Nanofiltration with optional permeate recycling from the pretreatment of synthetic fabric

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Abstract

The company Global Safety Textiles Limited (GST) in Murg/Germany is a leading manufacturer of woven fabric for airbags. The weaving section orders polyamide yarns from different suppliers which use significantly different preparation agents. For the weaving process itself, the yarns need to be protected by means of a film of sizing agent which consists of polyacrylic acid. Subsequently, for removing the sizing agent and the preparation agents, the flat woven fabric is washed in a continuous washing machine. Until 2006, the wastewater resulting from this washing operation was discharged to the municipal wastewater treatment plant (MWWTP) of Murg. This was associated with significant problems. On the one hand, the percentage of the discharged load of organic compounds was high and on the other hand, a number of chemical compounds of the wastewater were insufficiently biodegradable and bioeliminable respectively.

After various investigations to reduce the COD load, GST decided to erect and to operate a plant for the pretreatment of a certain wastewater stream from the washing machine. This is the high-loaded wastewater stream from the so-called chemical compartments which contains the major part of sizing agents and preparation agents. The low-loaded wastewater from final rinsing of the fabric is discharged to the MWWTP without prior pretreatment.

The wastewater pretreatment plant consists of a nanofiltration and a vacuum evaporation unit where the concentrate from nanofiltration is further concentrated for subsequent external disposal (incineration). Thus, the COD load of GST discharged to the MWWTP was significantly reduced. As a consequence, the COD concentration of

the treated wastewater of the MWWTP is more than 50 % lower. So the pretreatment of a selected and segregated individual wastewater stream is as a success story.

1 The company Global Safety Textiles Limited (GST) in Murg / Germany

The textile industry in the upper Rhine region has a long tradition. So, the history of GST is reaching as far back as to the 19th century. In addition to the site in Murg, the company operates two more sites in the same region which are located in Bad Säckingen and Maulburg. The production sites in Europe outside Germany are in Poland, in the Czech Republic and in Romania. Further, the company operates production sites in the USA, Mexico and South Africa. For a number of years, GST is part of the South Korean Hyosung Group [1].

According to its statement, GST is a market leader for the development and production of airbags and woven fabric used for the manufacture of airbags. As such woven fabric needs to resist to extremely high pressure in case of emergency, i.e. in case the gas generator is ignited, synthetic yarns are used. Amongst others, GST produces polyamide woven fabrics for all applications such as for the head, breast, shoulder and knee area. Nowadays, the cars from well-known car manufacturers are equipped with four to twelve airbags. [2]

1.1 The production process of GST in Murg

In case of a frontal impact, the front airbags for driver and front-seat passenger provide particularly high protection. For this application, GST in Murg produces so-called flat woven fabrics which are two-dimensional. [3] The cutting and sowing of the fabric manufactured in Murg is carried out at other sites of the company. Besides flat woven fabric, so-called OPW (One Piece Woven) fabric is produced in Murg. This is a double-layer woven fabric which is produced in one step and which thus not have seams. [4]

The weaving section of GST sources the polyamide yarns from different external suppliers. Due to their production process, these yarns contain about 0.8 weight-% of

[1] https://www.global-safety-textiles.com/de/unternehmensgruppe/historie
[2] https://www.global-safety-textiles.com/de/unternehmensgruppe/historie
[3] https://de.wikipedia.org/wiki/Flachgewebe (accessed on 07.08.2018)
[4] https://www.global-safety-textiles.com/de/produkte-und-services/airbaggewebe

preparation agents of different composition (see Chapter 1.3). After sizing, weaving and wet processing, the polyamide fabric produced from the yarns is used for the production of airbags. The process sequence carried out in Murg is shown in Fig. 1.

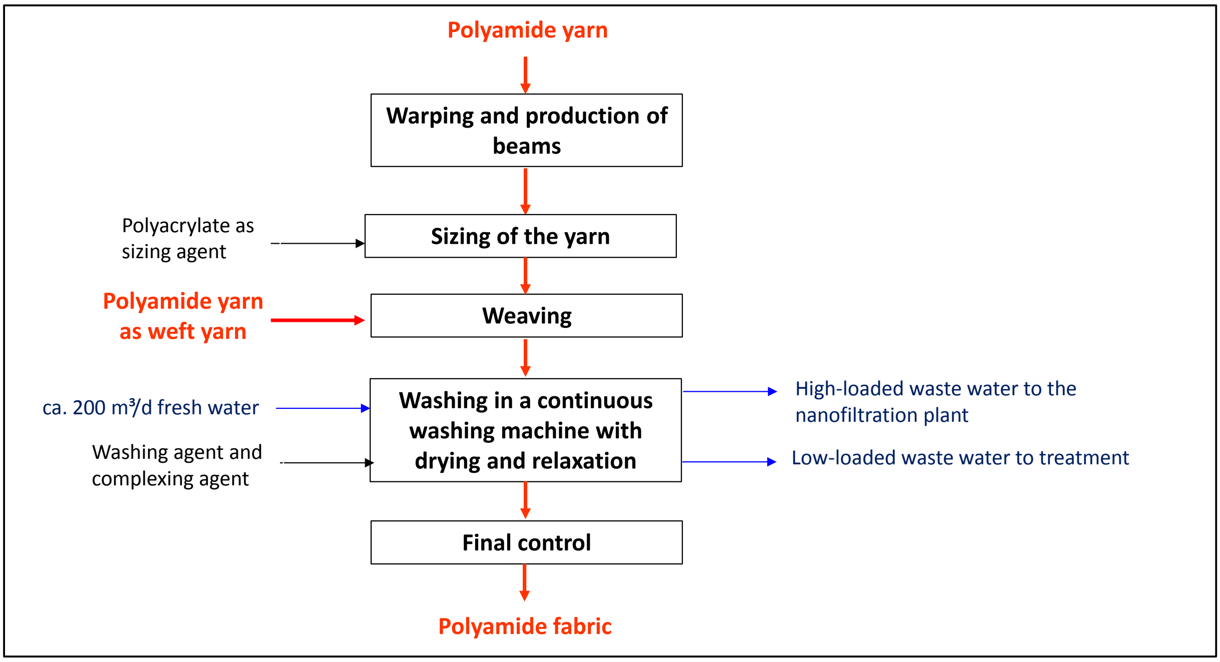

Fig. 1: Process sequence of the production in Murg with indication of the most relevant input and out mass streams

First, the yarns are warped and wound on warp beams. In order to protect the warp yarns against the high mechanical stress during weaving, they are coated with a polymer film. The compounds used for this purpose are called sizing agents. In case of GST, unbranched polyacrylic acid is used at an add-on of 0.4 – 0.6 weight-%. After weaving, the sizing agent has done its job and has to be removed.

1.2 Wastewater from washing the polyamide fabric

The preparation agents and the sizing agent are removed to a high extent in a continuous washing machine (Fig. 2). For this purpose, auxiliaries containing washing agents and complexing agents are used. The alkaline pH of the washing liquor is adjusted by means of caustic soda.

Fig. 2: Photo of the continuous washing machine for polyamide fabric at Global Safety Textiles Limited in Murg

The washing process is completely carried out in the counter-current mode. As indicated in Fig. 3, there are two individual wastewater streams resulting from the washing process.

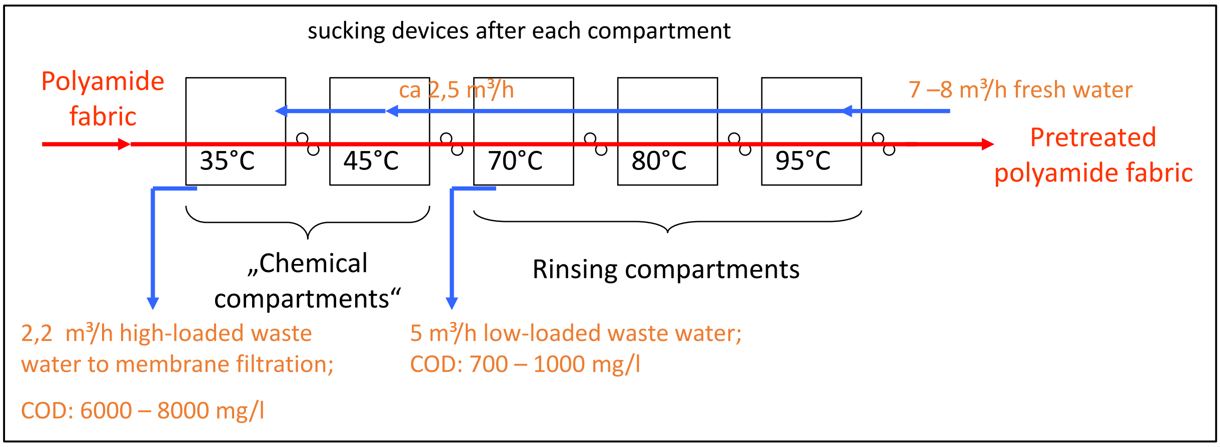

Fig. 3: Scheme of the continuous washing machine for washing-off preparation agents and the sizing agent from polyamide woven fabric

From the rinsing compartments, about two thirds of the wastewater flow (low-loaded) is generated. The remaining third is the wastewater from the so-called chemical compartments which contains most of the preparation agents and sizing agents (high-loaded). About 0.2 – 0.3 weight-% of the preparation agents cannot be washed off and remain on the fabric whereas the sizing agent is removed to more than 95 %. The low-loaded rinsing water has a chemical oxygen demand (COD) between 700 and 1000 mg/l whereas the COD of the high-loaded wastewater stream from the chemical compartments varies between 6000 and 8000 mg/l. The specific water consumption of the washing operation is 8.8 l/kg.

Fig. 4 shows the input of fresh water and chemicals as well as the two wastewater streams from the continuous washing machine.

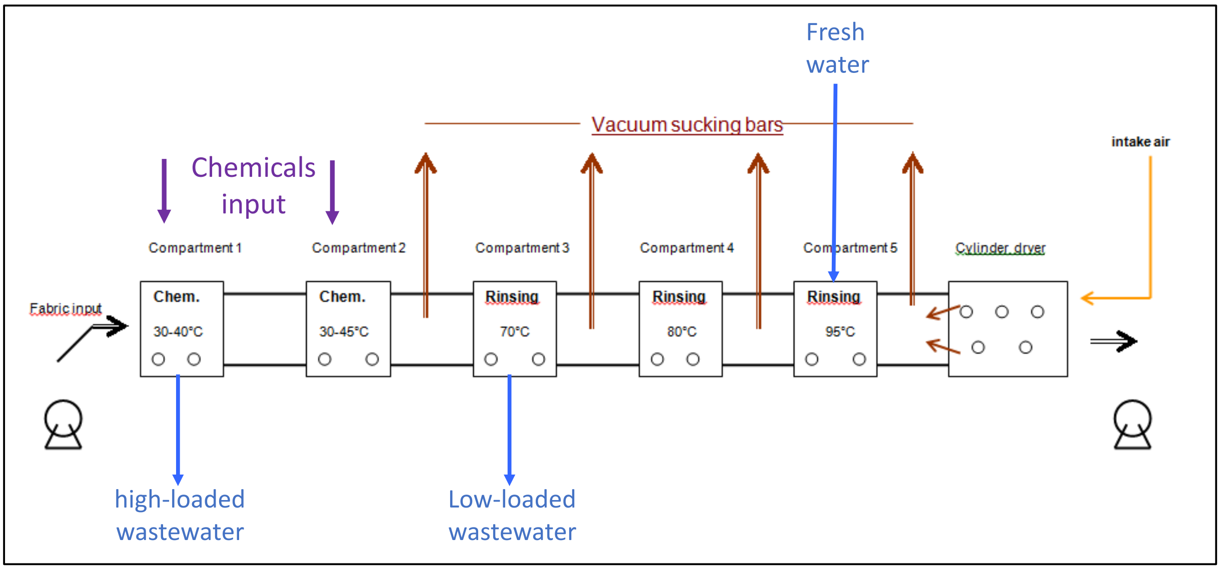

Fig. 4: Scheme of the fresh water input, wastewater output and sucking devices of the continuous washing machine

The low-loaded wastewater stream is pumped to an equalisation tank from where it is discharged to the municipal wastewater treatment plant (MWWTP) of Murg. By means of an automated sampler, every day 24 hour flow-proportional composite samples are taken and analysed for COD. Earlier, prior to the pretreatment plant established in 2006, all the wastewater had been discharged to the MWWTP. However, investigations of the biological degradability and eliminability respectively revealed comparatively low rates. Therefore, at an early stage, it was intended to minimise the pollution load of the wastewater discharged to the MWWTP of Murg.

1.3 Chemical compounds in the wastewater resulting from continuous polyamide fabric washing

As described above, the pollution load of the wastewater results from the preparation agents, the sizing agent and the textile auxiliaries used for the washing process (washing agent and complexing agent). For the selection of an appropriate and efficient wastewater pretreatment process, detailed information of the aforementioned chemical compounds were collected.

From the material safety data sheet, it could be seen that the sizing agent consists of polyacrylic acid. Concerning the preparation agents, an expertise, prepared by Mrs Claudia Schafmeister from the company Textil + Ökologie in 85221 Dachau/Germany, describes the composition of the preparation agents used for the different polyamide yarns (Schafmeister, 2005). For confidentiality reasons, the main components of the preparation agents are mentioned but not information of the individual yarn suppliers. The most relevant components of preparation agents are lubricants (ca. 50 – 60 %), emulsifiers (ca. 10 – 20 %), anti-static agents (ca. 10 – 20 %), yarn compacting agents (ca. 10 %) and additives (corrosion inhibitors, biocides, anti-splash agents). As lubricants, mineral oil, fatty acid esters (common esters and which are sterically hindered or do have longer chains), ethylene oxide/propylene oxide adducts (EO/PO adducts), silicone oils, polyol esters or polyester/polyether carbonates. Surfactants serve as anti-static agent and emulsifier. For better yarn compacting, EO/PO adducts are used.

The types and add-ons of chemicals used for preparation agents are well-protected knowledge of the yarn producers. For the polyamide fabric, only polyamide flat yarns are used. They contain only one primary preparation agents (spin finish). Mineral oils are not applied for lubrification. In contrast, fatty acid esters are largely used. They are easily biodegradable. The same is true for triglycerides and for most of the surfactants used.

The fatty acid esters lubricants used by one of the yarn suppliers (at a percentage of 50 % of the preparation agent) belong to the so-called “conventional fatty acid esters”. This means that the chain length is in the range of C_{14} to C_{18}. In this case, anionic surfactants (secondary alkane sulphonates) are used as emulsifiers, oleic acid triethanolamine as anti-static agent (10 %) and oleic acid ethoxylates as yarn compacting agent (20 %). The yarn supplier stated that the preparation agents are stable at the condition of the continuous washing process (high pH and temperatures near the boiling point).

Concerning biodegradability/bioeliminability, the yarn supplier mentions a value of about 80 % as an estimate from the different components. This estimation appears to be plausible. The add-on of preparation agents is reported to be in the range of 0.6 – 0.8 weight-%.

The add-on of preparation agents of several polyamide yarns of the second supplier varies between 0.6 – 1.0 weight-%. These agents contain fatty acid esters as lubricants. The main difference of all the preparation agents for these yarns is the EO/PO ratio of the yarn compacting agent (< 10 weight-%). Concerning the lubricant components, mainly conventional fatty acid esters (> 60 weight-%) and little silicone oil (< 5 weight-%) are used. As emulsifier (20 weight-%), a formulation of anionic and non-ionic surfactants are taken, and anionic surfactants as anti-static agent. Also these preparation agents are stable at high pH and temperatures. Silicone oils are non-biodegradable and may cause problems with respect to scaling of the membranes.

In contrast to the preparation agents described above, the ones supplied by the third supplier are based on natural oil (fatty acid triglyceride) which showed a biodegradation rate of 86 % (Zahn-Wellens Test). Further, no emulsifiers, anti-static agents etc. are contained. As consequence, in contrast to those above, these preparation agents are water-insoluble. Such natural oil and fats are esters of glycerin and fatty acids, which are saponified under the conditions of the washing process. The cleavage results in the formation of glycerin and sodium salts of fatty acids which are known as anionic soaps or sodium soaps. In wastewater, they precipitate with hardness minerals (calcium, magnesium) as insoluble lime soaps. This precipitate adsorbs to about 70 % to activated sludge and, in case of anaerobic sludge stabilization, they end up in anaerobic fermenters. There, depending on the chain length, their degradation is more or less complete.

The wastewater of GST was analysed in detail with respect to halogenated compounds by means of the sum parameter adsorbable organic halogens (AOX). However, no indications for the presence of such compounds were found.

Not only the preparation agents and sizing agent but also the chemical compounds contained in the applied chemical products were considered in detail. As complexing agent, an aqueous solution of a salt of an aminophosphonic acid is used. The supplier did not submit information on the biodegradability and bioeliminability respectively for this compound but it is known that such phosphonates are insufficiently eliminated in biological treatment plants. The chemical products containing washing agents are a formulation of fatty alcohol ethoxylates and fatty alcohol polyglycolethers which show a bioelimination rate of more than 80 % in 28 days (Zahn-Wellens Test according to OECD 302 B).

2 Wastewater treatment problems of the MWWTP of Murg

2.1 Wastewater disposal situation in 2006

It is hardly surprising that the wastewater of an indirect discharger like GST with high COD loads and heavily biodegradable compounds causes significant problems in the MWWTP concerned. Further, at that time a much more complex chemical recipe for washing the polyamide fabric had been applied.

Before the pretreatment plant described in this paper had been taken into operation, the situation in the MWWTP of Murg was dramatic. At that time, the annual COD load discharged by GST was about 200 t. The MWWTP of Murg is designed for 900 kg COD per day. With about 320 working days, the GST percentage of the COD load was about two thirds. In order to reduce this percentage, GST had reduced the add-on of sizing agents and the quantity of chemicals used for the washing process as far as possible.

Specifically with respect to GST wastewater, the dosage of pure oxygen and of lime was installed. Lime needs to be added in order to adjust the pH which is reduced during nitrification of ammonium. The additional costs for these measures were covered by GST.

2.2 Investigations to reduce the COD load of GST

For reducing the discharged COD load from polyamide fabric washing by treatment techniques, GST tested various available techniques (precipitation/flocculation, UV treatment, oxidation with hydrogen peroxide) (Egle, 2005). Each of these techniques showed disadvantages. One technique showed low efficiency whereas another was too complicated or too expensive. The combination of nanofiltration and evaporation of the concentrate under vacuum appeared as the best solution as the thus minimized quantity of residue can be disposed of externally. However, for large quantities of concentrate, this technique combination may not be economically viable.

After first trials with the combination of nanofiltration and concentrate evaporation under vacuum, GST decided to invest in this solution although some filtration trials with hollow filter modules showed cracks of some of the elements after a few weeks of operation. Such hollow filters, also called capillary membranes or hollow threads, can be manufactured to lengths of more than 200 cm and are compacted to modules with a range of filtration area between a few square millimeters and about 100 square meters. Thereby, the ends of the elements have to be closed in order to avoid hydraulic shortcut. Thus, a large filter area can be achieved within very small space. [5] Although first filtration trials with the hollow filter modules were not successful, it was demonstrated that the process was suitable in principal to concentrate the organic wastewater compounds. Due to the final report of the joint project "Development and use of ceramic nanofiltration membranes for the production-integrated environmental protection demonstrated at textile wastewater" of the German Aerospace Center dated 30.05.2001, the focus were laid on ceramic membranes.[6] Thus, for the pilot test carried out for several weeks these newly developed ceramic membranes with a pore size of 0.9 nm were used. Finally, GST decided to invest in the combination of nanofltration and evaporation under vacuum of the resulting concentrate.

3 Pretreatment of the wastewater from the chemical compartments

After the successful performance of the pilot test, GST started to plan the implementation of the plant for the pretreatment of the high-loaded wastewater resulting from the chemical compartments of the continuous washing machine.

[5] https://de.wikipedia.org/wiki/Mikrofiltration#Hohlfasermodule (accessed on 06.08.2018)
[6] http://www.cleaner-production.de/fileadmin/assets/27943_-_Abschlussbericht.pdf

3.1 Erection and commissioning of the pretreatment plant in 2006

The nanofiltration plant was provided by Andreas Junghans – Anlagenbau und Edelstahlbearbeitung GmbH & Co. KG in Frankenberg/Sachsen [7] with ceramic membranes with a very small average pore size of 0.9 nm. According to the definition concerned, nanofiltration membranes have a maximum pore size of 2 nm. [8]

The project was scientifically supervised by Prof. Dr. Horst Chmiel from the Gesellschaft für umweltkompatible Prozesstechnik (upt) mbh which was a research institute of the University of Saarbrücken/Germany. [9] The nanofiltration plant was complemented by an evaporation unit provided by H_2O GmbH in Steinen/Germany. [10]

The total investment costs for the pretreatment plant including construction costs were 266,000 Euro. The project was financially supported with about one quarter of the investment costs by the Ministry of Environment and Traffic of the German federal state Baden-Württemberg (Egle, 2005) and was permitted according to paragraph 16 of the German Clean Air Act by the competent authority (Regierungspräsidium Freiburg).

3.2 Description of the pretreatment plant

The scheme of the pretreatment plant as a combination of nanofiltration and evaporation is shown in Fig. 5. As described above, this plant pretreats the high-loaded wastewater stream from the chemical compartments of the continuous washing of polyamide flat woven fabrics.

[7] http://www.ajunghans.de/
[8] https://de.wikipedia.org/wiki/Nanofiltration (accessed on 06.08.2018)
[9] In the meantime the institute is not existing any more
[10] https://www.vakuumverdampfer-h2o.de/produkte/vacudest

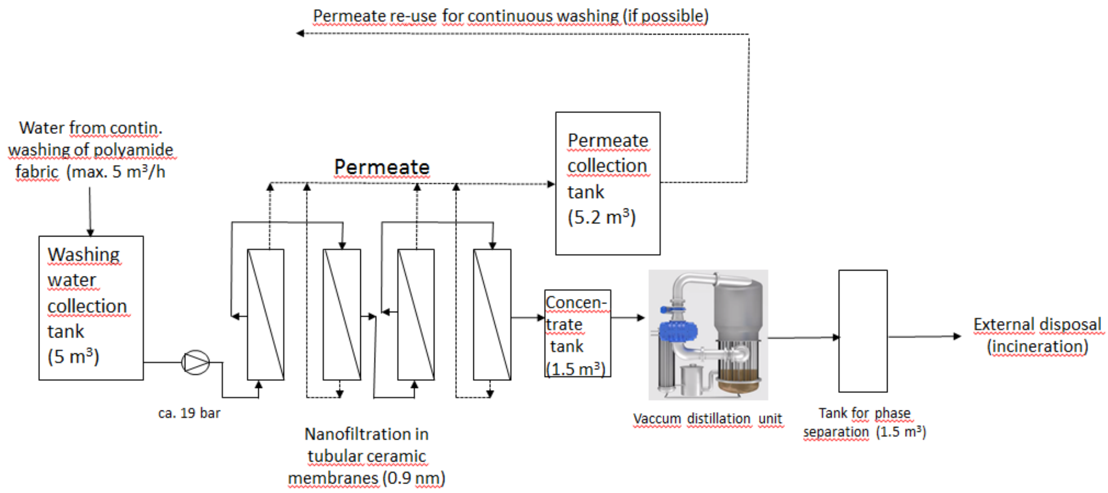

Fig. 5: Scheme of the nanofiltration and evaporation unit

First, the washing water is collected in a stainless steel tank with a volume of 5 m^3. From there, a pump delivers the wastewater via a pre-filter for removal of coarse suspended solids, especially fibres, to the nanofiltration unit with a membrane area of 37 m^2 and a capacity of 5 m^3/h. The membrane unit consists of a series of four modules which contain the ceramic membranes (19 channel tubes) with an average pore size of 0.9 nm. The circulation pump is operated at 19 – 20 bar. Fig. 6 shows the total view of the nanofiltration unit and Fig. 7 a 19 channel tube.

Fig. 6: The four stainless steel modules of the nanofiltration plant provided by Andreas Junghans – Anlagenbau und Edelstahlbearbeitung GmbH & Co. KG in Frankenberg/Sachsen

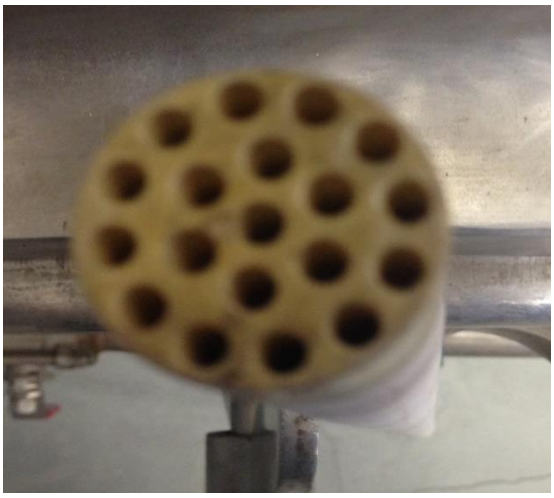

Fig. 7: One single ceramic module (19 channel tube) of the nanofiltration plant

The permeate from the four modules is collected in a tank with a volume of 5.8 m^3. While permanently charging wastewater, the concentrate is circulated until the target water content is reached. One cycle lasts about 6 hours. Then, the nanofiltration plant is cleaned by means of a washing lye. The filling time for the washing lye just tales about three minutes.
Fig. 8 shows the milky concentrate from the nanofiltration unit.

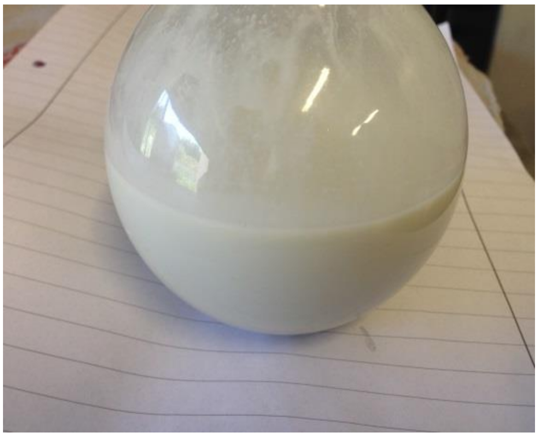

Fig. 8: Milky concentrate from the nanofiltration plant which is subsequently evaporated under vacuum

The concentrate is collected in a tank with a volume of 1.5 m^3 from where it is fed to the evaporation unit. This consists of a heat exchanger to heat the concentrate to a temperature of 90 – 100 °C under vacuum of about 0.5 bar (Fig. 9). The distillate is discharged to the MWWTP of Murg.

Fig. 9: The milky concentrate from the nanofiltration plant is de-watered under vacuum in an evaporation plant provided by H_2O Ltd. in Steinen/Germany

The evaporation residue is pumped to a collection tank with a volume of 1.5 m^3 in which the different phases of the residue can be separated. When the plant was put into operation, there were four different phases. Today, this is not the case anymore. The reason for this change may be the modified washing recipes (other chemical products) or modified preparation agents. Therefore, the whole evaporation residue is filled into intermediate bulk containers (IBC) which are sent for incineration via a disposal company. The evaporation residue is not a homogenous liquid. Fig. 10 gives an idea concerning the complexity of the evaporation residues (see the different components).

Fig. 10: Photo of the concentrate after evaporation with a water content of 3 -5 % which is collected in intermediate bulk containers (IBC) for external disposal (incineration)

Originally, the permeate from the nanofiltration unit was recycled to the washing process. As spots have been detected on the fabric and as this effect was not observed without permeate recycling, the permeate is currently not recycled but is discharged to the MWWTP of Murg.

The specific flow of wastewater from the chemical compartments for washing the polyamide fabric is about 3 l/kg which is fed to the nanofiltration unit. This corresponds to a daily average flow of high-loaded wastewater of 28 m^3/d (8865 m^3/a). The quantity after nanofiltration is 5 % of this flow maximum, i.e. 1.4 m^3/d (443 m^3/a). This quantity is evaporated to 21 m^3/a which is 0.25 % of the wastewater flow from the chemical compartments. Thus, the concentrating factor is 422. All the values mentioned above are for 2017.

3.3 Costs of pretreatment of the high-loaded wastewater

In 2017, the costs for wastewater pretreatment comprised of electricity consumption both for nanofiltration (14184 Euro/a; 16 Cent/kWh) and evaporation (6379 Euro/a; 16 Cent/kWh) and of the costs for concentrate disposal (4830 Euro/a, 230 Euro/m^3). Thus, the total costs are 25,393 Euro/a, which correspond to about 3 Euro per cubic meter of treated high-loaded wastewater.

4 Conclusion after twelve years of pretreatment plant operation

As a reward to all the efforts, the wastewater treatment situation of the MWWTP of Murg was and is significantly improved. Today, the COD concentration of the wastewater discharged is 20 – 40 mg/l which is less than half before operating the pretreatment plant (before 2006). Thus, the erection and operation of the nanofiltration and evaporation plant for the pretreatment of high-loaded segregated wastewater from continuous washing of polyamide fabric is a success story. This is also a result of the robustness of the ceramic membranes; most of the modules which have been installed in 2006 are still in use.

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