incineration. The procedure is advantageous, because the wastewater is used as energy source in the incineration plants as the heat produced can be utilized. The possibility of incinerating waste solvents is determined by their halogen and sulphur content. Temperature of incineration also plays an important role in the incineration process design. If the solvent does not contain these components, the wastewaters can be burned without danger of corrosion. However, this is a rare occurrence, therefore separate facilities are built for the burning of waste solvents or already existing hazardous waste incinerators are used to avoid formation of dangerous by-products such as dioxins during the incineration. The halogen-free waste solvent’s calorific value is equal to or close to the petroleum-based fossil fuel liquid waste’s (30000 to 40000 kJ / kg). Such wastes can be used as auxiliary fuels in high-temperature industrial technologies (e.g. cement and ceramics production) or as auxiliary feeding flame in the hazardous waste incinerator and in the afterburner, ensuring the necessary temperature [3].

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 make this method competitive [2, 4].

Evaporation of PWW is a distillation process, where water is the volatile substance, leaving the concentrate as bottom residue to be disposed of. The aim of this operation is to reduce the volume of PWW or to concentrate mother liquors. The volatile steam is collected in a condenser and the condensed water is, if needed recycled after subsequent treatment. Operating under vacuum decreases the boiling temperature and enables the recycling of substances that would otherwise decompose. Evaporators are usually operated in series, where the condensation heat of one stage heats the condensate of the preceding stage [5].

Proper maintenance of the heat exchangers is crucial. Encrustations, fouling and corrosion disturb the heat transfer to the liquid and decrease the energy efficiency. The concentration of contaminants, or surrogate parameters (TOC, pH, conductivity, etc.) must be continuously monitored in the condensate need to prevent the transfer of pollutants [5].

It can be concluded, the driving force for implementation of vacuum evaporator is the recovery of materials from PWW streams and the minimisation of the waste volume sent for treatment [5].

Evaporation is unique different from other separation processes, in that the water is removed from the contaminants rather than the other way round. Before recent technological developments, the capital and energy requirements have made widespread industrial application of for evaporation processes limited in the wastewater treatment and recycling of the regenerated solvents. Evaporation was only used if all other treatment methods had failed or could not be applied. The heat pump vacuum evaporator offers reduced electrical energy consumption, and superior reliability for low to medium flow produced water treatment applications. Evaporation occurs under high vacuum conditions [4, 6-11].

The aim of this study is to examine the COD reduction of process wastewater from fine chemical industry with vacuum evaporation. The COD content must be reduced under the emission limit, which is 1000 mgO₂/L [12]. Objective function can be defined in order to find the appropriate separation technology: COD rejection and yield must be maximized, common optimization is necessary.

The COD rejection can be calculated by the following equation [11]:

$$COD_{\text{Rejection}} = \left( 1 - \frac{COD_{\text{Distillate}}}{COD_{\text{Feed}}} \right) \times 100 \quad [\%] \quad (1)$$

Yield is calculated according to Eq. (2)

$$Y = \left( \frac{V_{\text{Distillate}}}{V_{\text{Feed}}} \right) \times 100 \quad [\%] \quad (2)$$

which is the ratio of the volume of the distillate ($V_{\text{d}}$) and the volume of the feed solution ($V_{\text{f}}$).

## 2 Material and methods

The average COD of the treated PWW is 7500 mgO₂/L. Chemical oxygen demand of feed and bottom product of distillation and permeate of membrane filtration are determined by the K₂Cr₂O₇ standard method. This method is fully corresponds to the International Standard ISO 6060:1991 [1]. The PWW contains nonionic detergents and its pH is 7.5.

LED Italia R150-v3 type vacuum evaporator is applied. The main parameters can be seen in Table 1 and in Table 2 [13].

The flowsheet of the pilot, heat pump evaporator can be seen in Figure 1.

40 L initial process wastewater was pumped into the evaporator. Six different pressures were investigated. During the experiments, applied pressure and boiling
Table 1. Technical characteristics of LED Italia R150-v3 type vacuum evaporator [13]

| Technical characteristic                                      | Details                                      |
|--------------------------------------------------------------|----------------------------------------------|
| Nominal production of distillate with water                  | 150 L/24h                                   |
| Model                                                        | R 150v3 FF# ; Superduplex stainless steel    |
| Electrical equipment                                         | R 150v3--3 (400 [V] 50 [Hz] 3P)              |
| Distillate heat exchanger                                     | Internal coil                                |
| Primary heat exchanger                                       | Heating jacket                               |
| Evaporation type                                             | Vacuum with a scraped system                 |
| Evaporation pressure                                         | Absolute pressure 40-50 mbar                 |
| Distillate temperature                                       | 33-35°C                                     |
| Drops separator                                              | Demister, grate type with packing elements   |
| Technology of heating/cooling                                 | Heat pump                                    |
| Heat pump compressor                                         | Reciprocating hermetic                       |
| Refrigeration fluid                                          | R 134a (ozone friendly)                     |
| Cooling of refrigeration fluid                               | Air cooled finned heat exchanger             |
| Vacuum system                                                | Liquid ejector                               |
| Electrical cabinet rating                                    | IP 54                                        |
| Noise                                                        | < 80 dB(A)                                   |

Table 2. Nominal performance of LED Italia R150-v3 type vacuum evaporator [13]

| Nominal performance                                           | Details                                      |
|---------------------------------------------------------------|----------------------------------------------|
| Electrical feed                                               | 230 V ; 50 Hz ; 1F                          |
| Maximum production of distillate with water                   | 170 L/24h ± 10%                             |
| Absorbed power                                                | 2.3 kW ± 10%                                |
| Specific consumption                                          | 0.325 kWh/L ± 10%                           |
| Produced heat                                                 | 2.3 kW ± 10%                                |
| Maximum air flow of finned heat exchanger                     | 1000 Nm³/h ± 10%                            |

Figure 1. Process diagram of LED Italia R-150 heat pump evaporator [14]
temperatures were measured. The examination was carried out until the best available yield. After the experiments the COD of distillate was measured in order to define the rejection. Finally, mass balance was also calculated.

3 Results and discussion

Figure 2 shows the COD rejection as a function of the yield. It can be seen, the maximal COD rejection value was reached at the yield of 85% and it was 88.7%. They represent a monotonous growing correlation.

In Figure 3, the COD values can be seen in the function of Ys, where the straight line means the emission limit. It can be concluded, 84.5% must be reached in order to reduce under the emission limit the COD of process wastewater.

Figure 4 and Figure 5 depict the yield as the function of boiling temperatures and the applied pressure. It can be seen that both graphs they are logically in good accordance with each other and the lowest pressure can result the best available yield.

It can be identified, the boiling temperature values with the corresponding pressure pairs are in acceptance accuracy with water phase [15, 16], see Figure 6.
4 Conclusions

Vacuum evaporation of washing nonionic detergents at pilot-scale setup is investigated. Evaporation rates are influenced by operating pressure between 40 and 50 mbar. The highest yield can be achieved at 40 mbar, where the boiling point is 32.8°C. The chemical oxygen demand is also the lowest using 40 mbar pressure: 850 mgO₂/L, which means 88.7% in COD rejection value. It can be concluded the COD value of process wastewater can be reduced under the effluent limit, so there is opportunity to recycle or reuse of this water.

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**Nomenclature**

| Symbol | Description | Unit |
|--------|-------------|------|
| COD    | Chemical oxygen demand | [mgO₂/L] |
| D      | Distillate   | [L]  |
| F      | Feed         | [L]  |
| PWW    | Process wastewater |      |
| T-bp   | Boiling point | [°C] |
| V      | Volume       | [L]  |
| Y      | Yield        | [%]  |

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**Figure 6** Water phase diagram [17]
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