



Application of several pretreatment technologies to a wastewater effluent of a petrochemical industry finally treated with reverse osmosis

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ABSTRACT

This work studies the adequacy of different reverse osmosis (RO) pretreatments applied to different petrochemical wastewater effluents. Three effluents from a caprolactam factory were analysed: ion-exchange resin washing effluent (RWE), batch reactor washing effluent and factory outlet effluent. Coagulation–flocculation, microfiltration (MF) and ultrafiltration (UF) were tested as RO pretreatments. Various inorganic coagulants (Aluminium Chloride, Iron (III) Chloride, Aluminium Sulphate and polyaluminium chloride), commercial coagulants (Nophos and ACO) and commercial flocculants (polyacrylamide, CH-30 and active polyfloc) were tested at different dosages and stirring speeds. The highest removal of suspended solids (SS) and the lowest turbidity were obtained for the ion-exchange RWE. Two combinations of coagulants and flocculants were chosen as the most suitable conditions for the coagulation–flocculation process. The ion-exchange RWE was further treated with a combination of MF followed by UF. SS were completely removed and turbidity decreased to 0.136 NTU. The silt density index at 15 min was reduced to 6.41.

Keywords: Petrochemical wastewater; Reverse osmosis pretreatment; Coagulation–flocculation; Ultrafiltration; Microfiltration

1. Introduction

Nowadays, the importance of wastewater reclamation is increasing due to water scarcity. Industries are the largest water consumers. Water consumptions are around 29 m³/ton for paper industries, 100 m³/ton for dyeing industries, 8 m³/ton for sugar industries, etc. [1].

Moreover, industries produce polluted wastewaters with a high content of hazardous chemicals. In the petrochemical industry, polyaromatic hydrocarbons and heterocyclic compounds are very common [2]. These effluents are often treated altogether. However, effluents from different processes can be reclaimed separately. Sometimes, this results in a better reclamation performance. In the present work, effluents from different processes in a petrochemical company were considered to be recovered separately.

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Reverse osmosis (RO) is a suitable technology for wastewater reclamation since it achieves high water quality production. It can be used for petrochemical wastewater reclamation [1–3]. RO water can be used in the factory for cooling, fire extinction, irrigation, etc.

However, the application of RO and other membrane technologies is limited by membrane fouling processes. Fouling causes permeate flux decline, it decreases process efficiency and it increases costs. Several studies attempt to identify what type of compounds produce severe membrane fouling [4]. However, it is sometimes difficult to identify all the pollutants in a wastewater effluent because of the large amount of compounds that are present. Petrochemical effluents present a wide variability in their composition and physicochemical parameters (pH, conductivity and chemical oxygen demand (COD)). Benito-Alcázar et al. [2] confirmed this variability with a similar petrochemical wastewater effluent that used in this work.

When fouling occurs, membrane cleaning becomes necessary. Reversible fouling can be removed with water; however, irreversible fouling can only be removed with chemical agents. Chemicals may damage the membrane surface. Moreover, cleaning and changing membranes is expensive.

Different technologies are used as RO pretreatments to avoid premature membrane fouling. RO membrane manufacturers and other authors recommend a turbidity value lower than 1 NTU and a silt density index at 15 min (SDI₁₅) value lower than 5. However, SDI₁₅ values lower than 3 are preferred for successful operation [5]. In the case of the SDI at 5 min (SDI₅), a value lower than 15 is recommended. These values can be achieved with different pretreatment methods such as chemical oxidation, granular activated carbon (GAC) filtration, chemical coagulation–flocculation, electrocoagulation, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and ultraviolet disinfection. Lora et al. [1] suggested the use of a combined UF and NF pretreatment to reuse wastewater in a petrochemical industry whereas Benito-Alcázar et al. [2] proposed to use GAC filtration. Gare et al. proposed physical and chemical pretreatment methods for RO systems [6].

Coagulation–flocculation is widely used as a pretreatment in industrial wastewater treatments. Garg et al. [7] used coagulation–flocculation with diluted black liquor from a pulp and paper mill, Verma et al. [8] applied it to a petrochemical wastewater, Garrote et al. [9] used it with tannery effluents and Santo et al. [10] used it in a refinery.

The most common coagulants in industrial and municipal wastewater treatment are inorganic compounds (metal salts of aluminium, iron, etc.). In this research, metal salts were used because of their high effectiveness and low cost [7,8,10–16]. Other authors used organic coagulants, such as natural gums, in the pretreatment of petrochemical wastewater [8].

The most widely used flocculants are polyelectrolytes. They can be cationic, anionic or non-ionic. Cationic polymers work well on negatively charged colloids and flocs whilst anionic polymers work well on positively charged particles. Non-ionic polymers perform better than charged polymers on uncharged particles and sludge. The use of one or another flocculant depends on the type of wastewater to be treated. Guida et al. [14] used an anionic polyelectrolyte for municipal wastewater whereas Verma et al. [8] used a cationic polyacrylamide (PAM) for petrochemical wastewater. Rennola et al. [12] employed anionic and cationic PAMs in the vinasses treatment as well as Wang et al. [11] did with a pulp mill wastewater.

Petrochemical industries produce high amounts of polluted wastewaters with hazardous petrochemical compounds. RO technology manages to produce a high-quality water stream suitable for reutilization. Traditionally, contaminated streams are mixed and treated altogether. In this paper, we propose to treat them separately to achieve high pollutant removal efficiencies. We study, several RO pretreatments applied to three different petrochemical effluents from a caprolactam production factory: an ion-exchange resin washing effluent (RWE), a batch reactor washing effluent (BRE) and the factory outlet effluent (OE). This last effluent results from mixing all factory wastewater effluents. In this research, a coagulation–flocculation process was combined with MF and UF to obtain a suitable feed effluent for an RO process. This sequence of coagulation–flocculation and MF or UF has been used in other industrial and municipal wastewater pretreatments [12,16–19]. However, it has not been applied to petrochemical wastewater effluents. There are other membrane technologies, such as NF, but they require more energy consumption than UF or MF. These are only employed when UF is not feasible.

The effectiveness of a coagulation–flocculation process depends on the type of coagulant and flocculant, their concentrations and the pH of the wastewater. Usually, these parameters are empirically determined. The tests performed in this work aim to identify the most effective coagulant and flocculant for each type of effluent within a petrochemical industry. In addition, the best dosages and stirring speeds were determined.

2. Materials and methods

2.1. Effluent characterization

Three wastewater effluents from a caprolactam factory were considered: ion-exchange RWE, BRE and factory OE.

During effluent characterization, conductivity, pH, suspended solids (SS), turbidity and COD were determined. For that purpose, standard methods were used [20–23]. SS were determined using the standard method UNE-EN 872 [20] with cellulose acetate filters with a pore size of 0.45 μm . The turbidity was estimated according to UNE-EN ISO 7027 [21].

The SDI is a parameter that measures membrane fouling potential of an RO feed. It was determined using cellulose acetate filters with a pore size of 0.45 μm and at a pressure of 207 kPa, according to ASTM D4189-07 [22]. The SDI can be estimated as shown in Eq. (1). Where t_i is the initial time in minutes required to collect 500 mL of filtrate and t_f is the final time in minutes required to collect 500 mL of filtrate after test time (t). Test time can be 5, 10 or 15 min.

$$\text{SDI}_t = \frac{\left(1 - \frac{t_i}{t_f}\right) \times 100}{t} \quad (1)$$

2.2. Chemical coagulation and flocculation

Coagulation–flocculation was applied to the three effluents considered in this work. The samples were prefiltered with a filter of 80- μm pore diameter. The best coagulant and flocculant concentrations (Fcs) and stirrer speeds were determined to achieve high removal of SS and turbidity.

Common inorganic coagulants were used e.g. Aluminium Chloride (AlCl_3), Iron (III) Chloride (FeAl_3), Aluminium Sulphate ($\text{Al}_2(\text{SO}_4)_3$) and polyaluminium chloride (PACl), all provided by Panreac (Spain). Verma et al. [8] used aluminium and ferric salts with petrochemical wastewater, Garg et al. [7] did it with diluted black liquor, Guida et al. [14] and Garrote et al. [9] used them with wastewater effluents from a tannery industry and Petrov and Stoichev [17] used them with wastewater effluents from a textile industry. Aluminium chloride was used in a pulp mill industry by Wang et al. [11], aluminium and ferric sulphate in a petroleum refinery by Santo et al. [10], PACl in the treatment of distillery wastewaters (vinasses) by Rennola et al. [12] and other inorganic coagulants in the treatment of municipal wastewater [14–16].

Commercial coagulants (Nophos and active catalytic oxidation coagulant (ACO)) for wastewater

treatment were also tested. Nophos (Dryden Aqua Ltd, Edinburgh) consisted of a dilute solution containing lanthanum salts, EDTA, cerium salts, activated alumina and an UV stabilizer. It acted as a coagulant as well as a flocculant. ACO (Dryden Aqua Ltd, Edinburgh) consisted of a solution containing activated polysilicates and titanium dioxide nanoparticles.

The flocculants tested were PAM, CH-30 and active polyfloc (APF). PAM is a commercial anionic flocculant. CH-30 is a commercial cationic flocculant. APF (Dryden Aqua Ltd, Edinburgh) consisted of a mixture of inorganic coagulants and flocculants such as aluminium salts, EDTA, lanthanum salts and an UV stabilizer. Santo et al. [10] used similar flocculants with a petroleum refinery effluent, such as NALCO 71408, a high molecular weight PAM. Other authors used other anionic and cationic flocculants [8,11,12,14]. These authors studied which were the best coagulants and flocculants for petrochemical industry effluents. They tested different concentrations and stirring speeds in Jar-tests [23].

The coagulation–flocculation process was performed using a standard Jar-test (ASTM D2035-80) [23]. Beakers of 1 L were used in the coagulation step and Imhoff cones of 1 L were used in the flocculation step.

In the coagulation step, the wastewater sample and the coagulant were placed in 1 L beakers with a mechanical mixing device. The flocculant was added to that mixture and it was mixed. The final sample volume was 900 mL. After that it was transferred to a 1 L Imhoff cone. In the final step, the flocs were allowed to settle for 30 min. The parameters analysed were the settled volume and the turbidity of the clarified liquid.

For the inorganic coagulants tested, the range of concentrations tested was from 200 to 700 ppm. This range is commonly employed for wastewater effluents from industries with similar values of SS, turbidity or COD to the ones reported in this study. Petrov and Stoichev [17] used concentrations ranging from 100 to 500 mg/L with a textile wastewater to remove basic colours from water; Garrote et al. [9] tested concentrations in the range of 100–200 ppm with a tannery effluent and Guida et al. [14] used concentrations ranging from 150 to 450 ppm with municipal wastewater. For commercial coagulants, manufacturers recommended dosages of 1–2 mL diluted to 10% [24]. The flocculant content was lower than that of coagulant. The range of dosages used for flocculants is around 2 ppm [10,14]. For commercial flocculants, recommended dosages 0.5–1 mL diluted to 10% were used, according to the manufacturer [24]. In the literature, concentrations around 20 ppm were used for highly polluted effluents [8,11,12].

The stirring speeds tested were in the range of 100–270 rpm for the coagulation step. On the other hand, flocculation required slow mixing. In this case, speeds of 30–50 rpm were used for 15 min. Settling time in Imhoff cones was 30 min. These conditions were similar to those employed by other authors in coagulation–flocculation processes [8,11,13–15].

It is recommended to adjust the solution pH by adding chemicals such as H_2SO_4/HCl and $NaOH$ to optimize the flocculation process [8,11,13,15]. In this work, pH was adjusted to achieve high SS and turbidity removal.

When the best conditions were determined, coagulation–flocculation processes were performed for each effluent. The final clarified effluent was analysed to evaluate its suitability for RO feeding. SS, turbidity, COD and SDI_{15} were measured.

2.3. Microfiltration and ultrafiltration

MF followed by UF was used for the clarified stream of the RWE obtained in the coagulation–flocculation process. MF and UF were performed according to the standard method ASTM D7285-06 [25]. Previously, liable flocs in the clarified stream were removed by prefiltration with a 20- μm filter cartridge.

The experimental set-up for MF and UF was described in detail by Benito-Alcázar et al. [2]. Firstly, MF with two membranes with a pore size of 0.25 μm was carried out. Polyvinylidene fluoride membranes were provided by Orelis Environnement. The MF was performed at a transmembrane pressure (ΔP) of 1.5×10^5 Pa and a cross-flow velocity of 1 m/s. The total volume treated was 23.5 L and the duration of the experiment was 15 h.

UF membranes of polyethersulphone were provided by Orelis Environnement. Their molecular weight cut offs were 100 and 500 kDa. The experiment was performed at a transmembrane pressure of 1.5×10^5 Pa and a cross-flow velocity of 1 m/s. The total volume treated was 19 L and the duration of the experiment was 3.5 h.

Permeate flux was measured and permeate and retentate samples were collected every 0.5 h for sample characterization (conductivity, pH, SS, turbidity, COD and SDI_{15}).

3. Results and discussion

3.1. Effluent characterization

The values of the characterization parameters (average values and range) of the three effluents considered

in this work are shown in Table 1. The characterization results for the three effluents considered in this work are highly different from each other. This suggests that they should be treated separately.

The average turbidity value of the RWE was much lower than that of the other effluents. The same occurred with the values of conductivity and SS. However, in the SS tests, cellulose acetate filters were blocked in few minutes. This suggested that pollutants may form a gel layer structure. RWE was slightly basic on average (pH 8.14). Nevertheless, this effluent had fluctuating pH values. These values were sometimes highly acidic (pH 4). Therefore, the coagulation process was expected to be completely affected, owing to the fact that the effectiveness of coagulants depends on the pH of the wastewater effluent. Besides, RWE presented a heavy organic load (COD = 14,598 mg/L). This was due to the fact that most common pollutants of the RWE were of organic nature (hydrocarbons, lubricating oils and organic fibres).

The BRE presented the highest content in SS (641.33 mg/L) and the greatest turbidity (202.36 NTU). BRE was basic, with an average pH of 11.80.

The OE presented the highest conductivity (5,890 $\mu S/cm$). This suggested a high content of ionic compounds from inorganic nature in the OE. The organic content (COD = 92 mg/L) was very low and it had the best values to release in the sewage system (COD < 125 mg/L) according to regulating agencies prescription [8]. SS and turbidity values were in between RWE and BRE.

It should be noted that SDI_{15} could not be measured for any of the three effluents due to their high fouling potential. Therefore, it was necessary a suitable pretreatment before feeding these effluents to a RO process.

3.2. Determination of the best conditions for the coagulation and flocculation process

3.2.1. Ion-exchange RWE

Experiments using aluminium chloride and iron chloride in combination with CH-30 did not produce any precipitate volume. This may be due to the significant decrease in the pH when the coagulant was added. From a slightly basic pH (8–9), it decreased to a highly acid pH (3–4). In the literature [26], the optimum pH values for aluminium and ferric salts at 25°C with a dissolved solids concentration of 140 mg/L are 5.32 and 8.2, respectively. Hence, RWE conditions were not suitable for these coagulants.

Aluminium sulphate and PACl at different concentrations and stirring speeds were used in combination

with PAM at 2 ppm and different stirring speeds. The results are shown in Table 2. In the case of aluminium sulphate, neither coagulation stirring speeds (C_{ss}) nor flocculation stirring speeds (F_{ss}) had a significant influence on the sedimentation volume in 30 min (V_{30}). The mean value of V_{30} was 43.22 mL and the standard deviation was 0.88. For PACl, the higher the PACl concentration was the greater sedimentation volumes were obtained. Low stirring speeds for flocculation were suitable for this effluent. Delgado et al. [15] evaluated the influence of PACl concentration on turbidity removal for municipal wastewater. They found that the higher the PACl concentration was the greater turbidity removal was achieved (for pH values between 5 and 9). Moreover, PACl removal results were better than those of aluminium sulphate and iron chloride. Santo et al. [10] obtained similar results with a petroleum refinery effluent. An increase of 80 mg/L in the coagulant dosage produced an increase of 40% in the turbidity removal efficiency. Therefore, the best conditions for RWE with common inorganic coagulants and PAM as flocculant were: [PACl] = 700 ppm, C_{ss} = 220 rpm; [PAM] = 2 ppm, F_{ss} = 30 rpm.

The coagulation–flocculation results for commercial coagulants are shown in Table 3. In this case, the low density of flocs prevented them from precipitating. Therefore, turbidity was considered instead of V_{30} . The results show that Nophos did not achieve any turbidity removal (Tables 1 and 3). ACO and APF results were similar at different dosages. Consequently, for ACO and APF the best conditions in terms of turbidity removal were: ACO = 1 mL (diluted to 10%), C_{ss} = 180 rpm and APF = 1 mL (diluted to 10%), F_{ss} = 50 rpm.

3.2.2. Batch reactor washing effluent

Table 4 shows the sedimentation volumes obtained for different stirring speeds, 200 ppm of aluminium sulphate and 2 ppm of PAM. Coagulation and F_{ss} did not have any significant influence on the precipitated volumes. An increase in F_{ss} at the highest C_{ss} tested

Table 2

RWE: sedimentation volume in 30 min (V_{30}) using 2 ppm of PAM as a flocculant

Coagulant	Cc (ppm)	C_{ss} (rpm)	F_{ss} (rpm)	V_{30} (mL)
Al ₂ (SO ₄) ₃	200	100	30	42.67
	200	100	40	42.67
	200	100	50	43
	200	200	30	42.33
	200	200	40	44.33
	200	200	50	44.33
PACl	100	180	50	7.67
	300	180	50	27.67
	500	180	50	48
	700	180	50	78
	700	220	30	88.67
	700	220	50	78

resulted in a slight increase in the precipitated volume. The opposite occurred for the lowest C_{ss} tested. The best conditions were those that corresponded to the lowest energy consumption: [Al₂(SO₄)₃] = 200 ppm, C_{ss} = 100 rpm; [PAM] = 2 ppm, F_{ss} = 30 rpm. However, the flocs were small, they had a low density and their settling speeds were very slow.

3.2.3. Factory OE

For the OE, the coagulation–flocculation results for a flocculant dosage of 2 ppm are shown in Table 5.

It can be observed that at equal coagulant concentrations (C_c), iron chloride sludge volumes were higher than those of aluminium chloride, except in the case of the highest C_c tested. In that case, flocs density was lower and the flocs floated instead of precipitating. Similar results were obtained by Haberkamp et al. [16] and Petrov and Stoichev [17]. They reported lower sedimentation volumes for AlCl₃ than in the case of FeCl₃. Moreover, the settling volume of iron was more compact and it

Table 1
Effluent characterization: average values and range

Parameter	RWE	BRE	OE
Conductivity (μS/cm)	207 [62.7–413.0]	3,120 [2,120–4,640]	5,890 [3,760–7,890]
pH	8.14 [4.12–11.10]	11.80 [11.66–11.99]	7.99 [7.69–8.28]
SS (mg/L)	8.67 [2–16]	641.33 [124–1,664]	46 [16–76]
Turbidity (NTU)	2.10 [0.073–6.95]	202.36 [54.89–497.25]	13.10 [5.89–20.30]
COD (mg/L)	14,598 [6,285–27,929]	–	92

Note: RWE: ion exchange resin washing effluent; BRE: batch reactor washing effluent; OE: factory outlet effluent.

Table 3
RWE: turbidity at 30 min of the clarified stream for a C_{ss} of 180 rpm

Coagulant	Flocculant	C_v (mL)	F_v (mL)	F_{ss} (rpm)	Turbidity (NTU)
Nophos	Nophos	0.05	0.05	50	4.793
		0.1	0.1	30	8.387
		0.1	0.1	40	8.463
		0.1	0.1	50	21.233
		0.2	0.2	40	27.209
ACO	APF	0.1	0.1	50	0.262
		0.2	0.1	50	0.201

Table 4
BRE: sedimentation volume in 30 min (V_{30}) for 200 ppm of $Al_2(SO_4)_3$ and 2 ppm of PAM

C_{ss} (rpm)	F_{ss} (rpm)	V_{30} (mL)
100	30	51.33
	40	48.00
	50	44.00
200	30	44.67
	40	49.00
	50	50.33

flocculant were: $[FeCl_3] = 700$ ppm, $C_{ss} = 180$ rpm, $[CH-30] = 2$ ppm, $F_{ss} = 50$ rpm. When PAM was used as an anionic flocculant and PACI was used as a coagulant, the stirring speeds of coagulation and flocculation did not exert a high influence on sludge volumes.

Therefore, in the case of PAM and PACI, turbidity was chosen to estimate the best stirring speed conditions (Table 6). It was noticed that the higher the C_{ss} was the lower turbidity of the clarified stream was achieved. The lowest turbidity value was obtained for the following experimental conditions: $[PACI] = 500$ ppm, $C_{ss} = 270$ rpm; $[PAM] = 2$ ppm, $F_{ss} = 50$ rpm.

decanted faster. Although higher flocculant dosages (4 ppm) were tested, this resulted in even a lower density of the flocs than in the case of 2 ppm of Fc. Furthermore, the higher coagulant dosage added, the greater sludge volume obtained. In this way, the best conditions selected when CH-30 was used as a

3.2.4. Effluent analysis after the coagulation–flocculation process

The best coagulation–flocculation process conditions selected for each effluent are shown in Table 7.

Table 5
OE: sedimentation volume in 30 min (V_{30}) for a flocculant concentration of 2 ppm

Coagulant	Flocculant	C_c (ppm)	C_{ss} (rpm)	F_{ss} (rpm)	V_{30} (mL)
$AlCl_3$	CH-30	200	180	50	21.95
		500	180	50	37.92
		700	180	50	107.53
$FeCl_3$	CH-30	200	180	50	31.83
		500	180	50	78.01
		700	180	50	83.87
PACI	PAM	500	100	30	46
		500	100	40	44.67
		500	100	50	43
		500	270	30	46.33
		500	270	40	43.83
		500	270	50	41.33

Table 6

OE: turbidity of the clarified stream for 500 ppm of PACI and 2 ppm of PAM

C _{ss} (rpm)	F _{ss} (rpm)	Turbidity (NTU)
100	30	5.339
100	40	5.694
100	50	4.714
270	30	2.638
270	40	1.774
270	50	0.910

For the RWE and PACI-PAM, the turbidity of the clarified stream was 0.109 NTU and its removal efficiency was 9.92%. The COD value was 6,255 mg/L (removal efficiency of 1.26%). The amount of SS was 2 mg/L (removal efficiency of 50%). Delgado et al. [15] achieved higher reductions in turbidity (80%) due to the lesser pollution of municipal wastewater and Santo et al. [10] also achieved high turbidity reductions with higher anionic Fcs (4.5 mg/L). For RWE and ACO-APF the turbidity value was 0.262 NTU. It was a similar value to that of PACI-PAM. Moreover, the pH of the clarified stream in both cases was close to a neutral value 6.67 and 7.02, respectively. In this way, both combinations were feasible to pretreat the RWE.

For the BRE, the effluent contained a high initial amount of SS (1,664 mg/L). The pretreatment with an 80- μ m filter and the Jar-tests were not effective to reduce the concentration of SS. For this reason, this wastewater effluent was not considered suitable for RO feeding.

For the OE, the following combinations were selected: FeCl₃-CH-30 and PACI-PAM. In the first case, the removal efficiency of SS and turbidity was 0%. Thus, this coagulation-flocculation process was not effective because it did not improve wastewater conditions. For PACI and PAM, SS and turbidity were partially removed. However, COD and pH values

remained almost equal. The clarified stream had a SS value of 12 mg/L and a turbidity value of 0.114 NTU with removal efficiencies of 75 and 99.63%, respectively. The COD value was 74 mg/L with a removal efficiency of 2.63%. In the case of vinasse, Rennola et al. [12] obtained different values using PACI-PAM. They achieved a 30% of turbidity removal with cationic PAM. In the case of the OE, anionic flocculants were more effective, owing to colloids having positive charges whereas in the vinasse colloids had negative charges.

In all the experiments of sample characterization after coagulation-flocculation processes, the SDI₁₅ could not be measured due to the fact that the 0.45- μ m microfilter was blocked after few minutes of filtering.

3.3. Microfiltration and ultrafiltration

MF and UF tests were performed for the RWE since it had the most suitable characteristics for RO feeding after the coagulation-flocculation process.

In the MF tests (Fig. 1), permeate flux (J_p) scarcely decreased over time i.e. membrane fouling was negligible. However, permeate flux decline was significant for both UF membranes (Fig. 2). The rate of permeate flux decline was similar in both cases: 23.25% in 3 h for the 500 kDa UF membrane and 21.93% in 3 h for the 100 kDa UF membrane.

MF and UF permeate characterization is shown in Table 8. MF achieved a 33.33% of removal efficiency for SS whereas UF achieved a 100% of removal efficiency for SS for the two membranes tested. For turbidity and COD, a 0% of removal efficiency was achieved for both MF and UF tests. Lora et al. also achieved low COD removal percentages (4%) with membranes of 0.2 and 0.05 μ m pore diameter [1].

The SDI was measured for the UF permeate streams (Table 9). The SDI₅ was below the value of 20 for both UF permeate streams. However, it was above 15, the value suggested by RO manufacturers and other authors [5]. The same occurred with the SDI₁₅.

Table 7

Best coagulation-flocculation process conditions for each effluent considered

Effluent	Coagulant	Flocculant	C _c (ppm)	C _{ss} (rpm)	F _c (ppm)	F _{ss} (rpm)
RWE	PACI	PAM	700	200	2	30
	ACO	APF	0.1 ^a	180	0.1 ^a	50
BRE	Al ₂ (SO ₄) ₃	PAM	2	100	2	30
OE	FeCl ₃	CH-30	700	180	2	50
	PACI	PAM	500	270	2	50

^aThese values correspond to the flocculant volume added in mL.

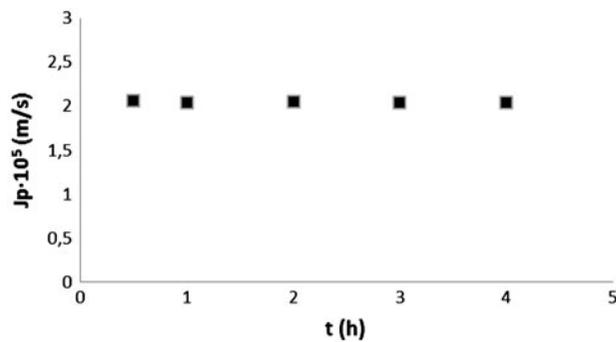


Fig. 1. J_p vs. time for MF membranes of 0.25 μm .

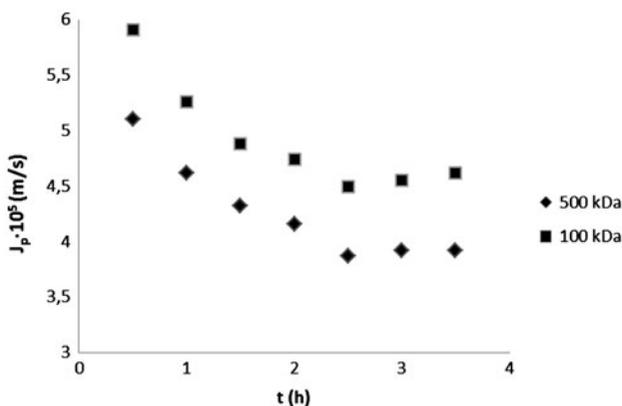


Fig. 2. J_p vs. time for UF membranes of 500 and 100 kDa MWCO.

Table 8
Permeate stream characterization

Membrane	SS (mg/L)	Turbidity (NTU)	COD (mg/L)
MF (0.25 μm)	4	0.105	9,540
UF (500 kDa)	0	0.136	9,600
UF (100 kDa)	0	0.136	9,620

Table 9
SDI for UF permeate stream

Membrane	SDI ₅	SDI ₁₅
UF (500 kDa)	17.89	>6.67
UF (100 kDa)	18.16	6.41

Although its value was near to the value suggested by authors ($\text{SDI}_{15} < 5$), it was above this value.

4. Conclusions

Ion-exchange resins washing effluent (RWE) was the most suitable effluent to reclaim and reuse in the factory. In this work, an improvement in the characteristics of the RWE was achieved by removing a large amount of pollutants. However, after the treatment of coagulation–flocculation coupled with MF–UF, an effluent with a SDI_{15} value above that recommended for RO feeding was achieved.

For RWE, the most suitable combinations for the coagulation–flocculation process were: $\text{ACO} = 1 \text{ mL}$ (diluted to 10%), $C_{\text{ss}} = 180 \text{ rpm}$ and $\text{APF} = 1 \text{ mL}$ (diluted to 10%), $F_{\text{ss}} = 50 \text{ rpm}$. UF experiments removed all the SS present in the RWE, although the SDI_{15} could only be reduced up to a value of 6.41.

A coagulation–flocculation process coupled with UF achieved a significant removal of SS, turbidity and COD.

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Symbols

ACO	—	active catalytic oxidation
APF	—	active polyfloc
COD	—	chemical oxygen demand
Cc	—	coagulant concentration, ppm
Css	—	coagulation stirring speed, rpm
Cv	—	coagulant volume, mL
EfOM	—	effluent organic matter
Fc	—	flocculant concentration, ppm
Fss	—	flocculation stirring speed, rpm
Fv	—	flocculant volume, mL
GAC	—	granular activated carbon
J_p	—	permeate flux, m/s
MF	—	microfiltration
MWCO	—	molecular weight cut off
NF	—	nanofiltration
ΔP	—	transmembrane pressure
PACl	—	polyaluminum chloride
PAHs	—	polyaromatic hydrocarbons
PAM	—	polyacrylamide
PES	—	polyethersulphone
PVDF	—	polyvinylidene fluoride
RO	—	reverse osmosis
SDI ₅	—	silt density index at 5 min
SDI ₁₅	—	silt density index at 15 min
SS	—	suspended solids
TOC	—	total organic carbon
UF	—	ultrafiltration
V ₃₀	—	sedimentation volume in 30 min, mL

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