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Reuse and recycling of secondary effluents in refineries employing advanced multi-barrier systems

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Abstract In this paper the reclamation and reuse of municipal secondary effluents, as well as the reclamation and recycling of refinery secondary effluents, are technically and economically evaluated. It is shown that both practices are feasible and sustainable, and that the reclamation costs depend largely on specific circumstances such as legal requirements, price policy, reuse application, raw water composition, etc. The reclaimed water is reused, or respectively recycled, as boiler make-up. Therefore both reclamation plants employ advanced multi-barrier systems including ultra-filtration and reverse osmosis. The employed processes have shown excellent performance with regard to the removal of critical parameters such as silica. For example, this parameter was reduced from 13 mg/l in the raw water to 7 µg/l in the boiler make-up.
Keywords Water recycling, water reuse, reclamation of secondary effluents, ultra-filtration, reverse osmosis, reclamation costs

INTRODUCTION

Basically there are two resources available for industrial water reuse and recycling. The first is comprised by municipal secondary effluents and the second by own (in-house) effluents from industrial processes. Which of these two options is the most feasible depends upon several factors such as water management policy and legislation, price policy (e.g. price of fresh water from municipal networks), the hydrological situation (degree of water stress), the availability of proper recipients, pollutant concentrations in the reclamation plant inlet, reuse/recycling applications, etc. Hespanhol (2008) discusses the two aforementioned industrial reuse options in a survey for the Brazilian State of Sao Paulo and comes to the conclusion that the reclaiming and recycling of in-house effluent is the preferable option due to the price policy of the public water suppliers. Further, he concludes that the dissemination of water reuse in Brazil can only be achieved through a strong institutional decision, followed by the enactment of comprehensive federal legislation. In China, which especially in its northern provinces, has far greater water stress, legislation is already more advanced. In this context, national water conservation policy prescribes that large industrial consumers have to reuse municipal secondary effluents. For example in Baotou (Inner Mongolia) the Baotou Donghua Power Plant is re-using reclaimed municipal secondary effluent as make-up water for its cooling water circuit, in order to both comply with the national water conservation policy (NDRC 2005) and to save costs for fresh water from the municipal network. The water is reclaimed and sold by a private company to the power plant. As the fresh water from the municipal network is much more expensive than reclaimed water, the power plant achieves considerable savings (Lahnsteiner 2007). In many cases, industry has to use both resources (in-house effluents and secondary municipal effluents) in its water management, especially when no other sources (ground and surface water) are available and reclaimed water from public sources is cheaper than fresh water from the public network. In this context the main objective of this paper is to present, discuss and compare two industrial case studies, i.e. the reclamation and reuse of secondary municipal effluent, and the reclamation and recycling of secondary industrial effluent (in-house effluent). Each of the case studies relates to a refinery.

METHODOLOGY

In both cases, advanced multi-barrier systems have been employed in order to meet the stringent quality requirements for the reuse, or respectively, recycling as boiler make-up water. Both reclamation plants are located in India, VA TECH WABAG India having been commissioned with their construction, operation and surveillance. The following represents a description of the two cases.

The Panipat reclamation plant for the recycling of industrial effluent as boiler make-up

The first case is located in Panipat City (Haryana State), 90 km northwest of Delhi. Annual precipitation totals approx. 500 mm, but over 70 % of this rainfall occurs during the monsoon months of July to September. Nevertheless, there is practically no water shortage in the Panipat region due to the availability of sufficient surface water (river water). The Panipat Refinery is located in farmland, which is irrigated by the Yamuna River. The Indian Oil Corporation Ltd. (IOCL) Panipat had to build a wastewater recycling plant as a response to the demand of the environmental authorities for zero discharge (Lahnsteiner 2007). This request was made due to the fact that no proper recipient is available in the Panipat area. Therefore, this plant has been installed to meet stringent governmental regulations and prevent the pollution of nearby water bodies and not because of the unavailability of water for industrial use. Water losses during the refining processes are compensated for by the use of fresh water from the Yamuna River. The reclamation of secondary municipal effluent was not considered due to both the availability of sufficient volumes of fresh water and the distance between the municipal sewage treatment plant and the refinery. The plant, which treats both secondary refinery effluents and different refinery/petrochemical process effluents (Tab.1), was commissioned at the end of 2006. A second, identical plant (repeat order for the same process and capacity) for naphtha cracker secondary effluent (along with cooling water blow-down and demineralisation regenerates) will be started up in July 2009 and in addition, evaporation and crystallisation for both Panipat reclamation plants will soon be on an operational footing, which meet the zero discharge target requested by the authorities.

Table 1. Panipat Refinery - wastewater flows

Panipat wastewater flows	
Secondary refinery effluent – ETP I	400 m³/h
Secondary refinery effluent – ETP II[1)]	300 m³/h
PX[2)]/PTA[3)] effluent including cooling tower blow-down	272 m³/h
Demineralisation regenerate from Panipat Refinery I	60 m³/h
Demineralisation regenerate from Panipat Refinery II[1)]	140 m³/h
Cooling tower blow-down from in-house Power Plant I	18 m³/h
Cooling tower blow-down from in-house Power Plant II[1)]	50 m³/h
Total wastewater	1,240 m³/h

[1)] Extension of refinery [2)] PX…..Para-Xylene [3)] PTA…..Purified Terephtalic Acid

The major design parameters of the blended wastewater flow (inlet to the reclamation plant) are T = 15 – 35°C, 150 mg/l COD, 10 mg/l BOD_5, 10 mg/l oil, 1,786 mg/l TDS and 98 mg/l silica. Basically, the reclamation plant (design capacity = 900 m^3/h) incorporates clarification (including silica adsorption on magnesium hydroxide), pressure sand filtration, ultra filtration (UF) and reverse osmosis (RO) phases. The RO permeate is polished by mixed bed ion exchange filters. It is then mainly recycled as boiler make-up water in the refinery power plant (Fig. 1).

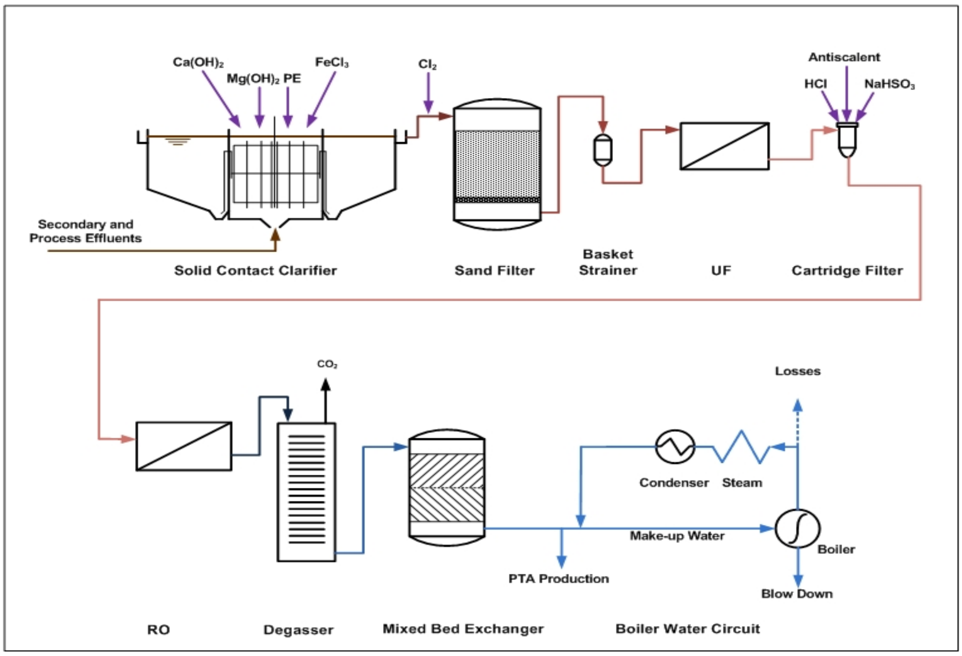

Figure 1. Panipat water reclamation and recycling process diagram

The Chennai reclamation plant for the reuse of municipal effluent as boiler make-up

The second case is located in Chennai, the capital city of the State of Tamil Nadu. Chennai City does not have perennial water sources. Rainwater is stored in reservoirs and is used for drinking and industrial purposes. The rainy season is restricted to about 45 days per year and average annual precipitation totals 1,200 mm to 1,300 mm. If the rains fail, the city mainly uses ground water. Owing to the fact that, especially during droughts, the available water sources are insufficient to meet drinking water demand, industry has to use alternative options such as the reclamation of secondary treated sewage and seawater desalination. The extraction of groundwater for industrial purposes is no longer permitted. At present, the sewage generated in Chennai City is being treated in nine treatment plants with a total capacity of 486,000 m^3/d. The Kodungaiyur STP is the largest plant (capacity: 110,000 m^3/d) and is located in the vicinity of the Manali industrial area. From this STP, 36,000 m^3/d of secondary effluent are supplied by the Chennai Metropolitan Water Supply and Sewerage Board (CMWSSB) to the following industries at a cost of 9.2 INR/m^3 (0.13 EUR/m^3): 23,000 m^3/d to Chennai Petroleum Corporation Ltd (CPCL), 11,500 m^3/d to Madras Fertilizer Ltd and 1,500 m^3/d to Manali Petro Chemicals. The 23,000 m^3/d provided to the CPCL Refinery are reused for cooling, irrigation and for boiler make-up water production. The refinery also recycles in-house effluents (9,600 m^3/d), which are utilised for the production of boiler make-up water and as cooling make-up. In total, 15,600 m^3/d are reused/recycled as boiler make-up and 5,760 m^3/d as cooling make-up. The losses caused by evaporation (e.g. in cooling) and irrigation, etc. have to be covered by the aforementioned amount of secondary effluent, fresh water from the public network (7,200 m^3/d for 62 INR/m^3 equivalent to 0.89 EUR/m^3) and in future, by seawater desalination. CPCL is dependent upon the use of alternative resources (municipal secondary effluent and seawater) as whenever there is a drought the authorities first cut off the water supplied to industry from the public network.

As noted above, the raw water source for industrial reuse at the CPCL refinery comprises secondary effluent from the Chennai Kodungaiyur Wastewater Treatment Plant, which employs an activated sludge process for carbon removal. The main design parameters of the secondary effluent (inlet to the reclamation plant) are T = 30 – 45°C, 208 mg/l COD, 82 mg/l BOD_5, 6.6 mg/l NH_4, 100 mg/l TSS, 18 mg/l PO_4, 1,900 mg/l TDS and 11 mg/l silica. The reclamation plant (design capacity = 475 m^3/h) is located adjacent to the refinery and is approximately seven kilometres from the Kodungaiyur STP. Basically it consists of biological treatment for nitrification and de-nitrification (sequencing batch reactors), coagulation, precipitation, flocculation, clarification, chlorination (disinfection, removal of residual ammonium), two-stage filtration (pressure sand filtration and multi-media filtration), ultra-filtration and reverse osmosis. The major part of the RO permeate is polished by mixed bed ion exchange filters located in the refinery and reused as boiler make-up water in the refinery power plant (Fig.2). The RO permeate is additionally reused as cooling make-up water. The plant was commissioned at the beginning of 2007.

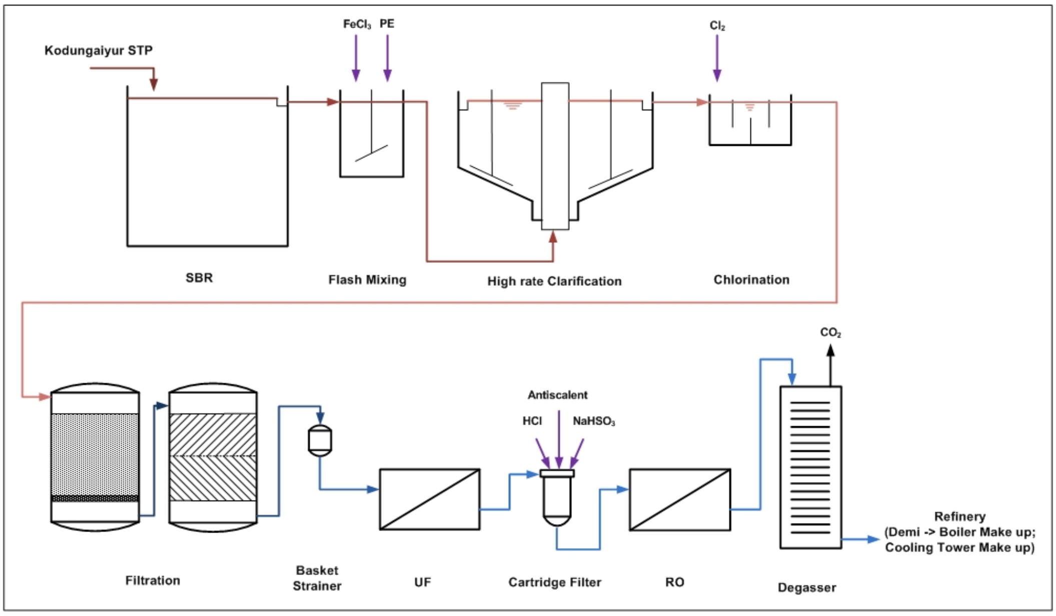

Figure 2. Chennai water reclamation and reuse process diagram

Membrane process steps of both plants

The same UF and RO membranes are employed in both plants. The ultra-filtration process steps consist of pressure-driven, inside-out, hollow fibre systems (Tab.2). Both systems are operated in a dead-end mode. The major task of the UF is the reduction of the silt density index (SDI) and the removal of turbidity, as well as suspended and colloidal matter, in order to minimise fouling of the downstream reverse osmosis process step. The UF membrane fouling caused by the aforementioned impurities is removed by regular backwashing with permeate. The backwash is enhanced once a day in both UF plants using chemicals (chemical enhanced backwash - CEB with caustic NaOCl and HCl). As can be seen in Table 2 the Panipat UF was designed with a gross flux of 54 $l/m^2 \cdot h$, whereas in the Chennai UF a 22% higher gross flux of 66 $l/m^2 \cdot h$ is employed. The Panipat UF was designed relatively conservatively, as this industrial application (secondary refinery effluent) was not piloted prior to full-scale realisation. Furthermore, the subject membrane was employed for the first time in this kind of wastewater and therefore the client requested a safety margin. A degree of full-scale experience with regard to secondary municipal effluent was already available and therefore a higher flux was applied. The resulting membrane areas are 16,416 m^2 for the Panipat UF and 7,200 m^2 for the Chennai UF.

In the Panipat reclamation plant, a two-pass RO system is employed in combination with a brine concentrator. The UF permeate is fed to RO pass I (three internal stages; low fouling composite membranes). The RO I permeate is further desalinated in RO pass II (three internal stages; low fouling composite membranes) and the RO I reject is fed to the brine concentrator (two internal stages; seawater membranes). The brine concentrator permeate is recycled to RO II. The recovery rate accomplished by this process configuration is 90 %. The RO II permeate is degassed and, in order to allow the further removal of dissolved solids, polished in mixed bed ion-exchangers containing strong acid cat-ion and strong base an-ion resins mixed in a single vessel. As previously mentioned, the authorities have stipulated that the refinery has to achieve zero discharge. However, temporarily the refinery has permission to dispose of the liquid waste produced in the reclamation process (R.O. brine). Currently the brine is blended with fire-fighting water, or used for irrigation (blended with low TDS water) of the free land along the refinery boundaries in order to provide green spaces around the refinery. Nonetheless, this official request will soon be met through the installation and operation of evaporation and crystallisation.

Table 2. Ultra-filtration design parameters

Membrane parameters	**Panipat - IOCL**	**Chennai - CPCL**
Membrane material	Hollow fiber polyether-sulfone	Hollow fiber polyether-sulfone
Average feed flow [m^3/h]	894	475
Design gross flux [l/m^2·h]	54	66
Design permeate flow [m^3/h]	760	428
Design net flux [l/m^2·h]	46	59
Recovery [%]	85	90
Skids	6 (+ 1 standby)	3 (+ 1 standby)
Pressure vessels/skid	18	15
Vessels total	108	45
Elements/vessel	4	4
Elements total	432	180
Membrane area/element [m^2]	38	40
Membrane area [m^2]	16,416	7,200

Due to the lower design TDS concentration, in the Chennai plant a single-pass RO system is utilised in combination with a brine concentrator. The UF permeate is fed to the first RO (two internal stages; low fouling composite membranes) and the concentrate of this stage is further treated in the brine concentrator (single internal stage; seawater membranes). The recovery rate accomplished by this process configuration is 90 %. Permeate from the two RO stages is blended in order to produce the required TDS concentration (80 mg/l). The blended permeate is degassed and pumped to the refinery for demineralisation and direct reuse as cooling make-up water. The brine from the Chennai RO is mixed with treated, low-TDS refinery effluent and reused in the fire-fighting water system and for horticulture.

RESULTS AND DISCUSSION

Figure 3 shows a typical diagram with regard to the major parameters (monthly average values of January 2009) TDS, silica and COD for the Panipat Reclamation Plant. TDS is mainly reduced in the reverse osmosis process step (from 1,148 to 12 mg/l; 99.0 %) and further cut in the mixed bed filter to less than 0.05 mg/l (total removal > 99.996 %). Silica is also mainly removed by RO (from 11.6 mg/l in the UF outlet to 1.4 mg/l in the RO I permeate and to 0.09 mg/l in the RO II permeate; 99.2 % removal in both RO stages) and is then reduced further to 0.007 mg/l (7 µg/l; total removal 99.94 %) in the mixed bed ion exchanger. This represents excellent removal efficiency, as 20 µg/l is the specified limit for boiler make-up water in various power plant guidelines such as VGB 2006. Colloidal silica is zero, as it is completely removed in the reverse osmosis stages. In the pre-treatment steps (coagulation/sedimentation, sand filtration), COD is reduced from 69 mg/l to 48 mg/l (30.4 %), it is then cut by a further 5 mg/l (from 48 to 43 mg/l) during UF (10.4 %) and from 43 to 0 mg/l in the course of reverse osmosis.

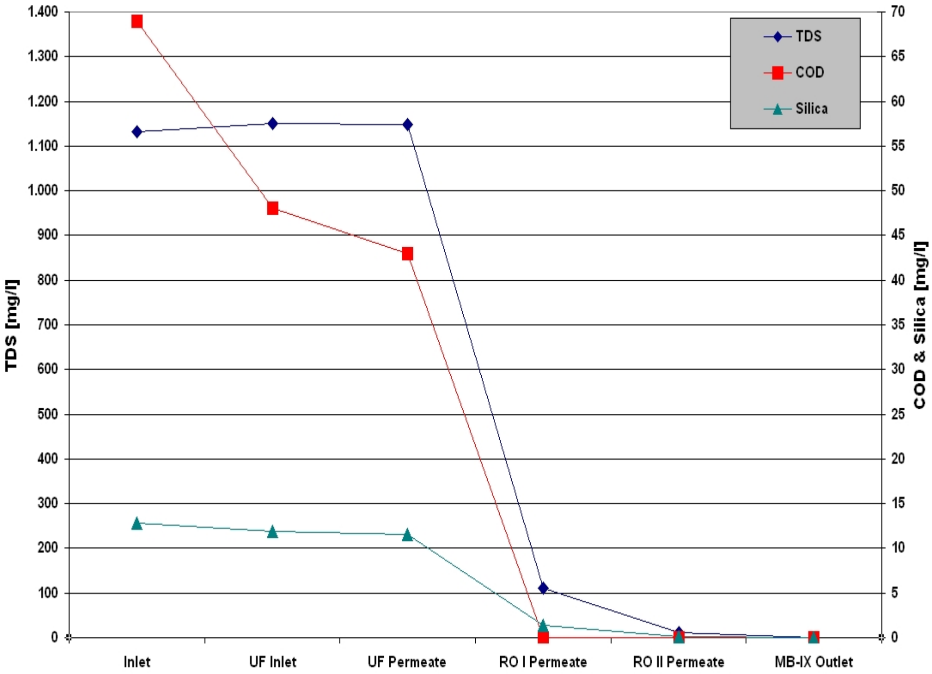

Figure 3. Removal of TDS, COD and silica – Panipat reclamation plant

The aforementioned COD reduction in the UF (5 mg/l or 10 %) means that approximately the same amount can be attributed to both the high molecular fraction of the UF inlet (origin: refinery/petrochemical effluent; assumed macro-molecules: polyesters on terephtalic acid basis, etc.) and hydrophobic compounds, which are adsorbed on the polyether-sulfone membrane. The UF design gross flux of 54 $l/m^2 \cdot h$ and a COD reduction of 5 mg/l, result in a specific COD removal rate of 270 mg $COD/m^2 \cdot h$, which can be regarded as moderate. Organic fouling can be removed relatively easily by CEB with caustic NaOCl (e.g. by saponification of esters), at least during regular operation. Since start-up in December 2006 the Panipat UF has been operated at design flux (and a little above). SDI outlet values have generally been within a range of 2.1 to 2.4 (inlet SDI is 6.7; the design outlet value is 3.0) and the turbidity values have been less than 0.1 NTU (limit of detection). No membranes have required exchanged thus far. The integrity tests showed that to date there have been only a few fibre breakages (e.g. in skid G: 36 in 72 membrane elements, i.e. 0.025 ‰ fibre breakages per year; December 2008). Figure 4 shows normalised (20°C) permeability values after 6 (May 2007) and 18 months (May 2008) of operation. As can be seen in this figure, which is representative for the first 24 months of plant operation, there is practically no difference in the permeability values after the mentioned periods. This means that a stable filtration performance has been accomplished in the first two years. However, after 26 months of operation, a permeability loss of approximately 25 % was observed. The main reason is that due to the request of the refinery, 50 - 100 m^3/h effluent from the Panipat Effluent Treatment Plant III (ETP III) has been additionally treated in the reclamation plant. This effluent contains increased COD concentrations in the 200 - 300 mg/l range, which fouled the UF membranes. The fouling has been removed by more frequent and intensified CEBs. The original permeability values however could not be recovered completely (as mentioned above: 25% permeability loss).

The reclaimed water is used mainly as boiler make-up water and additionally as process water for the production of purified terephtalic acid (PTA), which is employed in the textile industry as a substitute for dimethyl terephthalate (DMT). The manufacture of PTA demands high-quality water, e.g. zero colloidial silica and low TOC for the preservation of the catalyst, which is needed for the chemical reaction, and practically absolute softened water for the end product quality (textile elasticity).

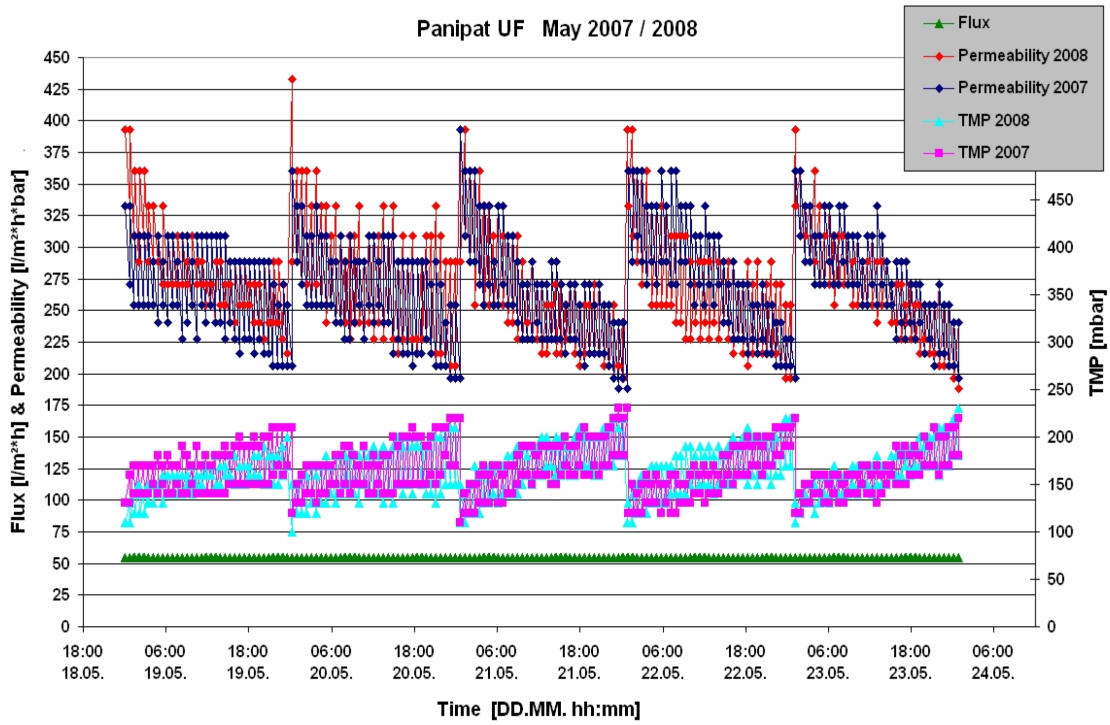

Figure 4. Panipat UF – filtration performance

Figure 5 shows a typical pattern for the removal of the major parameters (monthly average values for September 2008) TDS, COD, NH_4 and silica at the Chennai reclamation plant. TDS is reduced by reverse osmosis from 840 mg/l in the UF permeate to 71 mg/l (91.5 %) in the blended permeate of RO stage I and the brine concentrator (design value: 80 mg/l) whereas silica is cut by RO from 24 mg/l to less than 1 mg/l (> 95.8 %). The COD is lowered by SBR treatment from 89 to 56 mg/l (37 %), in coagulation/sedimentation, in chlorination and filtration from 56 to 38 mg/l (32 %) and from 38 to 28 mg/l in ultra-filtration, i.e. a reduction of 10 mg/l. This means that approximately 26 % of the UF inlet COD is of high molecular nature (origin: secondary municipal effluent; macromolecules: mainly humic acids, proteins, poly-saccharides). The design gross flux of 66 $l/m^2 \cdot h$ and a COD reduction of 10 mg/l result in a specific removal rate of 660 mg $COD/m^2 \cdot h$, which is much higher than in the Panipat UF. However as is the case in the Panipat UF, this organic fouling can be removed relatively easily by CEB with caustic NaOCl.

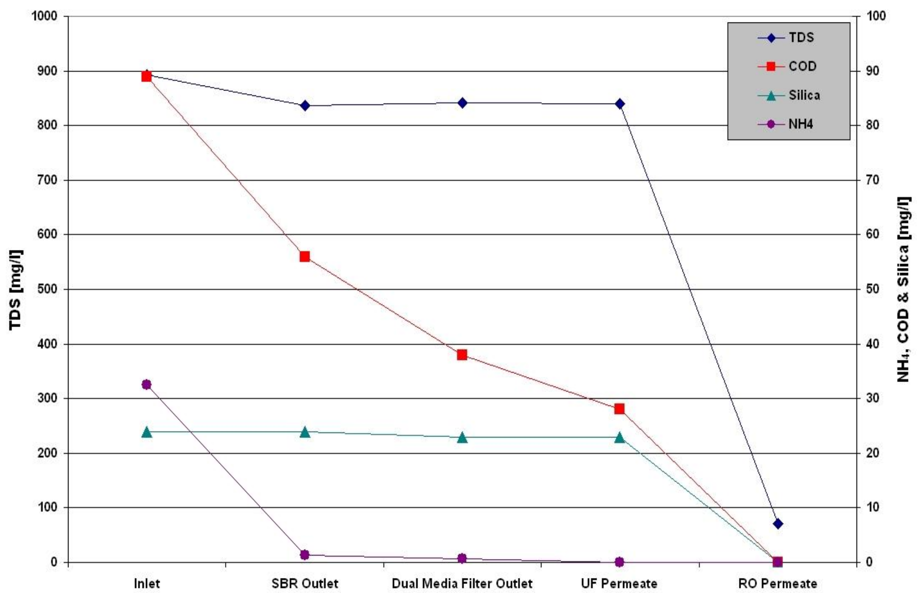

Figure 5. Removal of TDS, COD, NH_4 and silica – Chennai reclamation plant

The Chennai UF was operated with a flux, which was slightly below design (2 - 4%) and so far no membranes have been changed. Generally it can be concluded that the results of the Chennai UF were comparable with that of the Panipat UF during regular operation.

In the Chennai RO some problems occurred due to increased salt passage. As a membrane autopsy has shown, parts of the membranes were damaged by debris, which passed the cartridge filters, and possibly by the oxidation of residual chlorine. This problem was solved by exchanging the damaged membranes (44%). Additionally there were some problems with bio-fouling, which was dealt with by means of intensified chemical cleaning and the use of a biocide.

Operating costs of both reclamation plants

The operating costs of both reclamation plants are presented in Table 3. As can be seen in this table, the reclamation costs (opex + capex) for the production of demineralised water (boiler make-up water) are 0.60 EUR/m^3 for the Panipat plant and 0.67 EUR/m^3 for the Chennai plant. The difference of 0.07 EUR/m^3 (10.4 %) can be mainly explained by the fact that more process steps are employed (SBR, 2nd filtration step) in the Chennai reclamation plant than in the Panipat reclamation plant. As mentioned above, a biological treatment step (SBR) has to be operated for nitrification and de-nitrification, which increases capital and electricity costs (for aeration, additional pumping and mixing) substantially. Moreover, in the Chennai case, the price of the secondary municipal effluent (including opex + capex for the pipeline and the pumps as well as CMWSSB's profit) has to be added to the reclamation costs, which results in total reclamation costs of 0.80 EUR/m^3. In the Panipat case the costs of the refinery effluent treatment pants (ETP I and II; oil removal, coagulation, dissolved air flotation, nitrification and de-nitrification) are excluded from the cost calculation, as effluent treatment is a minimum legal requirement and this resource is already owned by the refinery.

Table 3. Reclamation costs

Costs for boiler make-up water	**Chennai Reclamation Plant Municipal secondary effluent**	**Panipat Reclamation Plant Refinery secondary effluent**
Total Investment [m EUR] [1)]	8.96	12.17
Electro-mechanical Equipment [m EUR]	7.47	9.74
Civil works [m EUR]	1.94	2.43
Produced boiler make-up water [m^3/d]	8,400	14,393
Manpower [EUR/m^3]	0.035	0.024
Chemicals [EUR/m^3]	0.129	0.123
Electrical Power [EUR/m^3]	0.171	0.154
Maintenance & other expenses [EUR/m^3]	0.005	0.005
Operating costs [EUR/m^3]	0.340	0.306
Capital Costs [EUR/m^3] [2)]	0.332	0.295
Reclamation costs for demineralised water [EUR/m^3]	**0.672** [3)]	**0.601** [4)]
Price of secondary effluent	0.132	
Total reclamation costs [EUR/m^3]	**0.804**	**0.601**

[1)]Including price raises indexed in line with annual inflation; [2)]Electro-mechanical equipment: 15 years, 10% interest; civil works: 25 years, 10% interest

[3)]Actual costs for RO permeate + calculated costs for demineralisation in mixed bed ion-exchange filters; [4)]Actual costs for the entire process

The costs for the RO permeates are 0.45 EUR/m^3 in the Panipat case and 0.54 EUR/m^3 in the Chennai case, which is cheaper than seawater desalination for comparable permeate production (8,400 m^3/d).

The installation and operation of the zero discharge facilities in the Panipat case will raise reclamation costs for demineralised water by approximately 0.13 EUR/m^3 (the main energy source consists of waste steam from the refinery power plant) or 22 %. This is a relatively large amount, but it has to be invested in order to protect the surrounding farmland and ultimately the population of the Panipat area. Last, but not least, a cost comparison between boiler make-up water produced from river water and recycled water is provided. In Panipat, boiler make-up water is additionally produced from the Yamuna River water by demineralization. The total specific costs are 0.36 EUR/m^3 (capital cost 0.15 EUR/m^3, operating costs 0.21 EUR/m^3; design TDS: 292 mg/l). These costs exclude the disposal of the regenerates, which are disposed of into the refinery ETP (and finally desalinated in the RO of the reclamation plant), and the price of the raw water (0.04 EUR/m^3), which is subsidized for industrial policy reasons. The cost comparison shows that the use of fresh water (0.36 EUR/m^3; disposal of regenerates and raw water price not included) is just 40 % cheaper than recycling (0.60 EUR/m^3).

CONCLUSIONS

The evaluation of recycling and reuse of secondary effluents in advanced multi-barrier systems shows that these practices are technically and economically feasible. The specific costs greatly depend on factors such as legal requirements, the price policy of public suppliers and the pollutant concentrations in the raw water. The comparison of the two cases analysed, shows that under the aforementioned specific circumstances, the recycling of industrial secondary effluent is cheaper (0.60 EUR/m^3) than the reclamation and reuse of municipal secondary effluent (0.80 EUR/m^3), which in turn is less expensive than the use of freshwater from the municipality (0.89 EUR/m^3). Furthermore, security of supply is guaranteed when municipal secondary effluent is reused, which is especially relevant in water stressed areas such as Chennai. In Chennai there is still considerable potential for the reuse of municipal secondary effluent, as at present only 7 % is reused. The use of fresh water from the public network as a single source is risky for industrial enterprises, as during droughts the industrial supply is the first to be cut off. Finally, it can be concluded that both applications are sustainable due to the saving of freshwater, the protection of recipients and the boost to security of supply.

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