

# Physicochemical treatment of pharmaceutical process wastewater: distillation and membrane processes

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## Abstract

*This work provides physicochemical solutions for the treatment of process wastewaters of fine chemical industries, that is, pharmaceutical industry. Economical methods are recommended for practical use, which can reduce the disposal ratio of the process wastewaters with higher values of chemical oxygen demand (COD) and Adsorbable Organically Bound Halogens (AOX) than the corresponding emission limits. Such treatment alternatives are also the part of environmental sustainability.*

*The work reviews the theoretical background of the problem and gives options for using the waste management hierarchy chart. Then the general features of pharmaceutical process wastewaters and the treatment methods are summarized. In the algorithm developed for process wastewater treatment, the distillation is the core of the physicochemical treatment alternatives. In the case of the real industrial case studies, the distillation and membrane filtration laboratory experiments and cost calculations prove the efficiency of the selected physicochemical treatment options.*

## Keywords

*waste management · solvent regeneration · distillation · membrane process · process wastewater treatment · COD reduction · cost calculation*

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## 1 Introduction

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 [1].

The other problems besides the large quantity of by-products are that

- the chemical process wastewaters 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,
- the biological treatment is often not officially authorized.

So other alternative methods must be sought to solve the problem [2, 3].

## 2 Strategy for process wastewater treatment methods – theoretical concepts

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 [4, 5].

In the 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. In our work we deal with the latter.

Benkő and co-workers [6] studied the separation of a highly non-ideal quaternary mixture. They compared two solvent recovery (extractive heterogeneous-azeotropic distillation -

EHAD - and ternary cutting) structures to waste incineration. According to the economic calculations the solvent recovery structures gave better results than the incineration. The problem was examined on the basis of environmental considerations, too: the best treatment structure was EHAD followed by the incineration and the last one was ternary cutting method. This example also showed that the developed regeneration structures could fulfil both economical and environmental requirements [7].

As it is mentioned in the introduction, the process wastewaters could not always be treated with conventional biological methods. The treatment technology, in this case the column performing EHAD, should be built in the factory or in its vicinity, for which there are already a number of existing industrial examples.

### 3 The features of pharmaceutical process wastewater

Pharmaceutical process wastewaters are very diverse in pollutants and their pH is usually not neutral - that is why they must be treated. It is known that in the pharmaceutical processes the raw materials never completely transform (in the sense that the starting material is completely converted into end products), but the transformation only happens to a certain degree, and a large quantity of by-product is produced, too.

In the environmental evaluation of a process the E-factor is a frequently used factor to characterize the environmental feature of different process alternatives. The E-factor is the ratio of waste quantity and the product quantity associated with the process, where the selected product is produced [8]. Hence this industry has typically a high E-factor. Thus, the pharmaceutical process wastewaters consist of starting materials, and the main products, as well besides the by-products.

In many cases, the pharmaceutical process wastewaters 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.

The treatment of these process wastewaters is a two-way effort. 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 COD reduction must be implemented with the biological treatment, even if there are quantitative and qualitative fluctuations in the composition of the process wastewater. In BREF (best available techniques reference document) the main target is the significant COD reduction (by 90%) [9].

Some of the contaminated solvents could be regenerated by different procedures but the relevant pharmacopoeia standards limit the possibilities of recycling and reuse. In some cases, the multi-regenerated solvent is used 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 because the pollutions prevent the maintenance of the constant quality.

If the pharmaceutical process wastewaters get into the surface waters they change the flow conditions, morphology and the habitat. They poison the wildlife of the rivers and can also cause thermal pollution. Since with the increase in water temperature the oxygen content decreases, aerobic organisms might be damaged and their numbers get significantly reduced. The lack of oxygen favors anaerobic degradation processes, which can lead to the disintegration of the biological balance [10]. Some thermophilic algae can also proliferate making these waters richer in organic matter, which can lead to eutrophication.

### 4 Process wastewater treatment methods

#### 4.1 Physicochemical treatments

A number of physicochemical methods are suitable for treating process wastewater, which primarily remove the organic solvents and reduce the chemical oxygen demand [11]. The selection of these methods depend on many factors, such as:

- composition of the process wastewater and the pollutant(s);
- environmental laws;
- economic parameters;
- local conditions.

Hereafter, applicability, advantages and disadvantages of the main physicochemical methods are described. The main physicochemical methods are: absorption [12], adsorption [12], ion exchange [12], extraction [12], evaporation [11], wet oxidation [13], distillation and membrane processes.

#### Distillation

Out of the various liquid waste treatment technologies the most widely used method is distillation [14]. 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 investment has reasonable and affordable cost compared to the various industry frameworks.

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 were developed [15, 16].

The distillation of volatile organic compounds (VOCs) significantly reduces the chemical oxygen demand of process wastewater (COD). The Adsorbable Organically Bound Halogens (AOX) could be removed with distillation but the process should be carried out carefully [11, 12]. 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 [17].

#### Membrane process

The advantages of membrane processes are the high separation efficiency, the flexibility and the energy-efficient operation [18, 19]. 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 [20, 21].

The pervaporation is one of the fastest developing membrane processes which could be applied as a unit of hybrid operations, as well. Pervaporation is the preferred method for anhydration of solvents, mainly alcohols [22].

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 [12]
- reducing process wastewater quantity by using hybrid separation technology [23]
- reducing the COD value of process wastewater [24].

These methods have not been used widely for purification of process wastewaters yet [11].

#### 4.2 Waste incineration

The most widely accepted form of disposal of pharmaceutical process wastewater is incineration. The procedure is advantageous since the process wastewater is used as energy source in the incineration plants: the produced heat can be utilized.

The possibility of incinerating waste solvents is determined by their halogen and sulfur content. If the solvent does not contain such components, the process wastewaters can be burned without danger of corrosion [25]. Since corrosion rarely takes place separate facilities are built for the burning of waste solvents or already existing hazardous waste incinerators are used.

#### 4.3 Strategy for process wastewater treatment methods – developed methodology

The strategy developed by Mizsey et al. [26] follows the principle of sustainability: obtaining valuable materials from process wastewaters should be considered a primary goal. So the very last step of the process is the release of the process wastewater into the sewer. Important concept for selecting the technology is that the process wastewater meets the criteria for release into the sewer. The current values can be found in 28/2004. (XII. 25) Ministry of Environment Regulation.

First, the AOX-value of the process wastewater has to be examined. If the water contains more AOX-causing components than the limit value and they are volatile then they should be distilled. After distillation it is necessary to examine the distillate, because it contains a high concentration of reusable volatile solvents. If the distillate composition is not adequate in the terms of recovery it must be disposed. In this case the incineration is much more economical since the treated process wastewater has less water than the raw, loose form.

If the AOX value of the process wastewater is under the limit it is appropriate to examine the COD. If the mixture contains many volatile solvents, it should be distilled. The volatile solvents of the bottom can be significantly reduced with distillation. At this point it is prudent to re-examine COD value of the bottom.

If the COD and AOX values of process wastewater meet the environmental regulations, then the bottom can be streamed into the sewer without paying a fine. If not, then the non-volatile materials must be removed from the mixture. This problem could be solved with physicochemical technologies (see previous section).

After the physicochemical method the process wastewater must be examined again to decide whether it can be released into the sewer. If the process wastewater still does not meet the criteria it must be decided weighing up economic considerations whether to use other treatments. Then the amount of environmental fines should be compared with the price of the cleaning technology.

### 5 Physicochemical treatment methods in practice

Table 1 contains the physicochemical characteristics of five different pharmaceutical process wastewaters. These are industrial samples. The methods of analysis are listed here. For the VOC analysis a gas chromatograph equipped with a flame ionization detector is used. The distillate water content is measured by Karl-Fischer titration. The COD is measured by ISO 6060:1991 and/or AOX value is also determined.

In Table 1 the pollutant component means in fact organic component. Studying the results found in Table 1, it can be noted that in each case, releasing the process wastewater into the sewer generates very serious environmental problems. The reason for this is the high COD content. The fine would be very significant and the incineration is also expensive because the samples have high water content. Thus, a cheaper alternative solution must be found.

#### 5.1 Distillation

Studying the technologies listed in Section 4.1 and the components of the process wastewaters distillation was selected for solving the problem. The volatile chemical oxygen demand (VOC-COD) can be enriched in the distillate [11].

A wide variety of process wastewaters should not be mixed in the experimental stage because later it is not possible to estab-

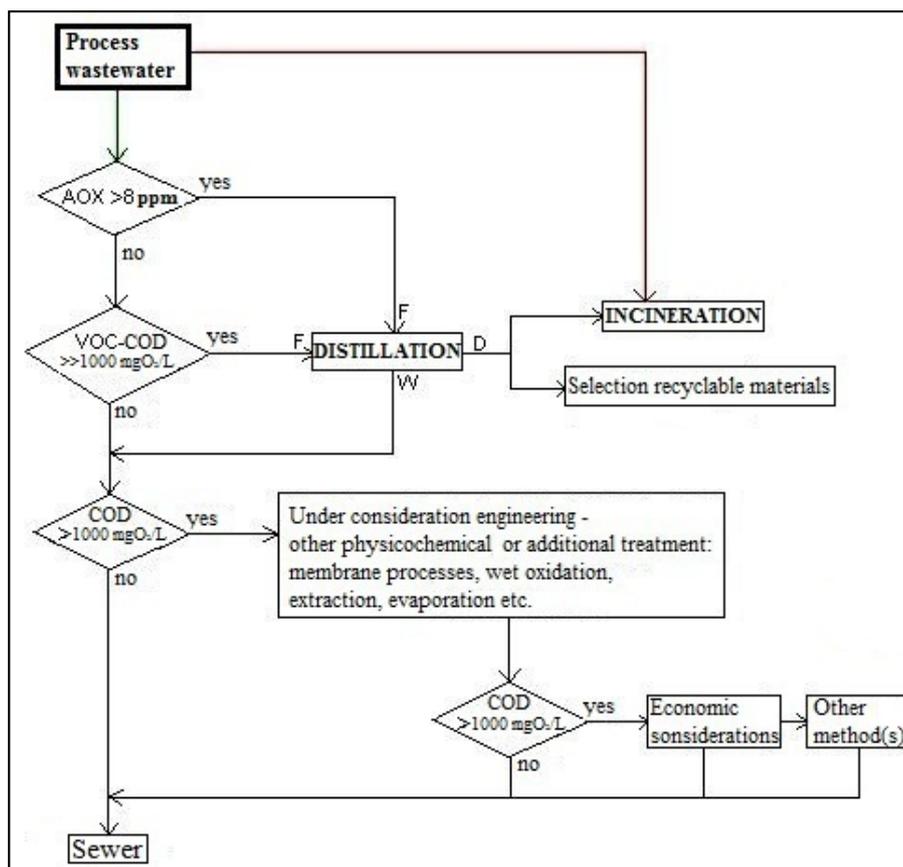


Fig. 1. Strategy for process wastewater treatment methods [27]

Tab. 1. Experimental process wastewater

Sample	Density [g/cm <sup>3</sup> ]	pH	Dry substance [wt%]	Pollution component [wt%]	COD [mgO <sub>2</sub> /L]	AOX [ppm]	Quantity [t/a]	E-factor
1	1.01	6.9	0.66	0.21 Acetone 0.44 Dichloromethane 0.42 Methanol	12400	7850	792	220
2	0.97	5.8	0.23	15.7 Ethanol	298000	-	648	270
3	1.02	5.5	9.31	26.2 Methanol	238000	-	96	40
4	1.01	7.0	0.00	3.14 Ethyl acetate 0.76 Ethanol	40000	-	26	26
5	0.97	7.0	0.70	0.42 Dichloromethane 7.92 Ethanol 0.16 Methanol	51000	2360	1440	230

lish, which one is the most difficult to clean and which one can cause scaling and/or corrosion.

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. In such cases the batch distillation can be used more effectively than the continuous distillation. Batch distillation can be realized so that total column is rectified or stripped. Continuous distillation is usually carried out when the feed enters the middle part of the column and the separation is taking place in both the rectifying (upper) and the stripping (lower) column sections.

It was found expedient to design the column in continuous mode and to make preliminary experiments with it because in the factory each process wastewater is produced in large quantities and the stripping column is also needed.

Enrichment of the distillate in pollutant components is well worth-while since then the incineration will be cheaper due to the lower water content. The AOX value of the bottom (Samples 1 and 5) must be reduced below the limit (8 ppm). This problem can be solved as shown in previous studies [11]. Based on the very high COD values for the five process wastewater samples it is not likely that the bottoms in either case could be reduced below the limit (1000 ppm), so even before the distillation it is worth considering the use of additional physicochemical treatment methods. In principle, the COD can be further reduced with membrane separation. In this case the greatest possible degradation should be achieved because the very sensitive membrane must be spared from pollution.

### 5.1.1 Laboratory experiments

The main parameters of the experimental column are the following: 1.2 m high, internal diameter of 4 cm with Raschig ring packing. The column had 9 theoretical plates. (According to measurement carried out by methanol-water mixture.) The feed was not preheated and it was pumped in the middle of the column. The column heating was controlled with a 1 kW efficiency heating plate.

Before the experiments a computer simulation was realized with ChemCAD 6.2.0. to reduce the required number of experiments, and the optimum reflux ratio, the mass- and bottom flow rate were determined based on the experimentally measured heating power. Furthermore pilot plant experiments were carried out with Sample 1 and 5 where the heating was optimized as well. Table 2 and Fig. 3 show the experimental results.

It was a difficult task to find the settings where the process was both in steady-state and in enrichment status in the cases of Samples 1, 4 and 5 (process wastewaters with heterogeneous azeotropic mixtures). In the experiment with Sample 4 the simulated optimal reflux was 10, but the enrichment was only over 20. This once again attests to that the computer could only assist

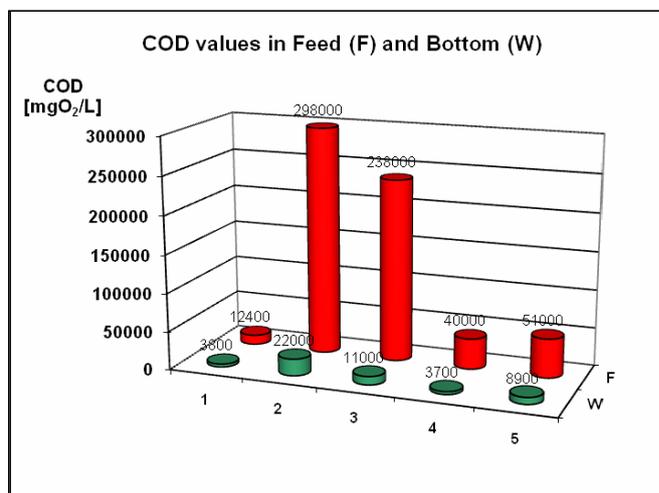


Fig. 2. Distillation COD reduction

in our work so it is important to verify the calculations experimentally.

However, we could reach our most important goal, namely the drastic reduction of COD, the bottoms still had to be treated with other methods because the COD was still over the legal limit. Based on our analytical measurements the halogen content (AOX) was reduced below the emission limit of 8 ppm.

### 5.1.2 Up-scaling

After the laboratory experiments pilot plant distillation experiments have to be carried out to determine whether industrial equipment can be designed. The distillation column should be designed so that one column can process higher amount of water. In this case there is no need to build a separate unit for each stream of process wastewater. Therefore, if the column size and the place of the feed is fixed, the desired purification with the correct selection of the reflux and D/F ratio can be achieved.

The energy requirements of distillation could be significantly reduced, if we were able to preheat the feed with the heat of the bottom [27]. Another unique feature of this distillation is that there is no need for designing a kettle separate from the column, since direct injection of the steam can be used for the heating of the kettle. The condensing steam also dilutes the bottom and further reduces the COD and AOX.

In some cases two-phased distillate is formed but it is not worth dealing with separately because the separation already works well enough and it would only complicate the column structure. Although, technological experience shows that the process wastewaters are often mixed, it is preferable to strive for a simpler operation.

Using our experimental results and the above observations was designed a column with seventeen theoretical plates and structured packing [28]. The feed tray location was at the middle of the column.

**Tab. 2.** Distillation results

Distillation results	1	2	3	4	5
Reflux	10	4	4	10	10
D - Pollution comp. [wt%]	65.3	75.6	99.8	11.9	94.1
D - Temperature [ <sup>0</sup> C]	87.3	83.2	64.8	93.5	76.5
D/F ratio	0.01	0.19	0.26	0.26	0.07
W - Pollution comp. [wt%]	0.14	traces	traces	0.06	0.32
W - AOX [ppm]	2	-	-	-	8.5E-03
COD reduction [%]	69	93	95	91	83

### 5.1.3 Membrane process

More experiments were carried out with Samples 2, 3, and 4 the process wastewater samples with no halogen content. Membrane filtration with CM-CELFA MEMBRANTECHNIK AG P-28 apparatus was applied to further reduce the COD of the bottom with ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO).

The membrane in the appliance was a circular plate of 75 mm diameter with an active surface area is 28 cm<sup>2</sup> 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<sup>3</sup>. A gear pump circulates the water between the membrane surface and the tank. The constant temperature is maintained by an ultra thermostat. Two kinds of thermometers were used: one measured the temperature of the liquid before the membrane and the other one after the membrane. 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 10 to 30 bars is created by nitrogen gas.

First a known quantity of liquid was poured in the tank and the quantity of the filtrate was measured as a function of time. Every time when a new membrane was used a test was carried out with distilled water before and after the filtration of process wastewater so we could draw conclusions based on the fluxes about the interaction of the sample and the membrane. The membrane was fouled when the flux of the second distilled water measurement was higher, or was falling through, if the flux was lower. The results of the COD values of the permeate could be read in Table 3.

**Tab. 3.** Membrane filtration COD reduction

COD [mgO <sub>2</sub> /L]	Distillation		Membrane filtration	
	F	W	W-NF	W-RO
Sample				
2	298000	22000	16600	3800
3	238000	11000	9600	-
4	40000	3700	1030	-

COD was not reduced by ultrafiltration therefore Table 3 does not include these experimental results. However, in the case of Sample 4 the limit was not reduced with nanofiltration, signifi-

cant decrease was achieved when reverse osmosis was applied.

In shortly it can be said that the membrane filtration of the bottom is rewarding when the chemical oxygen demand is close to the limit value and that significant scaling and fouling were not experienced.

Before selecting the utilization of the technology initial and operating costs and process wastewater charges should be examined.

## 6 Process wastewater charge calculation

The cost with annual material flow of the raw process wastewater and the bottom of distillation was calculated.

The fee for the sewage disposal (the usage of the sewers) consists of several parts: sewage disposal charge, water load charge and value-added tax (VAT). In 2010 the sewer usage charge (SUC) was 340.25 Ft/m<sup>3</sup> [29]. The disposal charge is a service charge and the water load charge is basically an environmental tax. The annual sewer usage charges for each samples are summarized in Table 4:

**Tab. 4.** Sewer usage charges (SUC) [29]

SUC [€/a]	F	W
1	1012	940
2	862	678
3	121	92
4	34	25
5	1916	1710

At first the actual case limit values have to be looked up. These can be found in 28/2004. (XII. 25) Ministry of Environment Regulation (Annex 4.) [30]. Table 5 contains the limit values and the specific penalty factors.

**Tab. 5.** Limit values and specific penalty factors [30, 31]

Parameter	Limit value	Specific penalty factor
COD	1000 mgO <sub>2</sub> /L	140 Ft/kg
AOX	8 ppm	140000 Ft/kg
pH	under 6.5; over 10.0	700 Ft/kg
Dry substance	2500 mg/L	140 Ft/kg

Studying Table 1 it is found that there are four unsuitable parameters in the raw process wastewaters COD, AOX, pH and dry substance. In the bottoms – in contrast to AOX – the COD is never under the limit. Dry substance and pH are not taken into account only the excess of COD and AOX were calculated. It is assumed that the factory filtered and neutralized these process wastewaters. Table 6 contains the fines.

**Tab. 6.** Fines [29, 30, 31]

Fine [thousand €/a]	F	W
1	408253	1.08
2	105.38	5.85
3	11.85	0.38
4	0.53	0.03
5	231844	5.56

Table 6 shows that the COD-fines of the raw process wastewaters are very high. For the halogen-containing process wastewaters the AOX and COD fines are added together. Noticing the high AOX-fines it can be said that incineration or alternative physicochemical treatment technologies are necessary for the treatment of these process wastewaters because disposal of the sewage could cause bankruptcy.

Adding the sewer usage charges (Table 4) and the fines (Table 6) the actual process wastewater fees (WWF) can be calculated.

**Tab. 7.** Process wastewater fees (WWF) [29–31]

WWF [thousand €/a]	F	W
1	408254	2.02
2	106.24	6.53
3	11.97	0.47
4	0.57	0.05
5	231846	7.27

The results shown on Fig. 2 appear in the process wastewater fees, too. Table 7 and Fig. 3 attest to the economic efficiency of the technology. It is essential to note that applying distillation the charges could be reduced up to 90%. Fig. 4 shows that the COD-fine takes up the largest part of the process wastewater fee.

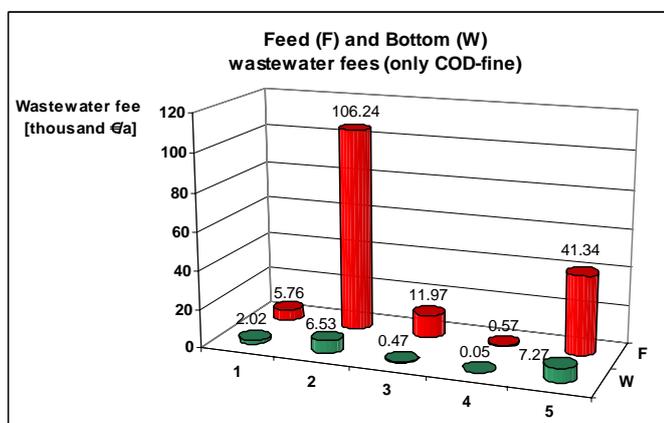
Distillation was also found economical since the fines can be reduced significantly and the payback time of the column designed by our research group is 2 years maximum [32, 33].

## 7 Summary

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 our goal is to minimize the use of materials and energy so that the amount of waste is also minimised. To find the best option, life-cycle analysis has to be carried out which is optimal in technological, economical, and social aspects.

In this work distillation and membrane processes are 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 environment 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 process wastewater problem.

Using membrane filtration process can be also a beneficial option for treating the bottom product of rectification to concentrate non-volatile pollutants. Such treatment can be an option if the bottom product does not meet the emission prescriptions. Without scaling and fouling of the membrane, the COD value can be reduced close to the emission limit.



**Fig. 3.** Process wastewater fees (only COD-fines) [29–31]

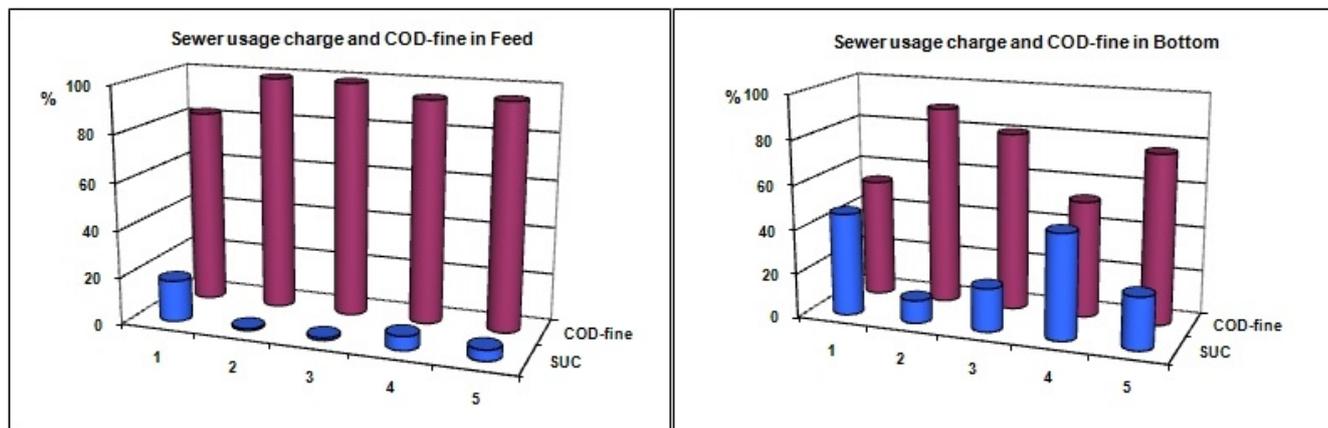


Fig. 4.

### List of Symbols

BREF	best available techniques reference document
D	distillate, overhead product
EHAD	extractive heterogeneous-azeotropic distillation
F	feed
NF	nanofiltration
RO	reverse osmosis
t/a	ton/annual
UF	ultrafiltration
VAT	value-added tax
W	bottom product
wt%	weight percent
€/a	euro/annual
AOX	adsorbable organically bound halogens [ppm]
COD	chemical oxygen demand [mgO <sub>2</sub> /L]
SUC	sewer usage charge [€/a]
VOC	volatile organic compound [ppm]
WWF	wastewater fee [thousand €/a]

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