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Optimization of the Sequence of Wastewater Treatment in the Cosmetic Industry

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Wastewater treatment in the cosmetic industry, which operates in batch mode, is a complex task due to the highly variable composition of the water to be treated. Among other parameters, n-heksan extractable material (HEM) and surfactants must comply with the specified limits. From theory, the advanced oxidation process (AOP) with a Fenton-like process is more suitable for surfactant degradation, while the coagulation/flocculation process (CFP) is more efficient for HEM removal. Determining the appropriate sequence of AOP treatment and CFP affects the quality of released water, the efficiency of each process step, and the consumption of required chemicals.
The objective of this research was to optimize the treatment sequence, the time required for each treatment, and the amount of sludge from wastewater treatment. For this purpose, AOP treatment and CFP laboratory tests were performed for different groups of samples and samples with high HEM and/or surfactant content. Based on the efficiency of the laboratory tests and the assessed wastewater composition (from mass and concentration balances), an optimization model was developed. The optimization model enables optimization of the wastewater treatment plant (WWTP) by feeding each of the streams to either i) AOP treatment, ii) CFP treatment, iii) AOP treatment followed by CFP treatment, iv) CFP pretreatment followed by AOP and CFP, v) bypass (i.e. the wastewater stream is not treated but mixed with treated streams). The optimal solution can be determined by minimizing the total annual cost of treatment or/and maximizing removal of pollutants. An additional analysis was performed considering the dilution of wastewater with freshwater after the treatment process. The results show that this last proposal is more economical but leads to questionable environmental impacts.

1. Introduction

The cosmetic industry generates a considerable amount of wastewater (WW) containing various contaminants such as polymers, dyes, surfactants, pH regulating chemicals, UV filters, antioxidants, etc. (Abidemi et al., 2018). Despite the widespread use of biological WW treatment methods, in some cases, this treatment is not a viable option due to the compounds present in WW, which are resistant and/or toxic to the biodegradation process. An advanced oxidation process can be used to treat recalcitrant organic compounds. Its main mechanism is the generation of highly reactive free radicals, such as hydroxyl radicals, which effectively degrade organic chemicals (Benatti and Tavares, 2012). The advanced oxidation process is a collective term for different processes, of which the one carried out with hydrogen peroxide and UV light was considered in this work (Bautista et al., 2008). The AOP process alone is usually not sufficient to remove the contaminants. For this reason, a two-step process is used - AOP followed by a coagulation/flocculation process (CFP). In cases where there is a high content of n-hexane extractable material (HEM), which are mainly oils and grease, the efficiency of the AOP process may decrease as these substances block the deep penetration of UV light into the wastewater, as described in Naumczyk et al. (2014). Since the H_2O_2 must be treated with UV light to obtain a hydroxyl radicals, the treatment process is less effective. In this work, an additional CFP is considered as an optional pretreatment process for the basic process if it is suitable (Tony et al, 2012). The efficiency of WW treatment is highly dependent on the composition of the WW, therefore a framework for optimizing the wastewater treatment plant has been developed in this work. The vast majority of published work considers either laboratory experiments describing AOP or coagulation/flocculation processes or simulations of these processes. This framework attempts to fill the missing link between laboratory experiments and computer aided

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approach to support more holistic decision making. This framework considers the mass and concentration balances of the wastewater collection system and the estimated efficiencies of different WW treatment sequences, namely: i) AOP only, ii) CFP only, iii) AOP followed by a CFP, iv) pretreatment with CFP followed by AOP and CFP. In the last case, the first CFP is carried out in an acidic environment, while the second CFP is carried out in an alkaline environment. In this way, the pretreatment CFP primarily removes the HEM, the AOP degrades larger organic matter and the second CFP removes the surfactants. The objective of this work is to select the proper sequence of the WW treatment process that will ensure that the pollutant limits are met while minimizing the overall cost of the WW treatment process.

2. Methodology

The optimization of the WWTP was carried out using the framework depicted in Figure 1. The main data needed for the optimization of the WWTP are the compositions of the wastewater streams and the estimated efficiencies of the different treatment processes as functions of WW composition. Estimating the WW composition is a challenging task due to the diversity of products manufactured in the cosmetics industry, the numerous containers that are washed with water, and the complexity of the WW collection system.

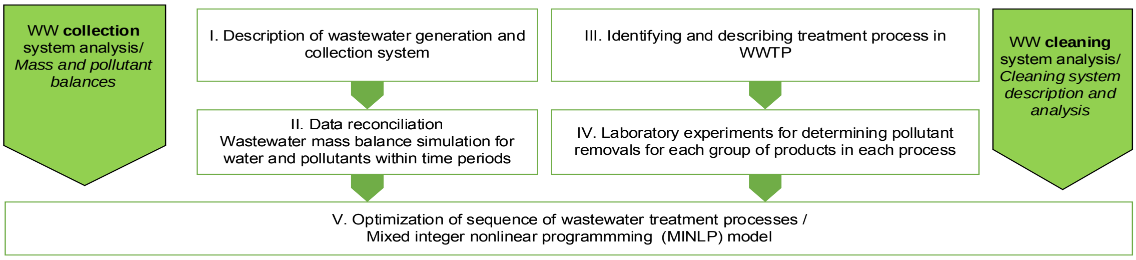

Figure 1: WW treatment plant optimization framework

I. **Description of wastewater generation and collection system.** To estimate the composition of the wastewater entering the treatment plants, the wastewater collection system should first be identified. This includes identifying all sources of WW, estimating the composition and timing of WW production, identifying the entire path to the WW collection tank, taking into account all intermediate tanks and all residence times along this path.

II. **Data reconciliation.** After identifying all major elements of the WW collection system, data reconciliation should be performed to obtain the nominal flowrates and pollutant concentrations of the WW prior to entering the WWTP. Due to the complexity of this step, a computer-aided approach is required, e.g. in the form of a nonlinear programming (NLP) model.

III. **Treatment processes in WWTP.** WWTP consist of several processes, and an understanding of each process principle is necessary to estimate pollutant removal in each process of the plant. Usually, the first principle models are too complex and impractical, therefore, surrogate models based on input-output relationships are used. In addition, it is highly recommended to form groups of WW types representing WWs with similar composition. The groups should be representative; however, their number should be kept as small as possible because pollutant removal ratio data should be obtained for each group in each WWTP process.

IV. **Laboratory experiments.** Laboratory or pilot-scale experiments should be conducted to obtain pollutant removal ratio data. Computer aided approach such as Design of Experiments may also help to reduce the number of laboratory tests required.

V. **Optimization of the sequence of WW treatment processes.** A mathematical model was developed to optimize the wastewater treatment cost. The following sets with elements were used:
   - *group* ∊ *GROUP* to represent wastewater from different groups of products with similar composition
   - *treat* ∊ *TREAT* for different wastewater treatment processes
   - *pol* ∊ *POLLUTANT* for different types of pollutants in the wastewater. In this study only HEM and SURF were considered.

The selection of treatment for each group $y_{\text{group,treat}}$ is done by inlet mass flow of pollutant $\dot{m}^{\text{in}}_{\text{group, treat, pol}}$ which is determined for each group, WW treatment, and pollutant, and is connected to the initial mass flow of pollutant $\dot{m}_{\text{group, pol}}$ (Eq (1)).

$$\dot{m}^{in}_{group,treat,pol} = \dot{m}_{group,pol} \cdot y_{group,treat} \quad \forall\ group \in GROUP,\ treat \in TREAT,\ pol \in POLLUTANT \qquad (1)$$

Each group can only be treated with one type of treatment, which is described by Eq (2).

$$\sum_{group,treat} y_{group,treat} = 1 \quad (2)$$

The outlet mass flow of pollutant after WW treatment is calculated from Eq (3) by multiplying $\dot{m}^{in}_{group,\ treat,\ pol}$ by the rate of pollutant removal $r^{in}_{group,\ treat,\ pol}$

$$\dot{m}^{out}_{group,treat,pol} = \dot{m}^{out}_{group,treat,pol} \cdot r_{group,treat,pol} \quad \forall\ group \in GROUP,\ treat \in TREAT,\ pol \in POLLUTANT \quad (3)$$

Assuming that the desity of wastewater and freshwater is equal to 1 kg/L, the pollutant concentration in the outlet WW after treatment and dilution is determined as ratio between the sum of the outlet pollutants flow and the sum of the total WW and freshwater mass flow (Eq (4)).

$$\gamma_{pol} = \frac{\sum_{group,treat} \dot{m}^{out}_{group,treat,pol}}{\sum_{group} \dot{m}^{water}_{group} + \dot{m}^{freshwater}} \quad \forall\ group \in GROUP,\ treat \in TREAT,\ pol \in POLLUTANT \quad (4)$$

The objective function (Eq (5)) represents the annual cost of WW treatment. The annual cost consists of the WW treatment cost, the freshwater consumption cost, and the additional environmental fee for WW discharge. The WW treatment costs consist of the operating costs of the WWTP, sludge incineration, and delivery of the liquid part of the WW to the municipal collection system. The additional environmental charge for the release of WW represents the cost of increasing the amount of WW that is diluted with freshwater. To calculate the cost at the annual level, the hourly cost is multiplied by the annual operating hours t^{op}.

$$Z = \left(\sum_{group} \dot{m}^{water}_{group} \cdot C_{group,treat} \cdot y_{group,treat} + \dot{m}^{freshwater} \cdot C^{freshwater} + \dot{m}^{freshwater} \cdot C^{WW\_release} \right) \cdot t^{op} \quad (5)$$

3. Illustrative case study

The described method is presented by means of an illustrative case study based on experiences from an industrial case study. The results presented focus mainly on the last step of the framework to show its strength. **I. Description of wastewater generation and collection system/II. Data Reconciliation.** The studied cosmetic industry operates in batch mode, therefore the timing, origin, quantity and composition of WW production should be determined for each WW source. To demonstrate the complexity of the WW generation and collection system in a medium-sized cosmetics company, 25 mixing tanks generating wastewater were identified. In addition, 4 intermediate tanks and a final WW collection tank were considered. Each tank is washed several times a day. The products were classified into 10 groups based on their similar composition (Table 1). In the cosmetic industry, there are several products, such as wash gel, that have the same basic composition but have different fragrances added. A group can also represent 40 different WW sources from different products (mixing tanks) that are cleaned in one day. The mass flow of HEM and SURF was determined based on the composition of the product after washing the tank and the amount of water used for washing.

Table 1: mass flowrates of water, HEM and SURF for each group

WW groups	$\dot{m}_{group,water}$/ (kg/h)	$\dot{m}_{group,HEM}$/ (g/h)	$\dot{m}_{group,SURF}$/ (g/h)
Group 1	37.2	35.2	7.1
Group 2	169.7	974.8	369.4
Group 3	75.6	195.7	128.5
Group 4	119.2	36.6	318.0
Group 5	396.4	1230.5	57.1
Group 6	164.6	73.7	145.7
Group 7	16.1	193.4	9.7
Group 8	176.9	6.7	82.6
Group 9	9.5	2.4	2.0
Group 10	3.3	1.1	6.3

II. Treatment processes in WWTP/ IV. Laboratory experiments. Five different pathways through the WWTP were considered: i) AOP only, ii) CFP only, iii) AOP followed by CFP, iv) pre-treatment CFP followed by AOP and CFP, and also v) WWTP bypass was considered. Table 2 shows the determined HEM and SURF removal for each group of WW in each WW treatment type. A removal ratio of 1 means that the pollutant is not removed in the particular treatment process, e.g. bypass.

Table 2: Pollutant (HEM and SURF) removal ratio for each group $r_{group,treat,pol}$

Product groups/ Removal ratio	r_{AOP} HEM / SURF	r_{CFP} HEM / SURF	r_{AOP_CFP} HEM / SURF	$r_{CFP\_AOP\_CFP}$ HEM / SURF	r_{bypass} HEM / SURF
Group 1	0.6239/1.0	0.1296/1.0	0.0057/0.214	0.0012/0.153	1.0/1.0
Group 2	0.6239/1.0	0.0532/1.0	0.0172/0.214	0.0146/0.153	1.0/1.0
Group 3	0.6239/1.0	0.0935/1.0	0.0066/0.214	0.00099/0.153	1.0/1.0
Group 4	0.6239/1.0	0.1352/1.0	0.0056/0.214	0.00121/0.153	1.0/1.0
Group 5	0.6239/1.0	0.0634/1.0	0.0114/0.214	0.0012/0.153	1.0/1.0
Group 6	0.6239/1.0	0.1282/1.0	0.0056/0.214	0.0012/0.153	1.0/1.0
Group 7	0.6239/1.0	0.0842/1.0	0.0073/0.214	0.0009/0.153	1.0/1.0
Group 8	0.6239/1.0	0.1653/1.0	0.0055/0.214	0.0015/0.153	1.0/1.0
Group 9	0.6239/1.0	0.1912/1.0	0.0054/0.214	0.0016/0.153	1.0/1.0
Group 10	0.6239/1.0	0.2156/1.0	0.0054/0.214	0.0018/0.153	1.0/1.0

III. Optimizing the sequence of WW treatment processes sequence. Based on the data presented previously and taking into account the cost parameters presented in Table 3, a sensitivity analysis was carried out in which the pollutant concentration limit was gradually reduced.

Table 3: Cost of individual WW treatment processes

Treatment	AOP	CFP	AOP_CFP	CFP1_AOP_CFP	BYPASS
Cost/ (€ /L)	0.007	0.0019	0.0089	0.0108	0

Figure 3 shows the results of the sensitivity analysis considering 21 optimization runs. As expected, lower pollutant concentration (i.e., higher treatment efficiency) leads to higher WW treatment costs. It should be noted that the company's pollutant concentration limit was set at 100 mg/L for HEM and 200 g/L for SURF. To reach this limit, the annual treatment cost was 104 600 €/a. The treatment plant operates five days a week.

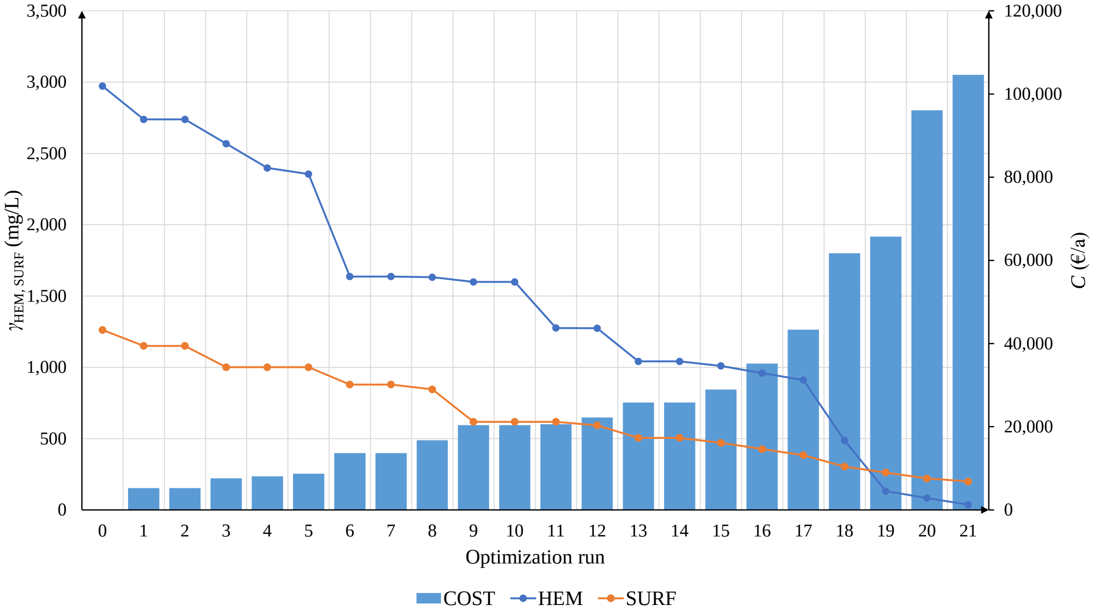

Figure 3: Sensitivity analysis of WW treatment cost by limiting the upper bound of HEM and SURF concentrations with no dilution

Since the limits for pollutants are given only as pollutant concentration and not as mass or volume, an additional sensitivity analysis was performed considering the option of diluting the WW with freshwater after the processes in the WWTP. This option may seem unrealistic; however, it is a very common option in business as usual. For the analysis, the cost of freshwater was set at 1 €/m^3 and the cost of WW discharge was set at 0.07667 €/m^3 to obtain a trade-off result. The results are shown in Figure 4. The comparison of Figure 3 and Figure 4 shows that diluting the effluent with freshwater leads to significantly lower costs while the same concentration limits are achieved. It is interesting to note that up to run 21, where the pollutant content is more than halved, the limits can only be achieved by dilution. The difference between the total cost and the freshwater cost represents the additional environmental fee due to the increased WW volume. For the lowest concentration limit, the costs decrease by 53 600 €/a (51 %) when dilution with freshwater is taken into account, and the total annual cost is only 51 000 €/a. However, this is a rather poor solution from an environmental point of view, as $15.9 \cdot 10^4$ m^3 of fresh water would be consumed on a daily basis. Even if the companies do not increase their freshwater consumption as much as in the presented case, this clearly shows that under the current conditions, a higher freshwater consumption is promoted for washing the equipment in the processes instead of minimizing the amount of WW produced. One of the main reasons for the high cost of wastewater treatment, apart from the cost of chemicals and energy, is the ever-increasing cost of sludge treatment due to the lack of suitable sludge treatment facilities.

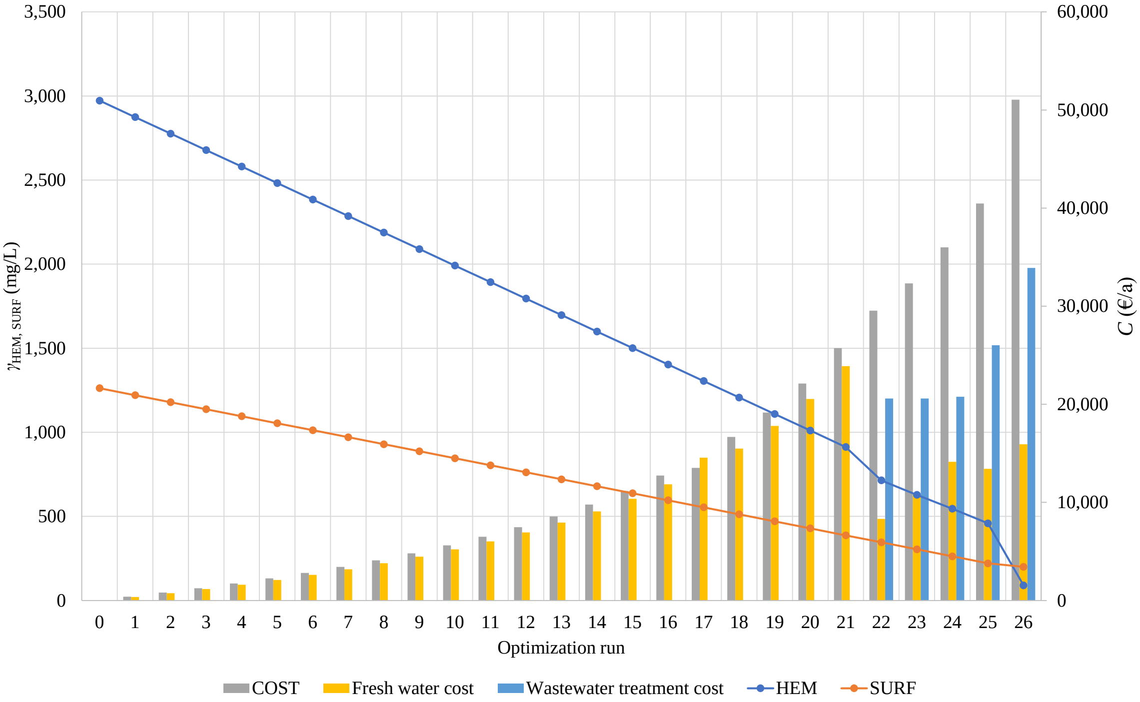

Figure 4: Sensitivity analysis of freshwater and WW treatment cost by limiting the upper limit of concentration of HEM and SURF using freshwater for dilution after treatment.

Table 4 shows the selection of wastewater treatment processes for all WW groups when the treatment plant is operated with and without dilution with freshwater. When dilution with freshwater is disabled, treatment processes with higher efficiency and higher cost are selected, e.g. CFP-AOP-CFP. On the other hand, dilution with freshwater leads to the selection of processes with lower efficiency and lower cost and increases the number of groups for which the bypass is selected. To obtain a trade-off result where no dilution is selected, the freshwater cost would have to be 19 times higher. The increased consumption of freshwater clearly shows how harmful the current practice is. It would make far more sense to limit the release of pollutants by mass or volume than to limit the concentration of pollutants in WW. This could be achieved either by making freshwater more expensive or, more sensibly, sludge treatment (incineration) should become cheaper to provide more environmentally friendly solutions.

Table 4: Selected processes in WWTP if only cleaning and dilution with freshwater is considered

Product groups	WWTP	WWTP+dilution with freshwater
Group 1	AOP-CFP	BYPASS
Group 2	CFP-AOP-CFP	AOP-CFP
Group 3	CFP-AOP-CFP	AOP-CFP
Group 4	CFP-AOP-CFP	AOP-CFP
Group 5	AOP-CFP	CFp
Group 6	CFP-AOP-CFP	BYPASS
Group 7	AOP-CFP	CFP
Group 8	CFP-AOP-CFP	BYPASS
Group 9	BYPASS	BYPASS
Group 10	AOP-CFP	AOP-CFP

4. Conclusions

A framework for optimizing the process sequence of wastewater treatment was developed. Advanced oxidation processes, flocculation/flotation processes and their combinations were considered. The case study presented shows that when only wastewater treatment processes are considered, the processes with higher cost but higher pollutant removal efficiency are selected. However, when the option of diluting the wastewater with freshwater is considered, the wastewater treatment processes are avoided as much as possible because the cost of freshwater is lower compared to the wastewater treatment processes. It should be understood that the cost of freshwater varies greatly depending on the degree of water scarcity in a particular country; therefore, different conclusions can be drawn. In the future, the possibilities of lower cost sludge treatment could lead to a more environmentally friendly solution by promoting wastewater treatment processes. In the future, the model will be extended to include the option of reusing treated wastewater.

Nomenclature

AOP – advance oxydization process
CFP – coagulation/flocculation process
HEM – n-heksane extractable material
SURF – surfactants
WW-wastewater
WWTP-wastewater treatment plant-

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