REUSE OF TREATED WASTEWATER FROM MUNICIPAL WWTP AS PROCESS WATER

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ABSTRACT

This paper addresses the water supply challenges faced by a white pigment powder production facility, relying on a nearby river, particularly during dry periods when minimum ecological flow may be compromised. The study explores an alternative water source from the municipal wastewater treatment plant (WWTP), emphasizing the use of membrane treatment, specifically ultrafiltration (UF) and reverse osmosis (RO). A pilot trial, initiated in March 2023, employs UF and RO devices in a container at the WWTP. Despite observed fouling during the summer, the results demonstrate optimistic water quality outcomes that consistently meet expectations. The paper underscores the importance of treating WWTP effluent and the specific considerations involved in membrane treatment for industrial processes. The ongoing pilot trial is discussed, focusing on the challenges of fouling reduction and the necessity of maintaining water quality. The study concludes by highlighting the significance of the chosen treatment method in ensuring a sustainable and reliable water supply for the complex white pigment production process.

Keywords: alternative water source, process water, pilot test, reuse, reverse osmosis, sustainability, ultrafiltration.

Introduction

Cinkarna Celje requires process water for its white pigment Titanium dioxide production process. Today, the factory draws water from a small river Hudinja located nearby. The company holds a water permit with two restrictions: the pumping quantity intake and the minimum ecological flow (Q_{es}). At normal water level, there is enough water for Q_{es} and production use of raw water from the river. However, during dry periods Q_{es} can drop below the established level, at which point water extraction is no longer permitted, and production must be immediately halted.

The production of titanium dioxide is highly complex, involving internal recycling loops and the preparation of intermediates necessary for production startup. It takes a minimum of 14 days from startup to the final product. The production consists of 21 fundamental processes and 31 supporting processes, all requiring water for their operation. Therefore, any water supply interruption results in an immediate production halt.

Short-term interruptions due to equipment malfunctions in specific process sections are adequately protected by environmental and equipment safety preventive measures and do not pose significant issues. However, longer interruption periods demand a complete production line drainage. If planned drainage using available water sources is employed, the process takes an average of 14 days. Under such conditions, negative environmental impact can be prevented, but economic damage due to production loss occurs.

In the event of an urgent, prolonged shutdown due to unavailable water sources, the consequences would be much more severe. To manage this risk, the company has:

- explored the possibility of utilizing surface and groundwater sources in the immediate vicinity,
- investigated options for storing a larger quantity of water in reservoirs during dry periods,
- examined the possibility of supplying water from existing reservoirs such as nearest large enough lakes (Šmartinsko and Slivniško),
- implemented and still implementing measures for maximizing water reuse,
- obtained a study to determine Q_{es} for water intake from the river Hudinja, submitted it with an application to the water agency, resulting in a favorable Q_{es},
- explored the possibility of defining a section of the river Hudinja as a candidate for a significantly modified water body.

Despite these efforts, a universal solution to the existing challenge has not been identified.

Solution with a sustainable approach

In recent years, Cinkarna has been transitioning towards sustainable production through various activities. In line with the principles of sustainable use of natural resources and the circular economy, the idea of using wastewater from the Wastewater Treatment Plant in Tremerje (WWTP) emerged. Despite the approximately 7 km distance between Cinkarna and WWTP in Tremerje, which presents a unique spatial challenge on its own, it proves meaningful considering the positive contribution. This approach not only addresses the risk of water scarcity but also improves the biological and hydromorphological condition of watercourses.

By using water from WWTP in Tremerje, the intake from the river Hudinja (currently at 350 $m^3/h \pm 10$ % during production) would be practically non-existent. This water would only be used during maintenance work at the Wastewater Treatment Plant when the discharge into the river Savinja is interrupted. Such maintenance activities are repeated twice a month, lasting approximately six hours each time. This means that water from the river Hudinja would be used for only 12 hours per month, or water from WWTP in Tremerje would be utilized for more than 96 % of the time. With the construction of an additional reservoir, this pumping could be entirely avoided.

If water from WWTP in Tremerje would be used for Cinkarna's needs, pumping from the river Hudinja would be discontinued. Therefore, the dam could be lowered to the minimal possible level, which can be easily lowered or raised within an hour. With the discontinued intake from the river Hudinja, the flow in the river could be increased, significantly improving hydromorphological conditions of the river Hudinja, especially during dry periods. Treatment capacity of municipal WWTP is 85,000 population equivalents with dry period flow 450 $m^{3/}h$. Currently production draws 350 m^3/h from the river Hudinja. From a quantity perspective, there is sufficient water available. However, an additional crucial parameter that distinguishes it from the current source is chloride levels. The presence of chloride in municipal WWTP is consequence of road treatment with salt. Peaks in chloride levels occur following rain after dry periods in winter. Chloride limit is in process in-line observed with conductivity i.e., conductivity of production water must be less than 800 µS/cm. In case of higher conductivity, water must be diluted with water containing less chloride i.e., has lower conductivity. Water with lower conductivity can be prepared with demineralisation, which is also necessary for the production process.

Under the existing cleaning system in Cinkarna, water pumped from the river Hudinja is first roughly treated in a sedimentation tank, followed by filtration on sand filters. Part of the water is used with this quality, while the remaining portion undergoes additional purification with ion exchangers.

The first step in treating water from the WWTP in Tremerje should be the coarse removal of undissolved substances, which would take place at the WWTP in Tremerje. Such a pre-filter is necessary to protect ultrafiltration membranes, as excessive concentrations of undissolved substances in the inlet water can irreversibly damage the membranes. Over the course of a year-long sampling period, it was found that the water discharged from WWTP in Tremerje contains an average of 8,4 mg/L of suspended solids. Most of these particles would be removed by the pre-filter at the WWTP in Tremerje, and finally, by ultrafiltration at the Cinkarna site. The water generated during pre-filter backwashing would be returned to the WWTP, and the water from ultrafiltration membrane backwashing would be directed to the existing water treatment system at Cinkarna. This would result in the removal of a total of 36,2 tons (calculated on a 100% dry matter basis) of suspended solids annually, which would otherwise end up in the river Savinja. Flowchart of proposed treatment process is shown in Figure 1.

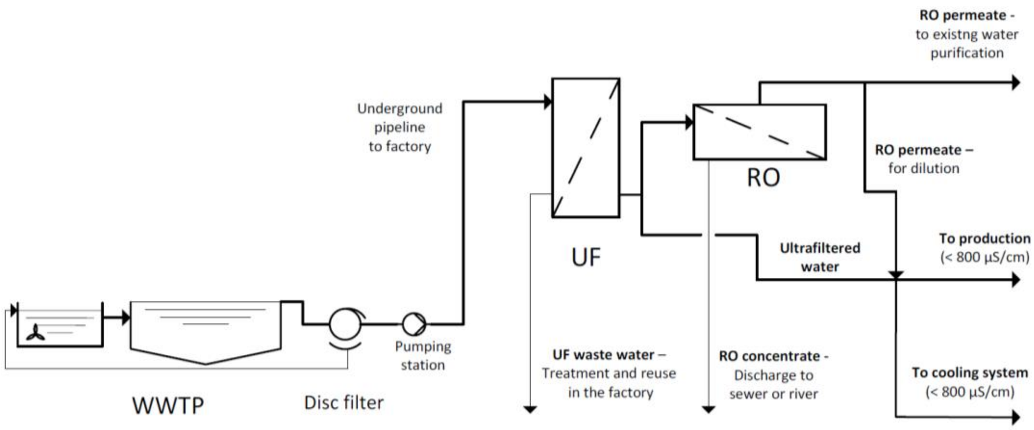

Figure 1. Flowchart of alternative water source for white pigment production

At the Cinkarna site, coagulation would precede ultrafiltration. By adding the coagulant $FeCl_3$, phosphorus and chemical oxygen demand (COD) in the water from WWTP in Tremerje would be coagulated. Both phosphorus and COD would be removed in the form of sludge after coagulation on the ultrafiltration membranes during backwashing. As a measure to increase the efficiency of ultrafiltration, it was envisaged to return the water from membrane backwashing to the existing water treatment system in sedimentation tanks. The purified portion or overflow would then be reused as process water, while the sludge would be pre-filtered with the existing plate filter press and disposed of as waste sludge. According to calculations, this would result in the annual removal of 13,8 tons of phosphorus and COD (calculated on a 100% dry matter basis), which would otherwise be discharged into the river Savinja as an effluent from the WWTP in Tremerje. Assuming a 25% share in sludge represents the removal of phosphorus (approx. 3,5 tons/year).

The water from which suspended particles have been completely removed would then be led to reverse osmosis for demineralization. Currently, demineralized water is obtained using ion exchangers. Due to the regeneration of exchangers, approximately 1250 tons/year of sulphate and 400 tons/year of sodium are currently discharged into the environment as wastewater. This waste load would be mitigated with the use of the new technique. In the case of pumping from the river Hudinja being used only twice a month for six hours, the amount of discharge sodium and sulphate from this source would be reduced by 96 % or even 100 %. However, it must be noted that in the implementation phase of reverse osmosis, unlike the previously mentioned positive impacts on the biological and hydromorphological conditions of watercourses, a negative aspect also arises. Due to the principles of reverse osmosis technology, higher concentrations of substances in the form of concentrate from reverse osmosis will be discharged into the river Hudinja compared to the water from WWTP in Tremerje. With optimal antiscalant dosing, high equipment efficiencies can be expected, with a predicted efficiency of 75 %. Such efficiency means that 75% of the influent water from reverse osmosis exits in the form of a product or permeate, and 25% as waste or concentrate. In our case, this means 56 m^3/h of concentrate.

Technology overview

Membrane technology for the processing of aqueous solutions and water treatment in general has a long history. One the more common membrane processes are ultrafiltration and reverse osmosis which are also foreseen for mentioned solution of wastewater reuse for process water.

Ultrafiltration is a physical membrane filtration process with pore sizes of 0,02 μm (nominal). This allows for the removal of all insoluble substances larger than the pore size, including 99,99 % of viruses and 99,9999 % of bacteria. There are no electrochemical interactions between the membranes and substances in the water, resulting in the water remaining chemically unchanged.

Separation in the module occurs through a sieving mechanism, where particles larger than the membrane pores are excluded. Water flow is established due to pressure difference on both sides of the membranes, passing through a multitude of small capillary tubes whose walls are porous membranes, flowing from the inside of the tube through the wall to the outside. Impurities remain inside the tube. The fact that impurities remain in a defined space is the fundamental advantage of inside-out filtration. It removes undissolved particles, as well as bacteria, parasites, and viruses. The purified water is called permeate (filtrate), which collects in a filtered water reservoir upon exiting the ultrafiltration unit.

Membrane fouling is prevented by performing periodic hydraulic cleaning (HC) (concurrent and countercurrent), which is automatically performed every 30-240 minutes, depending on the quality of the raw water, and lasts up to two minutes. In addition to periodic HC, periodic chemical enhanced backwash (CEB) is performed, where small amounts of chemicals are added to the washing water. Depending on the quality of the incoming water, a solution of sodium hydroxide (up to pH 12) and occasionally sodium hypochlorite (up to 200 ppm) is added to the water as the first phase of chemical cleaning, and hydrochloric acid (up to pH 2) as the second phase of chemical cleaning.

Membrane fouling control is conducted by measuring the pressure difference at the inlet and outlet of each UF branch (Trans Membrane Pressure - TMP) and must not exceed the threshold value. Since TMP depends on the flow through the membranes (calculated as specific flow - flux in $L/m^2/h$) and temperature (which affects the viscosity of water), membrane permeability (flux/TMP × temperature factor) is also calculated for comparison.

To control membrane leakage, an air integrity test is used, measuring the airflow, recommended as occasional control, triggered by the operator as needed or per protocol. The process occurs automatically. During testing, water production is not possible. The air test lasts for half an hour per unit. The frequency of execution depends on the requirement for bacteria and virus removal. In facilities with low risk, it is typically performed only during regular annual servicing.

The introduction of air during membrane cleaning with water and chemicals is used to assist in reducing chemical and water consumption for washing in water sources with higher turbidity.

Reverse osmosis is used to demineralize water and it is a highly effective water purification technology that operates on the principle of osmosis, but in reverse. It utilizes a semi-permeable membrane to remove contaminants, impurities, and particles from water, producing clean, purified water suitable for various applications. In the RO process, pressure in range 8 – 60 bar is applied to the water, forcing it through the membrane, while allowing only pure water molecules to pass through, leaving behind dissolved solids, salts, and other contaminants. To prevent scaling and fouling of the membrane, antiscalants are often added to the feed water. Additionally, crossflow filtration is employed, where a portion of the feed water flows parallel to the membrane surface, carrying away concentrated impurities, while the rest passes through the membrane. This process has yields between 40 % to 90 % purified water, depending on the specific application and operating conditions.

Pilot trial

Around the world, there are well-established working plants for the post-treatment of treated municipal wastewater. While we have some experience in membrane treatment of drinking water and production of process water from “fresh” water it is essential to note that treating fresh water differs from treating used water despite of fact, that it was cleaned biologically in well operated municipal WWTP. Therefore, a pilot trial was deemed a proper approach to obtain optimal data for the design, and this approach was agreed upon with the end user.

We have prepared a conceptual project addressing the possibility of capturing wastewater, transporting it to the Cinkarna site, and treating the water to the quality required for the technological process of TiO_2 production. The conceptual project involves cleaning with mechanical pretreatment, ultrafiltration, and reverse osmosis. To confirm this technology, a pilot plant for testing was installed at the WWTP in Tremerje, in agreement with the water operator in Celje, and has been in operation since early April 2023. The anticipated monitoring period is one year. The pilot device in container, as shown in figure 2, includes both envisioned stages of preparation:

- ultrafiltration with a single membrane module with a surface area of 64 m^2, like those used for filtering drinking water (capillary membranes with an inner diameter of 0,8 mm),
- reverse osmosis with three membrane 4-inch modules, in practice, larger systems typically use eight-inch modules, but the operating conditions remain the same.

Figure 2. Container with pilot device at WWTP Tremerje

The inlet water for the UF unit shown in the figure 3 is the effluent from the WWTP in Tremerje. It is pumped through an internal hydrant system, which is supplied from the effluent channel of the WWTP without additional filtration. The theoretically dimensioned flow rate through UF is 3,8 m^3/h, equivalent to a specific flow rate of 60 $L/m^2/h$. The unit has been operating steadily at 50 $L/m^2/h$ for four months. In addition to stable operation, the main challenges of ultrafiltration include preventing biofouling, adequate coagulation for organic matter removal, and phosphorus removal.

Figure 3. Pilot ultrafiltration unit with one UF membrane module

We prevent membrane biofouling with periodic CEB, where in the first stage we add sodium hypochlorite at a dose of 200 ppm Cl_2.

We coagulate organic matter by adding Fe^{3+} in the form of $FeCl_3$ solution. A sufficient reaction time is ensured. COD at the inlet of the pilot device mostly ranges between 15 mg/L and 25 mg/L. Sometimes it jumps over 30 mg/L. At the outlet of UF, we achieve values between 10 mg/L and 15 mg/L. Sometimes it jumps to 25 mg/L. Fe^{3+} is dosed based on spectrophotometric absorbance measurement at 254 nm, which detects organic substances. Overdosing Fe^{3+} is undesirable due to the RO that follows after UF.

At the inlet of the pilot device, water contains around 1,1 mg/L of phosphorus, sometimes even up to 1,8 mg/L. Phosphorus is precipitated before UF and removed by adding Fe^{3+}, same as organic substances. We have received clear guidelines from the membrane manufacturer for the necessary amounts of Fe^{3+} based on the concentration of phosphorus. Since the concentration of both pollutants removed by adding Fe^{3+} ions fluctuates, it is difficult to predict the appropriate dosing. An additional problem is that currently the device is not equipped with process measurement of phosphorus concentration. The desired concentration of phosphorus at the outlet of UF is $<0,5$ mg/L. This limit allows discharge of RO concentrate into the watercourse (the limit is 2,0 mg/l), where the concentration increases fourfold at an efficiency of 75 %.

A portion of the water filtered through UF is demineralized on the reverse osmosis membranes at a flow rate of 0,8 m^3/h. Currently, there are no issues with the quality of the RO permeate, but the challenge lies in the stability of operation or membrane fouling. The inlet conductivity fluctuates between 400 and 1200 μS/cm. It is expected to reach up to 1600 μS/cm during periods of intensive road salting. The fluctuation in inlet conductivity presents a challenge in monitoring the membrane condition, as normalization procedures sometimes lack precision. So far, we have conducted one successful CIP wash after five weeks of membrane operation. It is desirable to extend the period between CIP washes as much as possible.

Another challenge in treating the treated municipal wastewater is mechanical filtration before UF. UF modules with an internal capillary diameter of 0,8 mm require mechanical filtration of 300 μm. We initially used a mesh pressure filter commonly used in drinking water treatment, but it became clogged and could not be cleaned. For now, we have replaced the filter with a RoDisc filter, which operates with a low pressure drop (up to 20 cm of water column). Such a filter works smoothly at low flows and after a full test we determined it is suitable for pre-filtration of this wastewater.

Conclusion

The use of treated wastewater from the WWTP in Tremerje as process water in the production of titanium dioxide will greatly relieve the river Hudinja and enable continuous production of titanium dioxide even during dry periods. An additional environmental benefit will be the reduction of sludge, phosphorus, and sulphate discharge. Preparation with membrane technology (UF followed up with RO) ensures adequate water quality. The initial results of the pilot test indicate the viability of the technology. Improved operational stability is expected in both stages of preparation. Improvement in the removal of organic matter and phosphorus on UF is necessary. Mechanical pre-filtration is an important stage in preparation and RoDisc has been deemed to be a suitable solution.