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Petrochemical Industry: Wastewater Treatment For Water Reuse

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Abstract In water and wastewater treatment, the integration of processes is currently employed. Generally, two or three conventional processes are combined with one membrane technology, to maximize the possibilities of water reclamation and reuse. At the present work, a pilot study integrating Electrodialysis Reversal (EDR) and Reverse Osmosis (RO) processes to the treatment of a petrochemical wastewater aiming the water reuse was performed. Before the treatment by EDR-RO, the wastewater had been previously treated by conventional processes (sedimentation + activated sludge + stabilization ponds) on-site in the petrochemical wastewater treatment plant. The RO pilot plant has a spiral-wound polyamide membrane, Dow Filmtec™ BW30-4040, with membrane area of 7.2 m², while the ED pilot plant has 75 ion-selective membrane pairs having a total area of 14.4 m^2 and platinum-coated titanium electrodes. The integrated process EDR-RO provided the recovery of high quality water with conductivity around 6 $\mu S.cm^{-1}$. The removal rates for contaminant were higher than 90% for most parameters monitored. The characteristics of the produced water were compared to the water commonly used at the cooling towers at the industry. The results showed that integrated process EDR-RO can be an alternative for process water production.

Keywords: Wastewater, Hybrid Process, Reverse Osmosis, Electrodialysis Reversal, Reuse

1. Introduction

The current scenario of water scarcity, as well as the reduction in water quality due to pollution of water resources, has been of concern to the industrial sector, especially for the petrochemical industry, which requires high quality water in their production processes (Bayat *et al*. 2015). Given this problem, there is a need to reduce the volume of water taken from the springs and, by reusing wastewater internally, to produce quality water that meets the intended purposes.

The petrochemical industry uses large volumes of water (Padaki *et al*., 2015), for instance, petroleum production and processing facilities use an average of around six barrels of water for each barrel of oil produced (Tom, 2005). The industry assessed in this study consumes an average of 2333 $m^3.h^{-1}$ of water (Hansen, Rodrigues and Aquim, 2016). This volume is mainly used in cooling towers, feeding high-pressure boilers, as process water, as water for fire and as potable water. The highest water consumption occurs in the cooling towers (Wang *et al*, 2014; Walker *et al*, 2013).

Therefore, as the water consumption is high, the amount of wastewater generated is also high, around 700 $m^3.h^{-1}$, presenting a high conductivity, hardness, calcium, chlorides, sulfates, iron, chemical oxygen demand (COD) and suspended solids, among other elements (Hansen, Rodrigues and Aquim, 2016). Thus, conventional treatments are used in order to frame the wastewater in the discharge standards. However, according to Colla *et al*. (2016), conventional treatments are not able to remove the high content of salts, thus impeding the reuse of water in the production processes. In this regard, separation processes by membranes, such as electrodialysis reversal (EDR) and reverse osmosis (RO) are proposed to recover water. EDR will remove ions from the wastewater by applying an electric current, which promotes the transport of the ions through ion-selective membranes (Tanaka, 2009). On the other hand, RO will retain the contaminant material present in the wastewater through a semipermeable membrane by using pressure as the driving force (Shenvi *et al*., 2015).

In the literature, studies are found that use combined processes to produce industrial process water, Koo, Mohammad and Sujá (2011) applied ultrafiltration (UF) and RO for the treatment of wastewater from a palm oil industry, in order to produce demineralized water to feed the boilers. The authors found that the system reduced the total dissolved solids (TDS) by 95%, the COD by 87% and the hardness by 92%. Petrinic *et al*. (2015) also applied UF followed by RO to the treatment of a wastewater from a metal finishing industry aiming reuse the wastewater in the production process. The results presented above 91% of removal efficiency for the evaluated parameters. The total suspended solids (TSS), sulfate, COD and biochemical oxygen demand (BOD) were removed by 100%.

Bayat *et al*. (2015) investigated the technical feasibility of employing a membrane bioreactor (MBR) to treat wastewater in a petrochemical complex in Iran. The results indicated that the treatment performed by the MBR system was effective and the water could be reused in the production process. Machado and Santiago (2014) applied the electrodialysis reversal technology in the treatment of wastewater generated in a Brazilian oil refinery, aiming water reuse in cooling systems. EDR was efficient in the removal of chlorides and dissolved solids by around 70%.

The objective of this research is to employ the EDR-RO hybrid process in the treatment of a wastewater from a petrochemical industry located in southern Brazil, in order to obtain a process water that meets the quality standards for reuse in cooling towers.

2. Materials and Methods

2.1. Wastewater characterization

The wastewater used in the experiments was collected in a petrochemical industry, located in southern Brazil, after tertiary treatment. In this industry, the conventional wastewater treatment plant (CWWTP) has primary (physical and chemical), secondary (biological – extended aeration activated sludge) and tertiary (eight serial stabilization ponds) treatments. The wastewater was collected at the output of the last pond.

2.2. *EDR – RO Hybrid System*

The Figure 1 shows the EDR-RO hybrid system, as well as the pretreatment applied to the wastewater.

The wastewater was subjected to a pretreatment with sand filter (SF) and activated carbon filter (ACF) prior to the EDR-RO hybrid process in order to remove coarse material and avoid damage to the EDR and RO equipments. The sand filter is filled with sand with an average particle size of 0.61 to 1.23 mm. The activated carbon filter has an average particle size from 0.71 to 2 mm.

An electrodialysis reversal pilot system was used for the assays, model EDR 2.0 - 300 1E 1s 2e, Hidrodex®, which has two stacks made of four platinized titanium electrodes at the tips, 75 anionic membranes, Hidrodex® HDX 200, and 75 cationic membranes, Hidrodex® HDX 100, alternated and separated by polypropylene spacers, totaling 14.4 m² of membrane area. The process conditions were: electrical potential of 250 V, dilute flow rate at 600 $L.h^{-1}$ and concentrate flow rate maintained at 200 $L.h^{-1}$, and operated in series (with 150 membranes). Electrode polarities are changed and dilute and concentrated channels are cleaned every 15 minutes. By using this mechanism it is possible to control fouling of the membranes, reducing the number of interruptions for maintenance.

The dilute from EDR was then treated in a RO pilot system manufactured by PAM Membranas Seletivas. The system consists of a spiral polyamide membrane module, model Dow Filmtec™ BW30-4040, with membrane area of 7.2 m^2. Assays were performed with a pressure of 8 bar and with permeate flow rate at 348 $L.h^{-1}$ and reject flow rate of 300 $L.h^{-1}$. Samples were collected at the end of the tests for the physical-chemical analysis of calcium, iron, magnesium, hardness, chlorides, sulfate, total suspended solids (TSS), total solids, total dissolved solids (TDS), turbidity COD, color, conductivity, nitrate, sodium alkalinity, and coliforms (total and fecal).

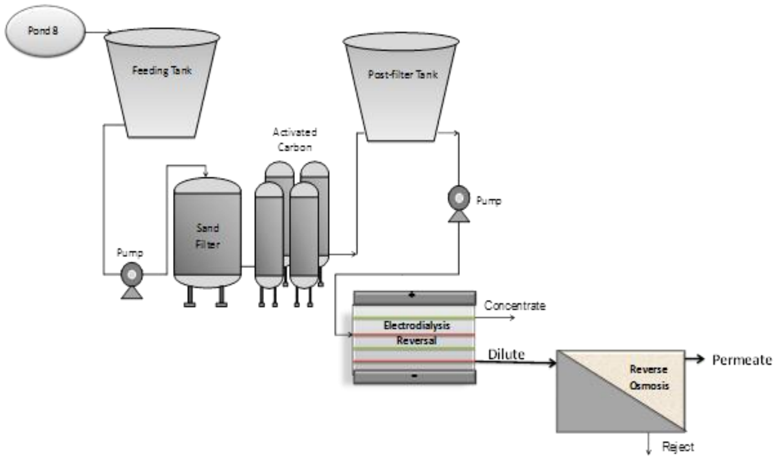

Figure 1. Flowchart of the filtration system and hybrid processes (Pond 8, Feeding Tank, Pumps, Sand Filter, Activated Carbon Filters, Post-filter Tank, Electrodialysis Reversal and Reverse Osmosis)

Table 1. Analytical monitoring of the parameters. EDR operating conditions: electric potential of 250 V, dilute flow rate of 600 $L.h^{-1}$ and concentrate flow rate of 200 $L.h^{-1}$. RO operating conditions: 8 bar, permeate flow rate of 348 $L.h^{-1}$ and reject flow rate of 300 $L.h^{-1}$.

Parameter	Feed (CWWTP)	Post-filter (SF+ACF)	EDR Dilute	Effic. EDR (%)	EDR-RO	Effic. EDR-RO (%)	Limit cooling towers
COD (mg $O_2.L^{-1}$)	26.00	21.19	10.22	51.77	<0.5	97.64	3.50
Color (Pt-Co)	111.0	80.57	54.50	32.36	0	100	n.e
Turbidity (NTU)	34.61	29.57	15.50	47.58	0.10	99.66	1.00
TSS ($mg.L^{-1}$)	36.18	23.94	21.80	8.94	<1.0	95.82	2.00
Total Coliforms (MPN/100 mL)	2.4 $x10^3$	2.4 $x10^3$	1.4 $x10^3$	41.67	Absent	100	n.e
Fecal Coliforms (MPN/100 mL)	7.5 $x10^0$	6.9 $x10^0$	Absent	100.0	Absent	100	n.e
Chlorides ($mg.L^{-1}$)	83.65	81.29	7.52	90.75	0.21	99.74	22.00
Alkalinity ($mg.L^{-1}$)	119.3	101.8	2.80	97.25	1.50	98.53	26.00
Calcium ($mg.L^{-1}$)	68.00	67.33	3.60	94.65	3.20	95.25	30.00
Magnesium ($mg.L^{-1}$)	32.33	31.32	1.03	96.71	0.45	98.56	0.50
Sulfate ($mg.L^{-1}$)	427.0	421.1	56.98	86.47	<0.07	99.98	22.00
Conductivity ($\mu S.cm^{-1}$)	1220	1215	233.6	80.77	6.08	99.50	165.0
Hardness ($mg.L^{-1}$)	100.3	98.65	12.70	87.13	<0.5	99.49	30.00
Nitrate ($mg.L^{-1}$)	0.59	0.59	0.08	86.44	0.01	98.31	n.e
Total solids ($mg.L^{-1}$)	1200	988.0	190.7	80.70	137.5	86.08	n.e
TDS ($mg.L^{-1}$)	1148	934.0	180.7	80.65	95.00	89.83	n.e
Sodium ($mg.L^{-1}$)	230.0	227.0	23.98	89.44	5.25	97.69	n.e
Iron ($mg.L^{-1}$)	0.93	0.64	0.34	46.88	0.01	98.44	0.10
pH	7.37	7.40	3.60	-	5.55	-	7.0-8.0

(<) limit of detection

Limits for the cooling towers set by the assessed industry

3. Results and Discussion

Table 1 shows the characteristics of the feed and wastewater after each treatment. All values were compared to the concentration limits set for the quality of the water to be used on cooling towers.

3.1. Post-filter (SF+ACF)

According to Henthorne and Boysen (2015), the filters (SF + ACF) have the purpose of removing the largest particles, thus avoiding damage to the equipments as well as of minimizing the incidence of fouling, biofouling or scaling in membranes. After the pretreatment, according to Table 1, it could be verified a higher removal rate for suspended solids, color and turbidity, which presented, respectively, a removal of 34%, 27% and 14%.

3.2. EDR test results

Notably, EDR performed well in removing the ions, as chloride salts, calcium and magnesium were extracted by over 90%. For sulfate, conductivity, hardness, nitrate, phosphate, total solids (TS), total dissolved solids (TDS) and sodium, the removal efficiency was above 80%. Iron was the only parameter that presented a lower efficiency. Although removals were higher for conductivity and sulfate, neither met the set standards for cooling towers. In addition, other parameters such as COD, TSS, iron, magnesium, pH and turbidity also exceeded the limits set by the sector. The removal efficiencies obtained in this study were similar to the results achieved by Machado and Santiago (2014), who also applied EDR to wastewater treatment, obtaining a removal efficiency of 90% for chlorides, 88% for TDS, 87% for conductivity, 83% for alkalinity, 60% for hardness, 92% for calcium, 57% for color and 85% for the sulfate. Treated water was recovered by 82%.

Goodmam *et al*. (2013) applied electrodialysis to the tertiary wastewater treatment, with the goal of producing high quality water for reuse in irrigation. The assessed ions and the electrical conductivity of the wastewater were reduced on average by 75%.

3.3. EDR – RO hybrid system

The removal rate obtained by using the hybrid system (EDR-RO) was greater than 95% for most of the parameters, as shown in Table 1. The calculations were based on the post-filter wastewater values. As to the chloride parameter, the removal efficiency was 99.74%. This result is in accordance to the specifications for cooling towers, since the parameters have concentrations lower than 0.21 $mg.L^{-1}$.

It was registered that magnesium removal reached a 98.56% of efficiency, while iron had it at 98.44%. Although these parameters are strictly controlled by the petrochemical industry, with high-quality criteria for water reuse in cooling towers, the established limits (0.50 $mg.L^{-1}$ for magnesium and 0.10 $mg.L^{-1}$ for iron) were attended, reaching concentrations as low as 0.45 $mg.L^{-1}$ and 0.01 $mg.L^{-1}$, for magnesium and iron, respectively. In addition, it must be highlighted that calcium, magnesium and iron parameters need to be very controlled, since these cations excess promotes a scale buildup inside the pipes, bringing damages to the entire system (Malakootian *et al*., 2010, Panigrahi and Ganapathysubramanian, 2015).

In regards to the conductivity and the TDS parameters, the removal rates were 99.50% and 89.83%, respectively. According to Suarez, Fidalgo and Riera (2014), these two parameters are directly related as both indicate the amount of dissolved salts. The results for the conductivity parameter meet the threshold specified by the industry. Compared to the experiment conducted by Koo, Mohammad and Sujá (2011), who applied a hybrid process of UF and RO to recover the wastewater of a palm oil industry in order to use it as demineralized water to feed boilers. The results showed a removal efficiency for TDS of 95.5% or greater compared to this experiment.

The chemical oxygen demand (COD) and coliforms (total and fecal) were removed by 97.64% and 100%, respectively. These parameters are in accordance with the quality specifications for reuse in cooling towers. Notably, organic matter must be controlled, since it cannot only cause an increase in the concentration of micro-organisms but their presence also leads to the growth of biofilms on the surface that results in corrosion in the system (Panigrahi and Ganapathysubramanian, 2015).

The values found for pH, as shown in Table 1, are below the threshold. Due to this fact, an adjustment is necessary prior to the reuse of industrial water in the production process. The pH control should be very strict, since a lower pH than the recommended may cause corrosion in the pipes, while a high pH can increase the potential for the formation of scales (Koo, Mohammad and Sujá, 2011).

The effectiveness in reducing turbidity and color parameters was of 99.66% and 100%, which is consistent with the thresholds for cooling towers, considering its main causes to be the presence of suspended solids (silt, clay, silica, colloids) and organic and inorganic matter (Al-Yaseri, Morgan and Retzlaff, 2013).

Finally, considering the proposal to apply the EDR-RO hybrid process in order to analyze the feasibility of reusing treated wastewaters, it is evident that the combination of techniques is indicated in removing the contaminants. The water treated by EDR-RO hybrid process comply with the criteria established by the petrochemical industry for reuse in cooling towers, except for the pH, which needs to be adjusted.

Conventional processes cannot produce water with a quality level as high as the one from water produced by processes with membranes. In addition, there are already wastewater treatment plants that use membrane processes, such as reverse osmosis, demonstrating the economic viability of these systems. In Brazil, for example, there is the Aquapolo, a company that treats domestic sewage from the metropolitan region of São Paulo - using conventional processes followed by membrane bioreactor and reverse osmosis - to produce water reuse. Currently, the Aquapolo supplies 650 $L.s^{-1}$ of process water to the Petrochemical Complex of the ABC Paulista Region (Ronconi et. al, 2012). Regarding our research, further studies will be performed in larger scale in order to assess the economic feasibility.

The results presented here are consistent with the ones reported by McGovern, Zubair and Lienhard (2014), who stated that hybridization EDR-RO produces a high-quality water. Unfortunately, in the literature, there are still a limited number of studies using the EDR-OR hybrid process.

4. Conclusions

The EDR-RO hybrid process seems to be a promising technology in the production of industrial water due to high removal efficiency of the evaluated parameters. The combined techniques meet industry requirements in a study for the reuse of wastewater from the petrochemical process in cooling towers.

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