Novel method for the removal of organic halogens from process wastewaters enabling water reuse

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ABSTRACT

The industrial production unavoidably generates waste in many cases but that should be recycled and reused following the principle of circular economy. New waste treatment methods or green technologies with zero waste should be developed in order to solve this problem. Since zero emission technology is a difficult task, it is rather typical that waste treatment process is developed. A typical example can be found in pharmaceutical industries because these plants generate wastewaters with high organic content, so-called process wastewaters (PWWs). These waters should be definitely treated before discharging, their organic content must be removed and then the PWW may be usually allowed into the sewer. Nowadays, the physicochemical methods are increasingly used since they have a smaller footprint compared with that of the biological treatments. On the other hand, the polluting organic substances can be recovered and recycled or reused. In our novel method, distillation is applied that is based on relative volatility differences of the individual components. The more volatile organic pollutants of the treated PWWs are obtained as the top product of the distillation, preferably in reusable form. The bottom product of distillation, namely the PWW should satisfy the discharge limits. Our novel innovative method is developed to remove and reuse the organically bound halogens and to reduce the chemical oxygen demand below the emission limit of PWWs. Our method is implemented and this well-planned industrial apparatus meets the requirement of the Sustainable Water Solutions and Circular Economy, and moreover the payback time of the investment is less than 2 years.

Keywords: Process wastewater; AOX removal; Dichloromethane; Distillation; Industrial column; Circular economy

1. Introduction

The treatment of process wastewaters (PWWs) is difficult, because there are other problems besides the large quantity of by-products [1,2]. In many cases the chemical PWWs create azeotropic mixtures, where the microbes in the conventional activated sludge are not able to convert the substances into their own nutrition. Furthermore, the biological treatment is often not officially authorized [3]. On the other hand, if the biological treatment is considered, there is no chance for the recovery of the polluting compounds. In many cases, the PWW fees are very significant and the incineration

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is also expensive because of the high water content of the samples. Therefore, cheaper alternative methods are needed to solve the problem [2,4,5].

The large amount of PWW with adsorbable organically bound halogens (AOX) content means serious problem in pharmaceutical industry. AOX is a sum parameter which indicates the overall level of organic halogen compounds (chlorine, bromine, and iodine) in water samples. The emission of AOX into the water in Europe by different industry sectors is shown in Table 1, highlighting the chemical industries in Table 2.

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 [6]. It is important to emphasize that many organic halogen compounds are persistent and/or toxic. The AOX method has several advantages, for example, it is a very simple and cheap measurement when it is compared with the alternative methods of measuring levels of individual compounds [6].

The advised treatment techniques of AOX removal methods from PWWs: chemical oxidation (pretreatment), wet oxidation (pretreatment), chemical hydrolysis, nanofiltration/reverse osmosis, adsorption [7–9], extraction, evaporation, pervaporation [10,11], stripping, and incineration and distillation [6,12]. Air stripping and its alternative method, steam stripping provides high efficiency up to 99.9% volatile organic compounds (VOC) and AOX removal [13,14].

1.1. Distillation for treatment of process wastewaters

The distillation of VOCs significantly reduces the chemical oxygen demand (COD) of PWW. The VOC-COD can be

enriched in the distillate [2,6,15]. The AOX could be removed with distillation too, but the process should be carried out carefully [16]. This study investigates a physicochemical approach for recycling wastewaters by applying distillation. The concept of this method is based on the difference of the relative volatilities of individual components in the wastewater. Fig. 1 introduces a distillation schema for treatment of PWW with AOX and/or VOC content. The main advantages of PWW distillation are the possibility of material recycling and removability of refractory and/or toxic organic compounds. The disadvantage is the energy requirements, which can be reduced significantly if the feed is preheated with the bottom product as a kind of energy integration [2,6].

The aim of this study is to introduce a method for treatment of PWW with ~6,000 ppm AOX concentration and ~16,000 mgO_2/L COD. Laboratory, pilot experiments, and industrial application are also demonstrated. The target of the treatment is to reduce the AOX below 8 ppm (discharge limit) and COD below 1,000 mgO_2/L to channeling the PWW. These emission values are the regulation limits, as it can be found in 28/2004. (XII. 25.) Ministry of Environment Regulation [18].

The emission limits for PWWs are extremely strict and the fine is high. If PWW of organic halide content is channeled by the company it can be either closed or punished with extremely high penalty. So it is essential for the manufacturer to develop such waste treatment method that is capable to fulfil the emission limits and maintain the economic and the environmental conscious industrial production.

According to the literature study, the largest phase of PWW can be recycled/reused using our elected method, which is distillation [2,15,19,20]. Fig. 2 summarizes the recommended treatment methods in the case of high content COD and AOX PWWs.

It can be stated, our method follows the principles of circular economy (see Fig. 3). Circular economy is an industrial economy that follows natural life cycles. In such way there is no waste production, but one product of the link becomes the resource of the following one leading toward a closed cycle [21]. The regeneration of PWWs can be solved locally in the factory with the introduction of waste treatments. The aim is to increase the recycle rate of the organic material of PWW

Table 1
The emission of AOX into the water by industry sectors/activities in Europe in 2010 [6]

Industry sector	Installation		AOX emission	
	No.	%	Ton	%
Urban wastewater treatment	232	62	1,045	25
Paper and wood	61	16	1,997	48
Chemical industry	33	9	353	8
Other sectors/activities	26	7	179	4
Other waste and wastewater management	22	6	591	15
Total	374		4,165	

Table 2
The emission of AOX into the water by chemical industries in Europe in 2010 [6]

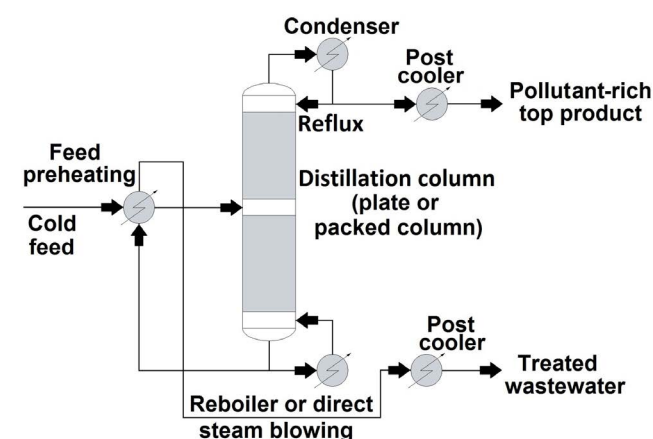| Chemical industry	Installation		AOX emission	
	No.	%	Ton	%
Basic organic chemicals	21	64	314	89
Basic inorganic chemicals	6	18	25	7
Other chemicals	6	18	14	4
Total	33		353	

Fig. 1. General schema of the process wastewater distillation [17].

and after that significantly less residual waste have to be disposed with incineration (cf. Fig. 2).

It is clear by now that the PWWs should be rather treated with physicochemical methods than with biological ones. In the case of PWW treatment, the most applicable physicochemical method is based on the differences of relative volatilities. In this case the volatile organic pollutants can be removed by heating.

Designing such a method is a process design activity. It needs creativity, innovation, experience, and simply to say engineering excellence.
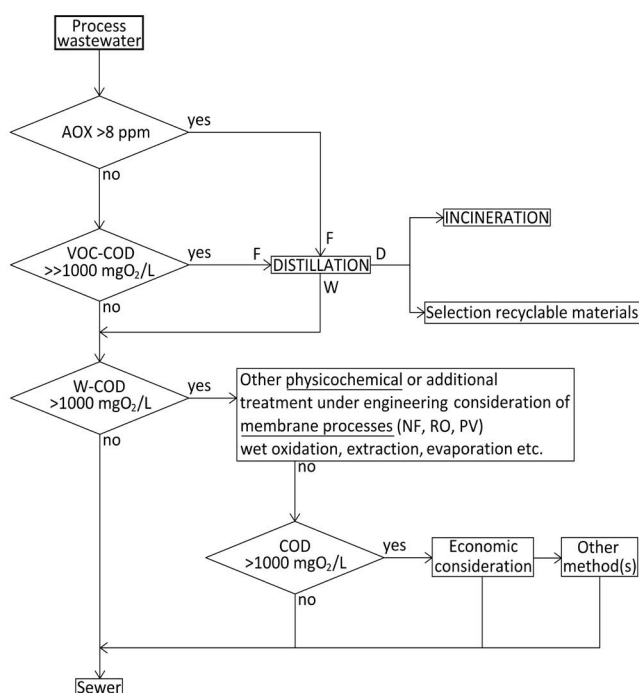

Fig. 2. Strategy for process wastewater treatment methods [17]. F: feed, D: distillate, and W: bottom product.

Fig. 3. Flowsheet of circular economy [21].

2. Materials and methods

Table 3 contains the polluting compounds of real industrial PWW samples from pharmaceutical sector. The amount of dry substance is not significant, but the COD values are so far from the emission limit. It can be seen halogen components, methanol, acetone, and dry substance cause the high COD in initial PWW. Furthermore, the average density is 1.02 g/cm^3 and pH is 6.7. Continuous operations were examined, because of the large amount of PWW, which is 570 ton/year.

The distillation of PWW is containing organic solvents, especially halogenated organic compounds behave as the distillation of mixtures with limited solubility. 99.8% of AOX is dichloromethane (DCM), further halogen compounds in the PWW can be found in Table 4. DCM is a toxic volatile compound which is found in the wastewater and ground water and widely used as a solvent in chemical industry. It is potentially carcinogenic for humans and induces cancer in animals [12]. It can be determined, every pollution compound belongs to the group of VOC [22,23].

They form minimum boiling heterogeneous azeotropic with water [24,25]. Fig. 4 shows the vapor–liquid equilibrium (VLE) of DCM-water mixture.

It can be seen 98.5 wt.% DCM means the azeotropic point. 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 a temperature which is always below than 100°C in the PWW distillation.

The process design steps are based on mathematical modelling and experiments. The modelling helps to reduce the

Table 3
Main parameters of process wastewater samples

Sample	Feed composition (ppm)			Dry substance	COD
	AOX	Methanol	Acetone	(%)	(mgO$_2$/L)
1	5,720	2,330	3,530	1.02	15,200
2	6,630	2,110	3,580	0.59	14,800
3	5,390	1,980	2,940	1.10	17,300
4	5,530	1,990	3,450	0.33	15,300
5	6,570	2,050	2,760	0.51	16,400
Average	5,968	2,092	3,252	0.71	15,800
Deviation	589	143	375	0.33	1,027

Table 4
AOX components in PWW

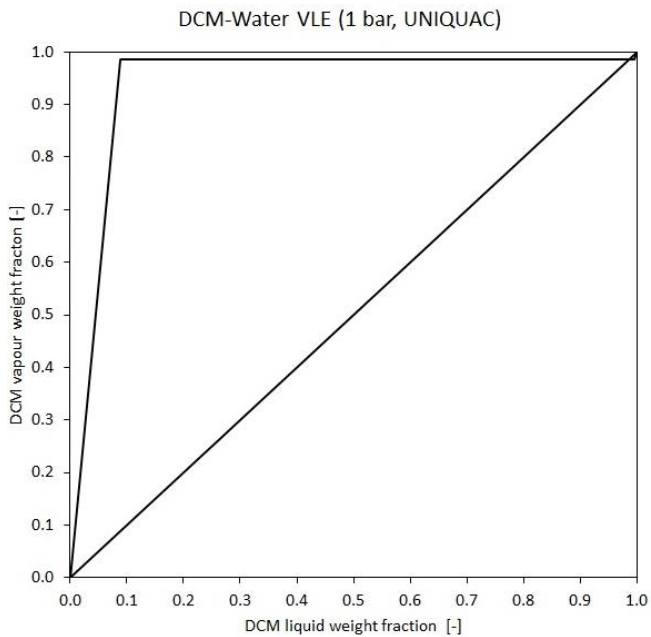| Component name	CAS	Ppm	AOX%	Azeotropic T-bp (°C)
Dichloromethane	75-09-2	5,956	99.8	38.1
Trichloroethylene	79-01-6	5.4	0.09	73.1
1,2-Dichloroethane	107-06-2	3.0	0.05	71.6
Chloroform	67-66-3	1.8	0.03	56.3
Tetrachloroethylene	127-18-4	1.2	0.02	88.5
Carbon tetrachloride	56-23-5	0.6	0.01	66.8

Fig. 4. Dichloromethane-water VLE diagram at 1 bar.

solution space and the promising alternatives can be selected. However, these alternatives must be tested and investigated by experiments. First, laboratory experiments and then experiments on the pilot plant scale were carried out.

Before the experiments, flowsheet simulations were carried out with flowsheet simulator (ChemCAD) to minimize the solution space, the required number of experiments and to find out the proper parameters of the unit operations. UNIQUAC method [26–29] was used for calculation of highly nonideal vapor-liquid equilibria. The optimal mass flow rates, reflux ratio, heating, and cooling requirements can also be determined [30]. 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 should be fed at the middle of the column.

Laboratory column was built to develop the treatment method (see Fig. 5).

The main parameters of the laboratory experimental column can be seen in Table 5. The column had 10 theoretical plates according to a measurement which was carried out with methanol-water mixture. The PWW feed was not preheated and the column heating was controlled with heating basket.

After the laboratory experiments pilot distillation had to be carried out to determine which industrial equipment can be designed [2]. Fig. 6 shows the pilot column for treatment of PWW.

The pilot column had 3 m high packing of Sulzer Mellapak 750 type structured packing, which was equivalent to 14 theoretical plates in our case. Direct injection of the steam was applied for the heating of the kettle type reboiler. In the pilot plant laboratory the feed was preheated with ultrathermostat but in the industrial design the heat integration was considered. Further information can be found in Table 6.
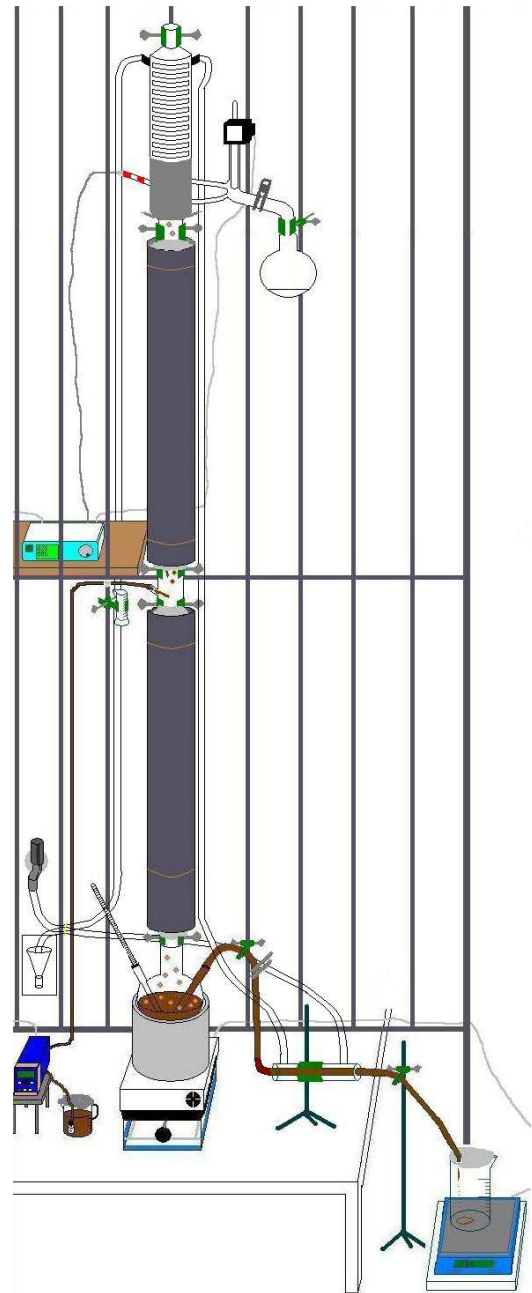

Fig. 5. Laboratory column in continuous operation [31].

Table 5
Main parameters of laboratory column

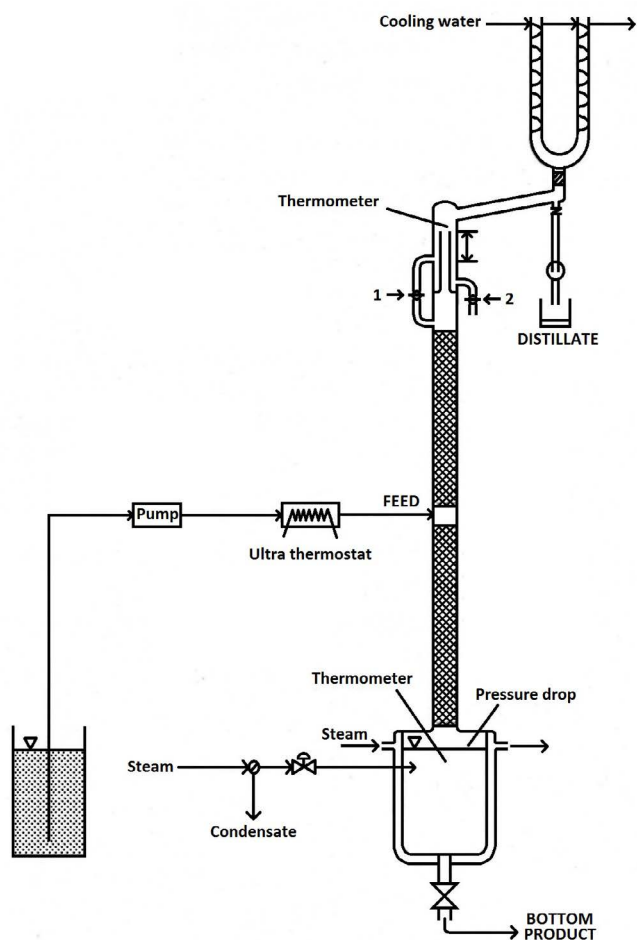|	
Height of column	0.7 m + 0.65 m
Diameter of column	0.04 m
Type of packing	Raschig-ring, 4 mm
Pump	Prominent GALA1005
Theoretical plates	10
Feed plate	5
Reflux timer	Iludest RT-2
Heating	heating basket (300 W)

Fig. 6. Pilot column with direct steam injection [17].

Table 6
Main parameters of the pilot column

Height of column	1.5 m + 1.5 m
Diameter of column	0.07 m
Type of packing	Sulzer Mellapak 750
Pump	Prominent GALA1005
Theoretical plates	14
Feed plate	7
Reflux timer	Iludest RT-2
Heating	direct steam injection (2 bar)

Fig. 7. Schematic figure of the industrial column.

The laboratory and pilot experiments were carried out with same steps. First of all, the column was heated up with reboiler until constant distillate and bottom temperatures in total reflux mode, then PWW was fed into column in modelled stream, in parallel reflux controller was switched on 3–4 h steady state was examined all case of settings. Every half hour, during the experiments sampling was executed. Temperatures, mass, and component flowrates were also examined.

On the basis of our experimental results and observations an industrial distillation column was designed with
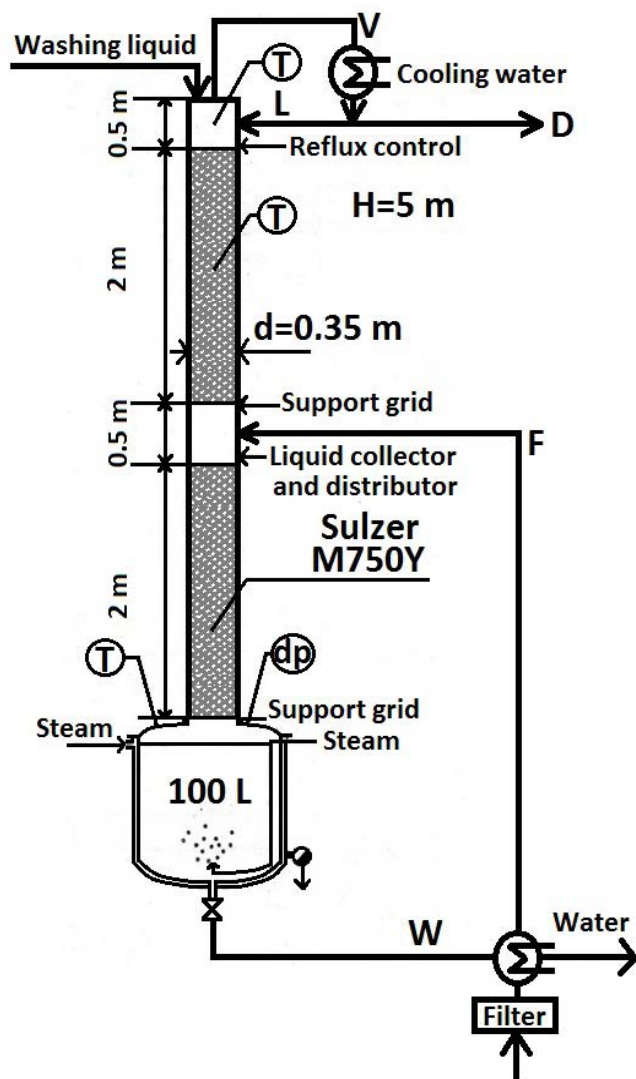
17 theoretical plates and structured packing. The main parameters of the column can be seen in Fig. 7. The feed tray location was located at the middle of the column and even 500 L/h PWW can be treated. Direct steam of 2 bar was injected into the bottom. The implementation of measurement was the same with pilot column case from heating up the column to steady state. The steady state was reached within 2 h.

The pollutant content of the feed, distillate and bottom product were measured with Shimadzu GC2010Plus+AOC-20 autosampler gas chromatograph with an Agilent CP-SIL-5CB (30 m × 0.32 mm × 4.0 μm) column connected to a flame ionization detector and EGB HS 600 headspace apparatus was used for sample preparation. The injector and detector were thermostated to 250°C and the column temperature was kept at 60°C. Pressure of carrier nitrogen, air and hydrogen gases were kept at 120, 60, and 50 kPa. The AOX was determined with Mitsubishi TOX-100 apparatus and the COD was measured by ISO 6060:1991.

3. Results and discussion

3.1. Experimental evaluation

In the evaluation part, the best available results are presented. Tables 7 and 8 show the optimized simulated tests and their measured results. It can be seen that the dry substance left in the bottom product, it was not detected in distillate. The simulation verification can be taken with objective function (OF), which is minimized the deviation of the simulated and the measured values.

$$\text{OF} = \sum_{i=1}^{n} \left(\frac{D \text{ or } W_{\text{measured}} - D \text{ or } W_{\text{simulated}}}{D \text{ or } W_{\text{measured}}} \right)^2 \qquad (1)$$

The standard deviations (SDV) of measured data are also given in Tables 7, 8, and 10. The comparison shows the accuracy also in laboratory, pilot, and industrial cases.

Table 9 represents the measured results of laboratory and pilot experiments too.

It can be seen, the AOX concentration of the PWW can be reduced below 8 ppm with applying continuous

distillation experiments. 63% reduction in initial COD value can be reached with laboratory experiment and 90% applying pilot column, but the value is above the emission limit (1,000 mgO$_2$/L) yet. The results of pilot experiment in the case of pollutant compositions and COD of PWW are more favorable because the condensation steam can dilute the bottom product and it can reduce further the COD and AOX [2]. The reflux ratio can be kept between 10 and 20 but at low distillate flow (1.5% and 3% of the feed) it does not result in a high reflux flow rate. Examining the streams, it can be determined the mass balance error can be kept under 2% in both cases.

3.2. Industrial implementation of AOX and VOC-COD removal column

Tables 10 and 11 show the results of industrial column test.

It can be seen the AOX was below detection limit (b. d. l.) and COD was also below the emission limit in bottom product (*W*). Furthermore, mass balance error can be kept under 2%.

After our modelling and experiments it can be stated, that in the case of the volatile organic pollutants can be removed

Table 7
Comparison of modelling and experimental results in the case of laboratory column

Laboratory column	Feed	Simulated data		Measured data				OF	
		D	*W*	*D*	*D*-SDV	*W*	*W*-SDV	*D*	*W*
AOX (m/m%)	0.60	95.95	0.001	95.92	0.02	0.0006	0.0001	1.18E-07	4.44E-01
Methanol (m/m%)	0.21	0.042	0.032	0.045	0.004	0.038	0.004	4.43E-03	2.49E-02
Acetone (m/m%)	0.33	0.001	0.077	0.013	0.001	0.043	0.02	8.56E-01	6.25E-01
Water (m/m%)	98.16	4.004	99.18	4.022	0.03	99.21	0.01	1.98E-05	8.19E-08
Dry substance (m/m%)	0.71	0	0.71	0	0	0.71	0	0	0
T (°C)	20	35.6	99.9	35.2	0.01	99.9	0.01	1.29E-04	0

Table 8
Comparison of modelling and experimental results in the case of pilot column

Pilot column	Feed	Simulated data		Measured data				OF	
		D	*W*	*D*	*D*-SDV	*W*	*W*-SDV	*D*	*W*
AOX (m/m%)	0.60	96.04	0.0003	95.99	0.04	0.0002	0.0001	2.41E-07	2.50E-01
Methanol (m/m%)	0.21	0.017	0.009	0.016	0.002	0.012	0.003	7.72E-03	6.25E-02
Acetone (m/m%)	0.33	3.51E-05	0.011	0.007	0.001	0.015	0.006	9.90E-01	8.22E-02
Water (m/m%)	98.16	3.945	99.27	3.987	0.2	99.26	0.3	1.09E-04	5.26E-09
Dry substance (m/m%)	0.71	0	0.71	0	0	0.71	0	0	0
T (°C)	30	36.9	99.9	36.5	0.01	99.9	0.01	1.20E-04	0

Table 9
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	5,810
pilot	5.00	0.16	4.75	10	2	120	150	1,640

Table 10
Comparison of modelling and experimental results in the case of industrial column (b. d. l.: below detection limit)

Industrial column	Feed	Simulated data		Measured data				OF	
		D	W	D	D-SDV	W	W-SDV	D	W
AOX (m/m%)	0.60	95.99	0.00001	95.91	0.03	b. d. l.	–	6.96E-07	–
Methanol (m/m%)	0.21	0.016	0.004	0.015	0.001	0.005	0.001	4.44E-03	4.00E-02
Acetone (m/m%)	0.33	3.28E-05	3.60E-02	0.084	0.04	0.009	0.003	9.99E-01	8.99E + 00
Water (m/m%)	98.16	3.994	99.25	3.991	0.3	99.28	0.04	5.53E-07	6.86E-08
Dry substance (m/m%)	0.71	0	0.71	0	0	0.71	0	0	0
T (°C)	30	36.7	99.9	36.3	0.01	99.9	0.01	1.21E-04	0

Table 11
Results of industrial measurements (b. d. l.: below detection limit)

Stream			R	PWW composition (W)			
F	D	W	$(-)$	AOX	Methanol	Acetone	COD
(kg/h)	(kg/h)	(kg/h)		(ppm)	(ppm)	(ppm)	(mgO$_2$/L)
510	7	497	10	b. d. l.	50	90	500

Table 12
Cost parameters of the apparatus [33]

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

with heating. Modelling and experiments prove that the best solution is based on the application of steam as heat source that stripes out the VOC. Special attention is given to the organic halides because this is the only way to remove them. Such treatment is carried out in a rectification column and the top vapor stream is condensed, after that a part of the condensate is taken away, distillate, and partially refluxed back into the column.

With this method we can get the treated PWW in the bottom of the rectification column having less pollutants than the emission limit. In the top, the distillate, the polluting organic compounds can be obtained in high concentration. As far as the organic halides are considered our method is the only way to remove them.

Every kind of possible PWW was tested and a flexible rectification column was designed. Flexibility means, that the column should be able to operate in a wide range of wastewater loads. On the basis of laboratory and pilot plant experiments the proper rectification column was planned and completed. Industrial experts were involved into the design and implementation steps so the column can operate according to the expectations.

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

3.2.1. 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, so 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, because direct steam injection can be applied for the heating of the kettle [2].

- On the other hand, the heat integration can reduce 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 DCM solvent because the column has rectifying section. So the process can adapt to circular economy concept with this recycle/reuse option.

3.2.2. Economic and social benefits of the method and apparatus

- Very high wastewater fee must be paid, if this PWW is channeled without any treatment by pharmaceutical company, so there is essential for the manufacturer to develop waste treatment method 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 [32]. It can be read 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 are supported by concrete data [33]. The investment cost of the optimized process was calculated according to the cost correlations of Douglas [34] with current M&S index. Investment costs of the distillation depend on different parameters: heat duties, the sizes of the column and heat exchangers, pump cost, and purity of the products. The operating costs contain the annual costs of the steam and water consumption. 8,000 h/year continuous operation was selected for the calculation of the operating cost. 10-year amortization of investment cost was assumed for the total cost estimation [35]. The above-mentioned heat integration and lower steam consumption result favorable operating cost. Table 10 shows that, the column's payback time is only less than 2 years.
- 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 three pharmaceuticals and one petrochemical references, the presented one in this text can be the only one in our public tender, which can demonstrate the technology.

It has to be stated that each case should be examined individually and experimentally since the dissolved substance can cause fouling in the column. Laboratory and pilot experiments are necessary to study the real vapor-liquid equilibria of PWW. Therefore, it is difficult to give the general limitations of the proposed method because it is different for every PWW case.

4. Conclusion

In the different process industries special PWWs arise that contain significant amount of organic compounds, among them organic halides. These compounds have a significant effect on the environment and only physicochemical methods can be considered as treatment. Applying steam to stripping out the pollutants, the PWWs can be cleaned until the discharge limit and the polluting materials can be gained as product of the method. For this purpose a rectification column with enough flexibility is designed based on modelling and experiments. Industrial case study proves that the method can be successfully applied fulfilling the principle of the circular economy.

The column in the industry is currently operating far above the expectations. Huge practical and engineering considerations have resulted in this success of the developed novel method. The DCM and AOX concentration of bottom product is under the detection limit because the application of direct steam results in a dilution effect. The distillate, after a simple phase separation, can be utilized in other plants as DCM solvent. Heat integration reduces the energy demands and the operating costs. The hot effluent wastewater is used for feed preheating thus this separation process enables 90% energy savings. The payback time of the column is less than 2 years.

The waste treatment can be achieved locally in the factory and the chemical sector can be driven toward the circular economy. Because of the reuse of materials the cycle of manufacturing processes can be closed. The featured method reflects to the popular "think globally, act locally" slogan.

Acknowledgments

Symbols

d	—	Diameter of the column
D	—	Distillate
F	—	Feed
H	—	Height of the column
No.	—	Number
R	—	Reflux ratio
T	—	Temperature, °C
T-bp	—	Boiling point, °C
W	—	Bottom product

Abbreviations

AOX	—	Adsorbable organically bound halogens, ppm
b. d. l.	—	Below detection limit
COD	—	Chemical oxygen demand, mgO_2/L
DCM	—	Dichloromethane
OF	—	Objective function
ppm	—	Parts per million
PWW	—	Process wastewater
SDV	—	Standard deviation
VLE	—	Vapor–liquid equilibrium
VOC	—	Volatile organic compounds

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