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A new concept for cosmetic wastewater treatment by a suitable classification and separation system

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ABSTRACT

A new approach for a successful treatment concept of industrial cosmetic wastewater is shown. Splitting the wastewater flow into various material streams based on fundamental characteristics enables distinct adapted treatment and disposal methods, respectively. Industrial wastewater still contains valuable and even recyclable materials that should not be disposed of as waste. A holistic treatment of the total wastewater flow comprising diverse material streams is very challenging due to a frequently changing product range. The developed concept provides a functional and yet simple approach by classifying material and wastewater streams that could be treated by distinct adapted processes. Most of the industrial wastewater achieved a quality that allows a cost-effective discharge via the municipal wastewater system.

Keywords: Cosmetic wastewater treatment; Technologies; Industrial effluents

1. Introduction

Wastewaters accrued by cosmetic manufactures are generally characterized by high organic loads and poor biological degradability (BOD_5) reflecting in high values of chemical oxygen demand (COD) levels and low BOD_5/COD ratios. Compounds such as suspended solids, fats, oils and detergents are main constituents of cosmetic wastewater [1,2]. Especially surfactants, disinfectants, dyes and even fragrances are usually not readily biodegradable and even toxic to microorganism [3,4]. Often, the manufactured product range is frequently changing so that in turn the composition of the resulting wastewater is varying accordingly. Due to this high variability, combined with the potential presence of less biodegradable and even harmful components, it is difficult, if not impossible, to find technological chains that provide efficient and for all conditions reliable treatment process. In recent years, detailed studies on enhanced physicochemical, chemical as well as biological techniques have been investigated and are shortly summarized, here.

1.1. Physicochemical techniques

Physicochemical methods focus mostly on coagulation followed by both sedimentation and flotation processes as pre-treatment to a subsequent biological treatment and sometimes also applied as post-treatment. Carballa et al. [5] determined ferrous(III) chloride ($FeCl_3$), aluminium sulfate ($Al_2(SO_4)_3$) and aluminium polychloride as suitable coagulants obtaining removal rates of examined pharmaceutical and personal care products of up to 70%. El-Gohary et al. [6] achieved total COD removals even of up to 78% by chemical precipitation methods. Especially the reduction of anionic surfactants (AS) utilizing lime and $Al_2(SO_4)_3$ as coagulant was less successful with 37% [7]. A more promising and cost-efficient option to the chemical coagulation is the electrocoagulation. Both Kong et al. [8] and Boroski et al.

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[9] obtained COD removal rates of up to approximately 86%. Mechanical treatment techniques such as filtration and decantation are usually used subsequently to eliminate agglomerated particles [5]. Drawbacks of coagulation processes are the need of additional chemicals and optimized operating conditions, demanding additional measures like adjustment of pH, floc density and water temperature.

Flotation is a less investigated process, suitable for the treatment of lipophilic and suspended particles [10]. Studies of Carballa et al. [5] already revealed a removal rate of 30%–60% of lipophilic compounds such as musks. Another main industrial application is the recovery of solvent extraction losses by dissolved air flotation [11].

1.2. Chemical techniques

Chemical treatment processes focus on advanced oxidation processes to reduce the COD significantly. In particular both Fenton oxidation and photocatalysis with titanium dioxide (TiO_2) are already investigated for the treatment of cosmetic wastewater. The Fenton reagent is predominantly used as pre-oxidation method for heavily polluted wastewaters [12] or as secondary treatment of physicochemical methods [13]. Because of its technologic simplicity, Fenton reagent, a solution of H_2O_2 and Fe^{2+}, is an often applied method to produce $OH^\cdot$ radicals. But a successful oxidation with Fenton reagent requires pH levels between 2.5 and 5 and an increased temperature [14,15].

Applied to cosmetic wastewater, it can – according to consulted literature – significantly reduce COD up to 85% [14], total organic carbon (TOC) up to 97% and total phenol content up to 99% [16]. Studies of Naumczyk et al. [17] revealed that Fenton oxidation has only a small effect on wastewaters containing antioxidants, which act as scavengers to $OH^\cdot$ radicals. Epically skincare products, the leading product class in cosmetics, are rich on antioxidants for skin protection and preservative [13].

Alternatively to Fenton reagent, heterogeneous photocatalysis reactions are also used to produce $OH^\cdot$ radicals. TiO_2 serves as semiconductor receiving energy from the absorption of photons. At the TiO_2 surface, organic compounds are adsorbed and degraded [18]. Due to the high costs of TiO_2, this process is only applicable for wastewater with low COD concentrations (≤800 mg L^{-1}) [19]. Thus, pre-treatment steps such as coagulation processes and/or biological treatment are usually required prior to its application [9].

In general, chemical oxidation aims at the mineralization of compounds to carbon dioxide, water and inorganics, which are thereby transformed into harmless products [20]. In most cases, they are arranged as polishing steps at the end of the treatment chain. Due to the need of additional chemicals as treatment reagents themselves or to adjust required conditions, e.g., a certain pH level, the shown treatment techniques are often associated with high operational costs.

1.3. Advanced biological techniques

Biological wastewater treatment is already known and successfully used for the treatment of municipal and other industrial wastewaters [21]. Concerning cosmetic wastewaters, the use of biological treatment methods is rather scarce. However, in some cases, biological systems can treat cosmetic wastewater effectively and cost-efficiently. To date, several studies to aerobic [22], anaerobic [23] or even aerobic and anaerobic combined treatment processes were investigated [24]. Most of them obtained positive results by conducting on laboratory-scale plants. Using an aerobic submerged membrane bioreactor on a pilot scale to remove CODs of approximately 2 g L^{-1}, COD and AS eliminating rates of up to 85% and 98%, respectively, were achieved [25]. A study of a full-scale side-stream membrane bioreactor researched by Monsalvo et al. [26] shows high removal efficiencies of up to 98% for COD and suspended solids. But generally, the successful application of biological systems demands readily degradable wastewater without inhibiting substances. In cases of elevated COD concentrations, physicomechanical pre-treatment and/or combined anaerobic–aerobic treatment is advisable or even required.

However, many of the described technologies and treatment processes suffer from limited applicability for wastewaters with higher COD levels than 10 g L^{-1}.

1.4. Specific challenges in the investigated cosmetic production

In this study, the cosmetic wastewater arises from a cosmetic industry company, which is a contract manufacturer, producing a range of products that is frequently changing. Consequently, the composition of the effluent water is also changing depending on the composition of these products. Extensive preliminary tests with cost-intensive physicochemical techniques as pre-treatment methods to subsequent biological techniques have already been conducted for the treatment of the total wastewater flow. Detailed evaluation of these preliminary tests are not part of this paper but will be briefly reviewed below. Especially flocculation experiments followed by sedimentation or flotation processes were systematically investigated by using 13 different flocculants under varying pH conditions. Both cationic and anionic polymers as well as various aluminium salts were examined as partly suitable coagulants. Lime was partially utilized as additional flocculation agent. However, the tests did not show reproducible and reliable results. Depending on the production process and thus the composition of wastewater, COD removal varied between 10% and 50% with different best-suited flocculation agents. Following, aerobic and anaerobic biological treatment techniques were conducted but hampered by various disruptive factors. For example, strong foam formation caused by surfactants particularly hindered the aerobic degradation processes and could only be suppressed by high dosages of antifoaming agents, which in turn inhibited the biologic activity. However, the major problem in the present case is the constantly changing composition of the resulting wastewater so that a viable and reliable treatment process could not be determined.

In contrast to previous studies, the focus of the present study was not on a collective treatment of an accruing total wastewater flow but rather on defining a classification and separating system to handle and treat distinct wastewater streams. Considering decisive characteristics, adapted treatment methods for each material and wastewater stream should be found.

Such a classification and separation system should be easy to implement and a cost-effective alternative for full-stream treatment or disposal of cosmetic wastewater.

2. Materials and methods

2.1. Case study – previous wastewater management

The current wastewater management is very simple but extremely expensive and environmentally not sustainable. The products are synthesized from raw materials and tap water that is demineralized by reverse osmosis (RO) as depicted in Fig. 1.

Apart from the production process itself, tap water is used for cleaning procedures, partially with the addition of cleaning agents or disinfectants and isopropanol. Regardless of type and level of contamination of the resulting wastewater, the combined effluent of all sources, with COD values of up to 70 g L^{-1}, is collected in a 25 m^3 storage tank. The factory discharges up to 70 m^3 wastewater per working week (Monday–Friday), which corresponds to an actual COD pollution load of up to 980 kg d^{-1}. The wastewater is disposed of as one cost-intensive wastewater stream by an external waste service company. Hazardous materials were collected separately but disposed via an external disposer in the same manner. Depending on the concentration of various parameters such as phosphorus (P), nitrogen (N), TOC or adsorbable organic halogen compounds the wastewater disposal costs vary between 50 and 100 € per ton. In parallel, tap water is used in sanitary installations and discharged via the local wastewater system.

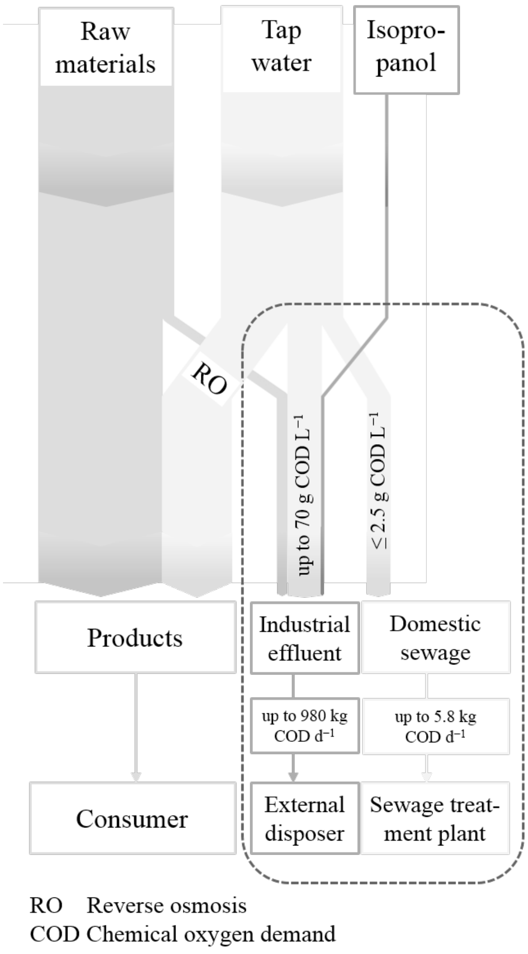

Fig. 1. Material flow balances (as total mass + resulting COD concentrations in the wastewater) of both the production process and wastewater concept of the concerned company prior to the investigations.

2.2. Wastewater sampling

Immediately prior to disposal of each 25 m^3 batch of wastewater collected in the wastewater tank, a 500-mL sample was taken. Overall 77 samples of different batches were collected. Samples from selected wastewater streams were collected separately at the point of occurrence. The samples were stored in dark and kept refrigerated under 7°C.

2.3. Analytical methods

All measurements were carried out using validated methods. A WTW Multi 340i was used for the determination of the pH value (SenTix41 probe) and the electrical conductivity (TetraCon325 probe). The COD, the total phosphorus (TP) and total nitrogen (TN) contents were analyzed spectrophotometrically by using HACH LCK cuvette tests. Conducted gas chromatography was performed on Agilent 7890A GC System. The varying characteristics of the total wastewater flow within a period of 8 months are given in Table 1. Especially the high variability of the determined COD values is depicted in Fig. 2.

2.4. Isoperibol calorimeter

The calorific values of selected samples from various batches of the solvent-based pre-rinsing water stream (PRWS) were determined by using a 6400 Automatic Isoperibol Calorimeter from Parr Instrument Company, Illinois, USA, following the DIN 51900-1:2000-04. Due to the high content of volatile compounds the experiments were performed without oven-drying. Cellulose acetate with a heating value of 23,661 kJ kg^{-1} served as suitable cover against undesirable evaporation processes of the tested materials. Benzoic acid served as standard reference material with a known heating value of 26,441 kJ kg^{-1}. All measurements were performed in triplicate.

Table 1
Varying characteristics of the total effluent from the respective company[a]

Parameter	Range
pH	2.77–11.6
Conductivity (µS cm^{-1})	436.0–5540
COD (g L^{-1})	4.914–90.21
Phosphate (mg L^{-1})	0.389–36.6
N-ammoniac (mg L^{-1})	25.8–592

[a] 77 wastewater samples were collected and analyzed in a period of 8 months.

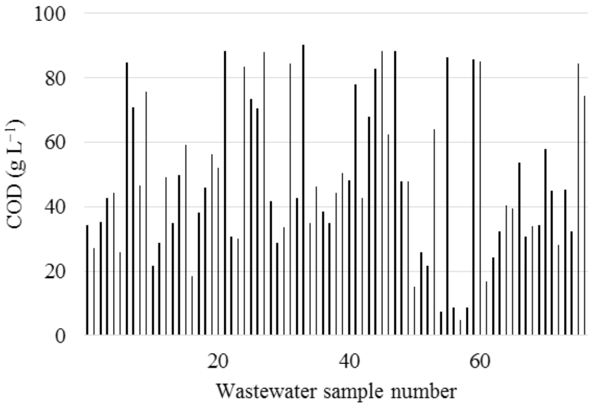

Fig. 2. COD values of various wastewater samples collecting within a period of 8 months.

3. Results and discussion

3.1. Determining the wastewater sources within the production process

The product portfolio is focused on liquids and aerosols, respectively, including, e.g., various shampoos, sunscreens, hairsprays and even disinfectants. Hence, the composition of the wastewater is strongly influenced by these produced cosmetics. There are three significant wastewater sources in the respective production plant.

Wastewater results from cleaning steps as part of both the actual production and the bottling process. The desired products are synthesized in large mixing vessels with a volume of up to 10 m^3 and subsequently bottled by bottling plants adapted to final product and package characteristics. The cleaning steps are conducted straight after emptying the vessels and bottling plants, respectively. The cleaning processes are predominantly performed automatically, requiring volumes of 200 L up to 1,000 L water. In a few cases, isopropanol is applied as cleaning medium instead of water, with a demand of up to 60 L per cleaning cycle.

The third wastewater source is the washing station where all kinds of used containers and equipment within the whole manufacturing process are cleaned. This includes intermediate bulk containers (IBCs), various barrels and buckets, which previously contained diverse raw materials. Membrane pumps and tubes are parts of the technical equipment that has to be cleaned regularly.

3.2. Separation of the total wastewater flow into various material streams

A classification into various streams by chemical constitution would not be practicable due to the continually changing product portfolio. For that reason, only a product-independent wastewater separation concept could provide the opportunity to achieve a reliable wastewater management and treatment system. A detailed analysis of the cleaning procedures revealed that the total wastewater flow could be subdivided into four material streams regarding their general quality and COD load. These four streams are an organic isopropanol stream (IPS), both a solvent-based (PRWS$_{\text{solv}}$) and an aqueous-based PRWS (PRWS$_{\text{aqua}}$) and at last a just slightly contaminated rinsing wastewater stream (RWS).

3.2.1. Isopropanol stream (IPS)

The IPS predominantly consists of isopropanol and residues from products with high contents of organic solvents or poorly water-soluble fatty ingredients such as nail polish remover, sun protection and hair-fixing sprays. The cleaning with isopropanol as rinsing medium is predominantly applied at the bottling line. The total used volume of isopropanol is about 1 m^3 per week. The bottling equipment cannot be heated adequately, and due to its complex pipe layout, the cleaning process is extremely simplified by using isopropanol as rinsing medium. On the contrary, the inner surfaces of the mixing vessels are flat and smooth and hence generally easier to clean than the bottling equipment. Isopropanol is a very costly cleaning medium compared with tap water so that the consumption of isopropanol is kept as low as possible. The measured COD of pure isopropanol is about 2.3 g O_2 g^{-1} [27]. Consequently, the used amount of just 1 m^3 isopropanol is responsible for a COD value of at least 33 g L^{-1} in a weekly total wastewater flow of 70 m^3. This calculation emphasizes the adverse impact of the IPS on the total wastewater quality.

3.2.2. Solvent-based pre-rinsing water stream (PRWS$_{solv}$)

The second material stream is a highly contaminated PRWS$_{\text{solv}}$ that also consists of residues from products containing fatty ingredients or organic solvents such as ethanol and ethyl acetate. Contrary to the IPS the enclosed product residues can be rinsed off from the inner surface of the mixing vessels and bottling lines within the first cleaning step with hot or even cold water. Since required rinsing volumes can be added manually into the respective equipment, the separation of this stream from following purging and disinfection streams could be realized easily. Individual water fractions will be discharged via available water drains or selected collection containers, respectively. In addition this stream contains product residues from products that are already bottled but are not complying with the quality standards, e.g., due to deviating filling quantities. These residues can be added manually to the desired pre-rinsing stream.

With a volume of less than 1 m^3 per week this stream is relatively small, but relevantly co-responsible for increasing the COD of the corresponding wastewater. For example, the conversion of 1 g ethanol (C_2H_5OH) to water (H_2O) and carbon dioxide (CO_2) requires 1.99 g oxygen (theoretical oxygen demand: 2.10 g g^{-1}) [28]. Even though solvent-based water streams are indeed readily biodegradable, wastewaters with increased COD values entail a costly disposal. Moreover, wastewater treatment methods based on physical separation processes (e.g., sedimentation, flocculation, filtration distillation) are not suitable for the separation of organic solvents from water streams. However, the separation of this solvent-based PRWS from aqueous-based water streams improves the general water quality of such aqueous-based streams and provides the opportunity to simplify their purification process.

3.2.3. Aqueous-based pre-rinsing water stream (PRWS$_{aqua}$)

The third wastewater stream is the PRWS$_{aqua}$ resulting from the first cleaning procedure of mixing vessels and bottling lines just as the PRWS$_{solv}$. However, this stream predominantly contains residues from products, which are highly water soluble. Most of these residues include detergent substances from various shampoos, shower gels or other cleaning agents. In addition, the washing station is also a source for PRWS$_{aqua}$ generated by primary cleaning steps of the washing procedure for the various containers and equipment. This stream may also contain organic solvents but only at a low ratio. So this raises the question, how this highly contaminated but still PRWS$_{aqua}$ could be separated from subsequent RWS at the washing station. The answer is quite simple as applicable: the automatic washing program, e.g., for the IBCs, will be programmed to run intermittently for a specified time and can only be restarted manually. Thus, from the technical aspect, the first water stream representing the highly contaminated pre-rinsing stream could be discharged and collected separately from the following rinsing stream. In order to actually collect the RWS, there is a need for a second option for water discharge.

With a ratio of approximately 30% of the total wastewater flow, the PRWS$_{aqua}$ is one of the most important wastewater streams. In contrast to the isopropanol and PRWS$_{solv}$, this stream is intended to be purified on site by a company-owned treatment process. For this, several promising mechanical, physical as well as chemical treatment procedures are currently evaluated with regard to their suitability and cost-efficiency. The final objective is to achieve a wastewater quality that permits a disposal to the local public sewer system.

3.2.4. Rinsing water stream (RWS)

The last but not less important is the RWS. Subsequently to the first cleaning step and after removal of the corresponding PRWS$_{aqua}$, both the mixing vessels and the bottling lines have to be flushed again with fresh cold or heated tap water. Depending on the composition and microbial sensitivity of subsequent produced or bottled products, a disinfection step is implemented occasionally. It is performed by using hot water with a temperature of ≥85°C to ensure a disinfection temperature of about 80°C inside the equipment. Alternatively, if a disinfecting agent is used as an additive to the disinfection solution, temperatures below 80°C could be applied. So the disinfection duration depends on both the type and the concentration of the disinfection solution. In the present case, an additive is used that contains an aldehyde usually in a concentration of 2 wt%. To achieve a sufficient bactericidal effect, the mixing vessels as well as the bottling lines need to be disinfected for 15 min. The water collected of both the second cleaning step and the disinfection procedure has been defined as "rinsing water" stream. As mentioned above, RWS also arises as a result of cleaning procedures of equipment and containers at the washing station. Subsequent to discharging the initial highly contaminated PRWS$_{aqua}$, the RWS could be collected separately.

Compared with the other wastewater streams, the RWS is only a slightly contaminated water stream usually containing no strong detergents, only traces of product residues and small amounts of the disinfection agent (Table 2).

Due to the low contamination level, a small proportion of the RWS can be reused for the first cleaning step but only for the same product line to avoid undesirable reactions between various constituents. Nonetheless, the general wastewater quality of the RWS is fairly consistent and thus independent from the product range. Rinsing water that cannot be reused has a composition suggesting a disposal via the local wastewater system.

3.3. Investigations and evaluation of potential approaches adapting to individual material streams

3.3.1. Investigations for the treatment of the isopropanol stream (IPS)

As mentioned above, the IPS contributes to a significant increase of the COD value of the total wastewater flow and needs to be collected separately. However, it should be classified not only as waste but also as recyclable and therefore

Table 2
COD loads of various PRWS$_{aqua}$ as well as RWS collecting at cleaning procedures based on selected produced and bottled cosmetics

Cosmetics	PRWS$_{aqua}$ COD (mg L^{-1})/ volume (L)	RWS[a] COD (mg L^{-1})/volume (L)	
	1st cleaning step	2nd cleaning step	Disinfection step
Bath essence I	27,573/200	110/100	≤50[b]/200
Bath essence II	9,507/100	496/100	–
Sunscreen	12,533/200	407/200	7,671[c]/200
Hair colorant	62,270/100	2,069/200	–
Shower gel	16,575/100	904/50	–
Total	24,081 (700)	2043 (1050)	

[a] The RWS comprises both the 2nd cleaning and the optional disinfection step.
[b] Using hot water with ≥80°C as disinfectant.
[c] Using an aldehyde-containing disinfectant as additive.

precious organic material. Isopropanol for cleaning purposes is commercially available and has a chemical purity of approximately 98%. The amount of product residues in the IPS probably is relatively small compared with the total volume of this stream. Cost-efficient ways of disposal could be the utilization as cheap carbon source for denitrification processes by external wastewater treatment plants or a thermal valorization. However, the recycling and reuse would be a more ecological and sustainable option. Therefore, the percentage of non-volatile components was determined by suitable evaporation experiments displayed below (Table 3).

Table 3
Evaporation residues of selected samples of different batches of the IPS[a]

Sample	Evaporation residues I at 23°C (wt%)	Evaporation residues II at 75°C (wt%)
1	1.6	1.5
2	0.5	0.3
3	0.4	0.2
4	0.2	0.1
5	32.7	31.5
6	5.9	5.7

[a] Experimental conditions: ~3 g of each sample of contaminated isopropanol were weighed on a watch glass and vaporized for a period of up to 5 h to obtain a constant weight at evaporation temperatures of 23°C (I) and 75°C in a drying oven (II), respectively.

Four of the six tested samples contain non-volatile residues with a quantity of ≤5 wt% (samples 1–4). Most of the volatile components were already vaporizable at 23°C, indicated by generally very similar results for the evaporation both at 23°C and 75°C.

Sample 6 has a slightly elevated low evaporation residue content of about 6 wt%, and only one sample (sample 5) contains a high content of non-volatile residues of 32.7 and 31.5 wt%, respectively. Each batch of the tested IPS has approximately a volume of 60 L. On average the total IPS of all these collected samples show a calculated evaporation residue of ≤7 wt% so that, e.g., a fractional distillation procedure represents a suitable recycling method for the resulting IPS.

Subsequently, a test distillation of a mixture of sample numbers 1–6 was performed. For this, a commercial rotary evaporator was used. The contaminated isopropanol containing, inter alia, several cyclic and acyclic siloxane residues was distilled in vacuum under reduced pressure (75 mbar, 40°C), and isopropanol was obtained as colorless liquid in a yield of 82% (Fig. 3).

Consequently, we started to collect the IPS on a large scale and sent representative samples of the IPS to several recycling companies for performing distillation trials with

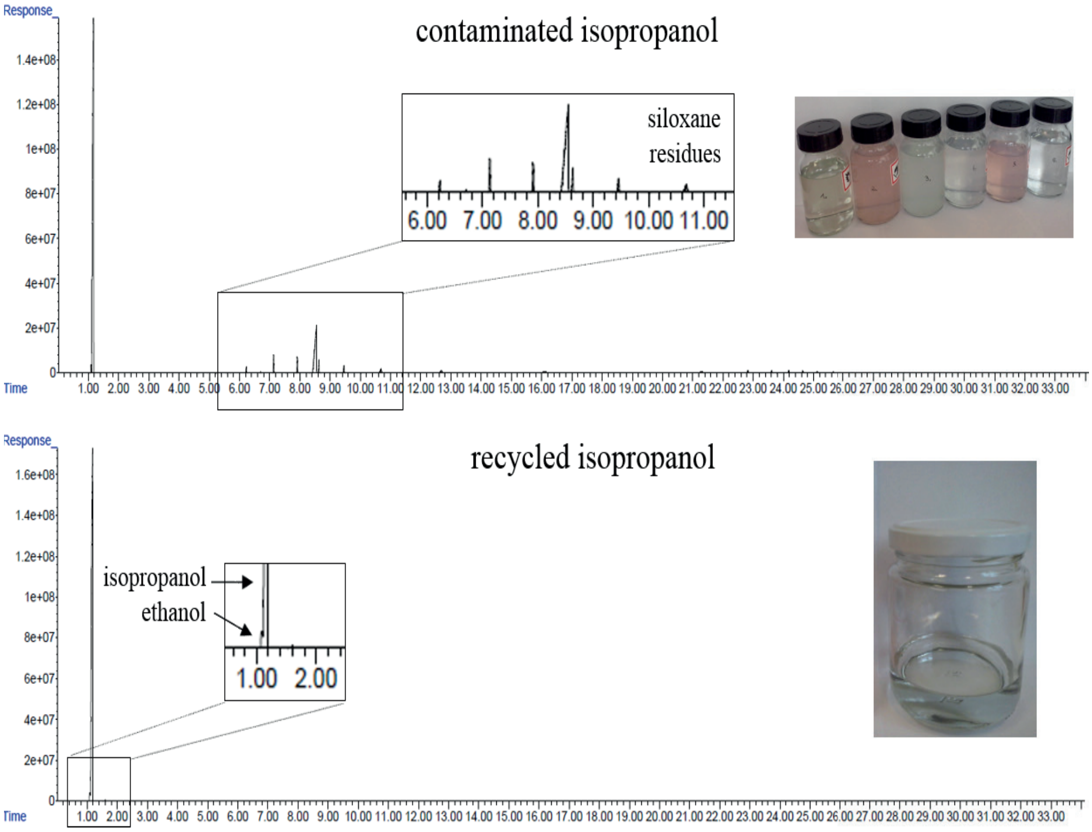

Fig. 3. Gas chromatography with flame ionization detector spectra of (a) collected contaminated isopropanol and (b) recycled IPS by distillation in vacuum under reduced pressure of 75 mbar at 40°C.

these collected samples. Fortunately, the laboratory reports generally revealed a good recovery rate of up to 85% yield (Fig. 4). The purity of the distilled IPS is about 83%–88% containing both water and ethanol as hard-to-remove components concerning their similar boiling points compared with isopropanol. The previously utilized isopropanol has a purity of ≥98%. The market price for such isopropanol averages between 0.80 and 1.20 € per kg. On top of that, there are costs for delivery as well as indirect costs for disposal. However, a purity of ≥83% of the recycled isopropanol is sufficient regarding its purpose as cleaning medium. Ethanol and water as undesirable minor components have no negative influence on the efficiency of the cleaning procedure. On the contrary, increased water content in the recycled isopropanol entails an increased disinfection effect. For this, the antimicrobial activity of isopropanol is optimal in concentrations between 60% and 90% [29].

With the contractual guarantee that the distilled isopropanol will be purchased from the corresponding recycling company, the transport and the actual recycling of the IPS will be conducted free of charge by this company. The price for the recycled isopropanol is more than 20% lower than the price of the previously used isopropanol. Moreover, with a recovery rate of up to 85% the isopropanol can be reused about four times until half of the initial volume of pure isopropanol (98%) will be used up. Thereby, the purity of recycled isopropanol does not drop below 83%. Beneficially, there is no further need to expensively dispose of the contaminated isopropanol as wastewater.

3.3.2. Investigations for the treatment of PRWS$_{solv}$

In comparison with the organic part of this stream, the water content is quite low. The resulting COD of this stream generally exceeds a COD value of 100 g L^{-1}. Since this PRWS$_{\text{solv}}$ comprises a large number of different solvents and components, a material utilization or even recycling, as in the case of the IPS, is no elimination option, here. The stream should be further disposed by an external company as comparatively inexpensive and still proper way of waste disposal. However, most of organic compounds are flammable substances with high calorific values. For example, the combustion of ethanol to water and carbon dioxide is an exothermic reaction with a higher heating value (HHV) of 26.8 MJ·kg^{-1} [30]. Depending on the ratio of combustible and incombustible components, this material stream may be used for energy generation.

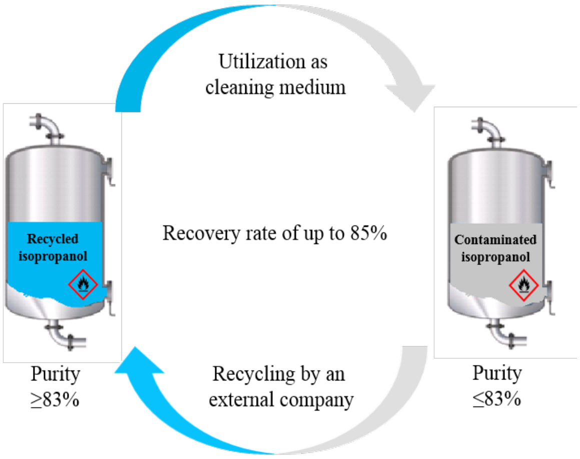

Fig. 4. Recycling and utilization loop of the IPS.

An energetic valorization has to meet the requirements according to the German recycling management and waste law [31]. Conditions to be met are: (a) the waste has to have a HHV of at least 11 kJ kg^{-1}; (b) achieving a combustion efficiency of 75%; (c) the resulting heat has to be exploited, e.g., by the operator of the incineration plant and (d) the resulting combustion residues have to be disposable.

Thereby, the resulting combustion efficiency is not only affected by the combustion material but also depends strongly on the incineration plant itself. Hence, to conform to requirement (b) as well as (c) prescribing the utilization of the resulting combustion energy is not only the responsibility of the concerning waste producer but also the responsibility of the external waste disposer. Requirement (d) cannot be examined with the actual available means. However, to ensure the compliance with condition (a), the HHVs of three selected samples were verified by determining the HVV with an isoperibol calorimeter (Table 4). All of them exceed the required value 11 MJ kg^{-1}, where the first two samples with values above 30 MJ kg^{-1} make this stream energetically very interesting.

In conclusion, the PRWS$_{\text{solv}}$ provides an enormous potential as suitable material utilized energetically by combustion processes. Due to an overall volume of less than 1 m^3 per week, an own incineration plant would not be an economic investment considering costs incurred by the need of the equipment, maintenance and probably additional staff. Thus, the challenge is to find an external but preferably local utilization company that demands less costs for both collection and disposal of the stream than the current wastewater disposal company.

3.3.3. Investigations for the treatment of PRWS$_{aqua}$

The PRWS$_{\text{aqua}}$ is a relatively homogenous solution with a very low content of suspended solids. Mechanical separation techniques such as centrifugation processes are not very promising. This stream indeed shows COD levels of up to ≥100 g L^{-1}, but contains hardly any residues of organic solvents. Hence, the suitability of distillation processes as treatment methods should be tested. Due to structural and

Table 4
Determining the higher heating values (HVVs) of selected samples of the solvent-based pre-rinsing water stream

HHV sample 1 (MJ kg^{-1})	HHV sample 2 (MJ kg^{-1})	HHV sample 3 (MJ kg^{-1})
$32.6 \pm 6.25{\cdot}10^{-2a}$	$34.4 \pm 3.86{\cdot}10^{-2a}$	$17.4 \pm 3.51{\cdot}10^{-2a}$

[a] Standard deviation σ according to $\sigma = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \mu)^2}{n-1}}$ where x_i (MJ kg^{-1}) is the measured value with $i = 1, 2, \ldots n$, and μ (MJ kg^{-1}) is the arithmetic mean.

technical settings, the $PRWS_{aqua}$ could be collected separately just at the production and bottling line, not at the washing station. After collecting a volume of about 6 m^3, a representative mixed sample was taken and analyzed immediately for COD. In parallel the sample was purified by distillation at a constant temperature of 40°C in vacuum under reduced pressure of down to 27 mbar (Fig. 5). The foaming was suppressed adding a suitable high-boiling polysiloxane. The distillation ultimately led to a distillate with a yield of 81% and a COD of less than 1 g L^{-1} corresponding to a removal rate of ≥98%. A resulting evaporation residue of 17% indicates an initial amount of 2% volatile compounds in the $PRWS_{aqua}$.

The results of the conducted experiments show that the amount of waste to be disposed of could be reduced by factor five. The evaporation residue with a share of 17% had to be further disposed of properly by an external company.

However, an essential pre-condition for the success is the absence of significant amounts of organic solvents due to their tendency to form azeotropic mixtures with water. Pre-treated wastewater with COD values of less than 1 g L^{-1} implies that all other variables are mainly complying with the legal limiting values for the disposal into the local common wastewater system.

Indeed distillation processes are comparatively both energy and cost-intensive purification procedures. However, the benefits are obvious; distillation is a treatment method that is relatively independent from the frequently changing product range; and it is the most appropriate method to reduce the COD on such a scale and comply with the required limits in only one treatment step.

In the case of obtaining distillates with COD levels that are out of range of legal limit values, the distillation can be used in combination with subsequent filtration processes, e.g., micro-filtration and ultrafiltration steps, to achieve the required limits.

3.3.4. Investigations for the treatment of RWS

The RWS is, as mentioned above, an only slightly contaminated wastewater stream, which is supposed to dispose via the local wastewater system. Compared with current wastewater costs with at least 50 € per ton, the discharge to the municipal sewer system costs <3 € per m^3. This would lead to a cost-saving of around 94% per ton of RWS. To verify the quality of the RWS, samples were collected separately from the total wastewater flow over a period of 3 weeks. Therefore, at first the concerning wastewater from the cleaning steps subsequent to the production was collected as well as the bottling process and secondly from the washing station as third wastewater source. In total we collected 10 representative samples of the requested rinsing wastewater from both the production and bottling process. One sample comprises a volume of 1 m^3 so that a suitable aliquot of 500 mL m^{-3} was taken. All samples were mixed together, and the resulting sample A was analyzed promptly for decisive parameters such as COD, BOD_5 and TOC (Table 5). Due to structural and technical circumstances, the sampling strategy at the washing station is different. Herein, four collected RWS samples of the cleaning procedures of various IBCs previously included products of different product classes were mixed. Therefore, the standard washing program for IBCs was interrupted after a certain time of 1 or 3 min corresponding to the contamination level of the respective IBC to discharge the $PRWS_{aqua}$. Following, the water outlet of the IBC was closed, and the

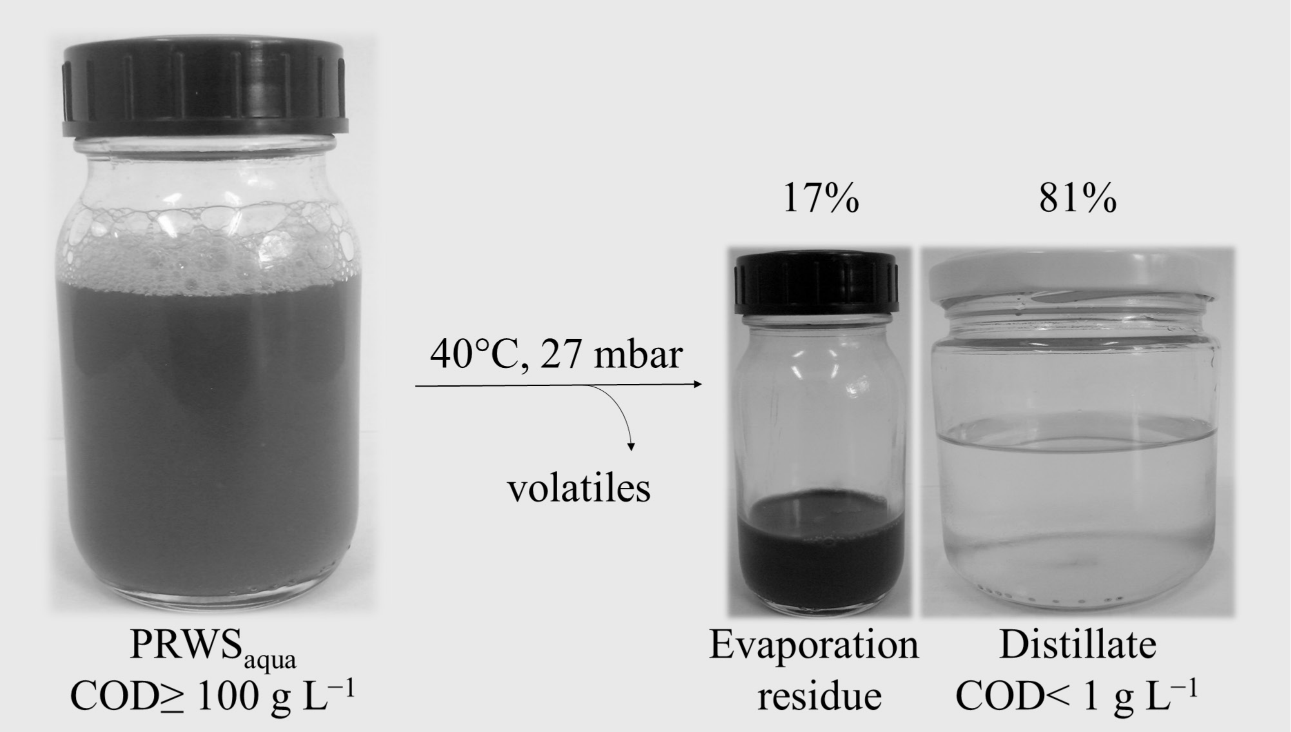

Fig. 5. Distillation experiments with $PRWS_{aqua}$.

Table 5
Characteristics of rinsing water streams (RWS)

Parameter	Sample A[a]	Sample B[b]	$\frac{A+2B}{3}$[c]	Discharge limits to domestic WWTP
pH	6.65	8.45	7.85	6.50–10.0
Conductivity (μS cm^{-1})	403	495	464	–
COD (g L^{-1})	4.91	1.67	2.75	2.50
COD$_{\text{filtrated}}$ (g L^{-1})	4.45	1.41	2.42	–
BOD$_5$ (g L^{-1})	3.70	0.74	1.73	–
BOD$_5$/COD	0.83	0.44	0.57	≥0.40
TOC (g L^{-1})	1.19	0.47	0.71	–
Phosphate (mg L^{-1})	0.40	1.37	1.05	50.0
N-Ammoniac (mg L^{-1})	5.33	3.46	4.08	100
Chloride$_{\text{filtrated}}$ (g L^{-1})	0.03	0.02	0.02	–
Sulfate$_{\text{filtrated}}$ (g L^{-1})	0.06	0.02	0.03	0.6

[a] Collected from cleaning steps at the production and bottling lines.
[b] Collected from cleaning steps at the washing station.
[c] Calculated values.

usually performed washing program restarted. After finishing the cleaning process, an aliquot of 500 mL was taken as representative sample. Four of those samples were mixed together to get sample B, which was analyzed similarly to rinsing water sample A (Table 5).

The volumetric ratio of the accruing wastewater from the production and bottling line cleaning compared with the washing station was determined as about one-third to two-third equivalent. Applying this ratio, composite values for the total RWS were calculated, ranging between the determined values of samples A and B. These calculated values represent a good approximation for an expectable quality of the resulting RWS. Thus the stated limits of wastewater discharges to the municipal sewer system also depicted in Table 5 are reached approximately. Based on these very promising results, it is recommended to examine characteristics of the real rinsing stream by conducting a full-scale experiment. The still elevated COD concentrations in the range of the upper discharge limit may lead to further optimization attempts, e.g., by adopting the cleaning procedures.

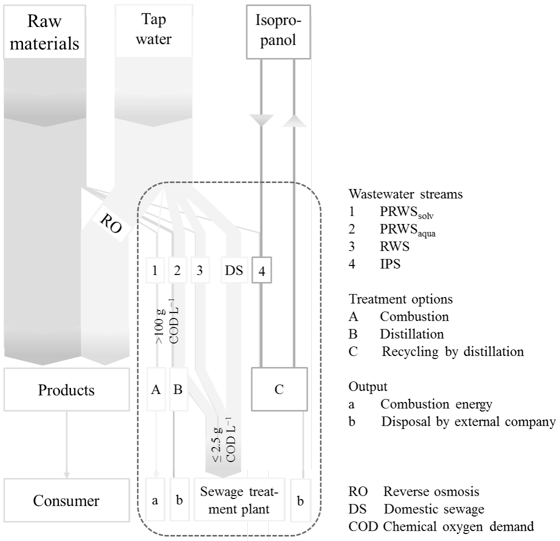

Fig. 6. Material flow balances of both the production process and the wastewater concept of the concerned company subsequent to the investigations.

4. Conclusions

The determination of general characteristics of the resulting effluent shows that a suitable classification and separation of certain material and wastewater streams is a promising approach for significantly reducing the wastewater costs and improving the general sustainability. The investigations resulted in a really simple separation system based on subdividing the total wastewater flow into four wastewater streams providing the opportunity for distinctive adapted treatment processes (Fig. 6).

These four streams are: (1) an IPS as totally recyclable material stream, (2) a PRWS$_{\text{solv}}$ resulted in an energy-providing combustion process, (3) a PRWS$_{\text{aqua}}$ purified by distillation processes achieving COD levels of ≤2.5 g L^{-1} and (4) an inherently low contaminated RWS. The pre-treated PRWS$_{\text{aqua}}$, the RWS as well as the domestic wastewater can be discharged without further processing via the local municipal wastewater system. Previous costs for the disposal of the total effluent varied between 50 and 100 € per ton. The costs for the disposal of the pre-treated PRWS$_{\text{aqua}}$ and the RWS via the municipal sewer system are less than 3 € per ton. With a percentage of more than 75% of both PRWS$_{\text{aqua}}$ and RWS, huge savings will be achieved.

In conclusion, we present a classifying principle based on plain chemical criteria that provides a favorable and easy-to-apply wastewater management system. Apart from a distillation plant to treat the PRWS$_{aqua}$ to achieve dischargeable wastewater there is no requirement for additional treatment equipment and facilities. The stream separation itself does not entail any additional costs. Capital expenditure and operational expenditure for a distillation plant are not calculated, yet. But compared with a company's own sewage treatment plant with costs in a million range, a distillation plant for the treatment of the PRWS$_{aqua}$ is probably cost effective. So far, both the combustible waste and the evaporation residues of the PRWS$_{aqua}$ will still be disposed by an external company.

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