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Efficiency of a coagulation/flocculation–membrane filtration hybrid process for the treatment of vegetable oil refinery wastewater for safe reuse and recovery

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Highlights

- This investigation highlights the oily wastewater treatment using hybrid processes
- Better pollutant retentions were obtained using ultrafiltration membranes
- CF/UF provided an efficient integrated membrane system for oily effluent treatment
- Treated effluent using CF/UF process was suitable for application in agriculture

Abstract (maximum 200 Mots)

Treatment of real (RVORW) and synthetic (SVORW) vegetable oil refinery wastewaters using membrane filtration system was experimentally studied. Experimental runs with SVORW were used to identify the best conditions to perform with RVORW treatment. The bench-scale experiment was carried out using a commercial ceramic 0.245 m² ultrafiltration (UF) membrane (150 kDa) in cross-flow filtration (CFF) mode at a flow rate of 3000 L·h⁻¹ and a trans-membrane pressure (TMP) of 1.2 bars. However, such membrane is vulnerable to fouling and it is insufficient to give water of good quality suitable for reuse. This investigation, aims to improve the purification performances of UF by exploring its combination with other treatment options, i.e. optimized coagulation/flocculation (CF) as pre-treatment and dead-end filtration (DEF) as post-treatment for better treated-water quality. According to the results, when using CF as pre-treatment under optimal conditions (2.4 g·L⁻¹ of aluminium sulfate, 60.05 mg·L⁻¹ of CHT flocculant, under initial pH of 9.23), the hybrid CF/UF process allows to achieve the best treated RVORW water quality with turbidity, COD and TOC removals reaching 100%, 98% and 97% respectively compared to those of CF and UF used separately, with membrane permeability of 135 L·h⁻¹·m⁻²·bar⁻¹ which is in agreement with an industrial application.

Keywords : Coagulation/Flocculation, Hybrid process, Membrane filtration, Oily wastewater

1. Introduction

Increasing growth of industries worldwide has led to excessive use of water resources in different processes. It is vital to reduce the exploitation of these resources by adopting new and efficient processes in industrial sector. In this direction, wastewater treatments have to be studied so as to facilitate the reuse of treated wastewater in different industrial processes (Dermentzis et al., 2011). One of the industrial sources of pollutants is the vegetable oil refinery, being significant water consumers and consequently large wastewater producers (Un et al., 2009). In fact, large amounts of wastewater and solid waste are produced during the soybean oil refining process, which usually includes degumming, alkalization, earth bleaching, and deodorization to remove undesired flavor-destroying minor compounds from the unrefined soybean oil (Rajkumar et al., 2010).

This wastewater, often referred to in the literature as “vegetable oil refinery wastewater” (VORW), has a high chemical oxygen demand (COD) and contains large amounts of sodium salts from free fatty acids soap stocks, oil, grease, sulphates and phosphates (Yu et al., 2018), which makes its treatment difficult. Regarding the organic load of VORW, the waste streams directly discharged into the environment without any efficient treatment poses a detrimental impact on public health and ecological systems (Pintor et al., 2016). In view of sustainability, highly loaded wastewater, such as VORW, have been considered more as a resource for water, value-added products, and even energy, rather than a waste. This has driven many researchers and scientists toward developing useful treatment technologies in accordance with the nature of oil in water mixture to produce treated water of a quality suitable for reuse and/or recycling (Jamaly et al., 2015 ; Zhang et al., 2010).

On the other hand, because of their low biochemical oxygen demand (BOD₅) / COD ratio, VORW cannot be treated by a biological treatment (Un et al., 2009). Furthermore, VORW transport presents a high risk of clogging in pumps and piping. For these reasons, VORW cannot be treated in a conventional municipal wastewater treatment plant since it may affect its operations (Un et al., 2009). Therefore, an appropriate treatment system of VORW is very important to minimize the release of such highly polluted effluents and to reuse them as an unconventional water source, and should provide efficient pollutant reduction, uses less treatment time, require simple installation, maintenance, and operation with the addition of little or no chemical compounds.

Treatment processes like gravity separation (Fischer et al., 1995) and centrifugal settling (Brar et al., 2006) as well as chemical methods using surfactants (Kang et al., 2011) are the most common technologies used for the treatment of oil/water mixtures. However, these conventional methods consume high amounts of energy while exhibiting poor removal efficiency for treating stable oil in water emulsions especially when the oil droplets are finely dispersed and the concentration is very low (Gryta et al., 2001). Some disadvantages associated with these approaches are complex operation, long processing time, high costs, etc..(An et al., 2017). These drawbacks emphasize the need for more novel separation processes.

Dissolved air flotation (DAF) is a widely used treatment method for oily waters. DAF is a process for removing suspended particles from liquid by bringing the particles to the surface of the liquid. Air is dissolved at high pressure in a saturator, and microbubbles are formed when water is released in the flotation cell at atmospheric pressure (Wang, 2006). Due to the collection and adhesion factors when dealing with flotation separation of very small oil droplets (2–30 μm), fine bubbles, quiescent hydrodynamic conditions in the separation zone and emulsion breakers before flotation are required (Gopalratnam et al., 1988). Therefore, studies concerning DAF are typically focused on coupling coagulation and DAF (Van Le et al., 2012). Nevertheless, the major disadvantages of this mechanically complex and intensive system that include (i) size and percent air, (ii) the higher energy consumption

as compared to conventional coagulation-sedimentation process (because of the recycle water pumping and air compressing requirement), (iii) the additional cost of chemical support aids (coagulants and flocculants) and (iv) the higher unit costs (Wong, 2013 ; Abboah-Afari and Kiepper, 2012), underline the need to investigate in new separation technologies that are less complex and less expensive.

Microfiltration (MF) and ultrafiltration (UF) have proven to be promising alternatives for conventional industrial separation methods, since they offer numerous advantages like high selectivity, easy separation, oil removal efficiency with easy maintenance, continuous and automatic operation, economic and fast operation, low energy cost and stationary parts with compact modular construction (Hafidi et al., 2004). These technologies have proved their efficiency in the treatment of different kinds of industrial wastewater; in pharmaceutical, textile, petrochemical and agri-food industries, as well as for oilfield produced water treatment and it is considered as the most useful technique in the treatment of stable emulsions particularly with oily wastewater (Decloux et al., 2005). Membrane based separation processes are used to obtain stable effluent quality without contaminants which can be reused and recycled in the process itself or in other applications (Cañizares et al., 2002). The possibility of using the microfiltration (Hemmati et al., 2012) and ultrafiltration (Wu et al., 2008) processes to treat the oil in water emulsions have been previously examined. Recently, Masoudnia et al. (2015) employed the microfiltration (MF) using polyvinylidene fluoride membrane for separation of oil/water emulsions. Many studies have been conducted on oily wastewater treatment with different types of organic and inorganic membranes (Gryta et al., 2001 ; Yan et al., 2006 ; Yan et al., 2009) However, most organic membranes offer several advantages such as low cost but they cannot withstand extreme conditions like high temperature and high pressure, and fly ash that limite the membrane regeneration (Kaur et al., 2018). In contrast, studies reported that ceramic membranes can support high temperatures and pressures owing to their excellent thermal and mechanical durability strength and good chemical resistivity that they can be used under harsher process condition for regeneration step (Parma and Chowdhury, 2014). Membrane fouling, which is caused by the accumulation of impurities, has always been a challenge for the development and the industrialization of membrane technologies (Schwarze et al., 2017). The fouling increases the cost due to the increase in energy demand, the use of chemicals for cleaning, and the frequency of membrane replacement. Thus, in order to reduce membrane fouling during oily wastewater treatment, the hybrid processes consolidating the advantages of pre-treatment are often preferred (Wu et al., 2017), including pre-coagulation, pre-adsorption, pre-filtration, and pre-oxidation etc... (Choo et al., 2007 ; Gao et al., 2011). Among the various pre-treatments, coagulation/flocculation (CF) is the most dominantly used due to its low cost, ease of operation and ability to significantly improve UF performance (Arhin et al., 2017). It is presumed that during coagulation, oil droplets and colloids are destabilized and clusters form larger flocs, which are easily retained by UF membranes (Xiangli et al., 2008).

The present investigation follows on from our previous study on the CF treatment of real vegetable oily wastewater (RVORW) using coagulation/flocculation process that investigates the relationship between the three variables (coagulant concentration, flocculent dosage and pH) and the two important process responses (COD and turbidity removals) in order to estimate the optimal conditions for maximum real VORW treatment using the Response Surface Methodology (Louhichi et al., 2019). Results previously found on real VORW are directly used in the present investigation, they showed that $Al_2(SO_4)_3$ was the best coagulant experienced allowing to obtain maximum COD and turbidity removals when it was directly used at a concentration of $2.4 \text{ g}\cdot\text{L}^{-1}$ followed by a CHT flocculant at a dosage of $60.05 \text{ mg}\cdot\text{L}^{-1}$ under initial pH of real effluent of 9.23 (Louhichi et al., 2019).

Furthermore, in the framework of an integrated water management strategy that will be developed in the Tunisian vegetable oil refinery (ZOUILA), the present investigation aims to identify the most effective treatment process allowing the supply of treated water suitable for recycling in industrial uses such as in the soap manufacturing sector as a step towards a zero liquid discharge system (this which is desired in our case by the company ZOUILA) or reuse in agriculture for the irrigation of

olive trees in the vicinity of the company ZOUILA thanks to the nutrients it contains. Finally, the treated water may also be discharged into the natural environment (terrestrial ecosystem) provided that it does not present a risk of toxicity to the ecosystem. For these reasons, the aim of this investigation was to identify the most efficient technology for complete removal of oil from synthetic (SVORW) and industrial (RVORW) oily wastewaters. Different treatment processes such as Coagulation/flocculation (CF) and membrane filtrations have been employed directly or in hybrid mode. The treatment processes were compared based in their efficiency in COD, TOC and turbidity removals. To our knowledge no study has so far been reported on hybrid coagulation-flocculation/ultrafiltration for the treatment of industrial vegetable oily wastewater.

2. Material and Methods

2.1. Real Vegetable Oil Refinery Wastewater (RVORW)

The investigations were carried out on real untreated vegetable oil refinery wastewater (RVORW) samples collected from the “Mutuelle Centrale de Services Agricoles et Industriels” company, mentioned herein as “Zouila” located in Mahdia (Tunisia) which generates on average 30 m³ of wastewater daily. The chemical refining processes involved by Zouila are summarized in Fig. 1. In order to study the physicochemical characteristics of RVORW and to carry out their treatments, samples were collected from Zouila according to the Standard Method for Examination of Water and Wastewater (APHA, 1998).

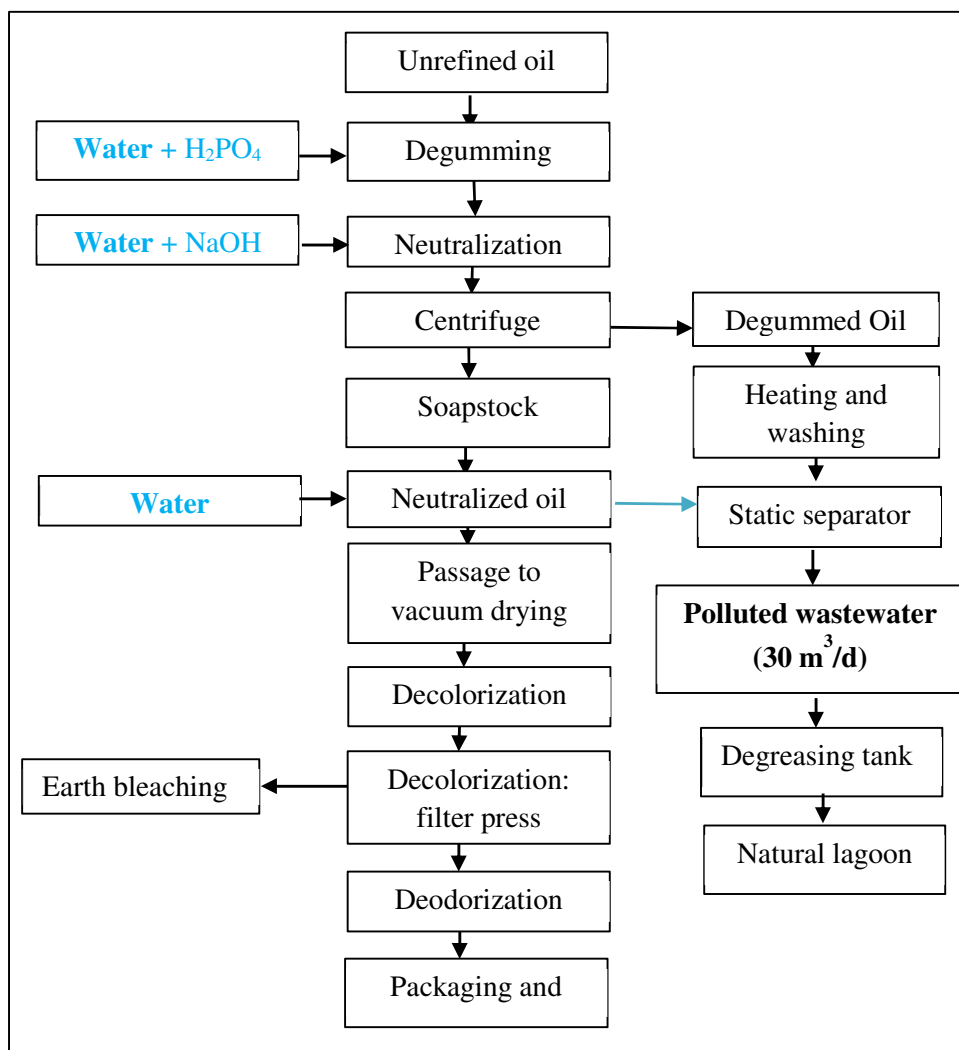


Fig. 1. Schematic diagram of vegetable oil chemical refining process adopted by Zouila company: source of oily wastewater.

2.2. Synthetic Vegetable Oil Refinery Wastewater (SVORW)

Oil / water (O/W) emulsions were prepared using soya oil ($2 \text{ g}\cdot\text{L}^{-1}$) mixed with a non-ionic surfactant (Tween 80) under a ratio of V/V in the distilled water. The mixture was homogenized using ultrasonic Homogenizer type SONOPULS HD 3200 with ultrasonic frequency equal to 20 kHz for 30 minutes at room temperature (Ahmad et al., 2011). In order to ensure large volumes of SVORW required for membrane filtration experiments, highly concentrated O/W emulsions are prepared (10x, 50x and 100x). The emulsions were subjected to the same homogenization conditions.

2.3. Coagulation/Flocculation experiments (CF)

Coagulation/Flocculation (CF) experiments were performed using a conventional Jar-test apparatus consisting of four beakers each with a volume of 1L (Velp Scientifica). Aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$) and Ferric Chloride (FeCl_3) were used as coagulants while CHT flocculant CV (CHT) and MF55, were used as flocculants. Jar tests were performed according to the standard procedure (ASTM D2035:2008) out in three steps in accordance with the operating conditions previously optimized in the laboratory (Louhichi et al., 2019) that have similar coagulation and flocculation durations to those found and

adopted by Chatoui et al. (2017) : (i) the coagulant was added to wastewater under rapid mixing 180 rpm during 5 min. (ii) After coagulation, the pH of water samples was adjusted to neutrality and flocculant was added under slow mixing during 20 min. (iii) Samples were allowed to settle down for 30 min.

Finally, supernatant was collected for COD, TOC and turbidity analysis. During CF of SVORW, the concentration of each coagulant was ranged from 0 to 5 g·L⁻¹, while the concentration of each flocculant was ranged from 0 to 500 mg·L⁻¹. Whereas, the CF treatment of RVORW was conducted using 2.4 g·L⁻¹ of Al₂(SO₄)₃, 60 mg·L⁻¹ of CHT flocculant CV at initial wastewater pH adjusted to 9 which were the optimal conditions (Louhichi et al., 2019).

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2.4. Membrane processes

2.4.1. Effect of the molecular weight cut off

Dead-End Filtration (DEF) appears as an useful tool to investigate appropriated MF/UF membranes and to choose the suitable molecular weight cut-off for the better oily wastewater treatment according to the permeate flux and feed quality. The DEF essays were carried out using Amicon stirring cell, a flat membrane with a membrane area of about 14 cm² at constant pressure of 1 bars under a gentle stirring using magnetic bar which limits the formation of a polarization layer on the surface of the membrane and shear denaturation. Several flat membranes of MF and UF have been tested (Millipore, OMEGA, RAWP ...) with pore sizes varied from 0.22 to 1.2 μm for MF and molecular weight cut off varied from 3 kDa to 100 kDa for UF. During each experience, samples was collected for COD, TOC and turbidity analysis.

2.4.2. Cross Flow Filtration (CFF)

Cross-flow filtration (CFF) is the industrial membrane filtration mode when the viscosity or suspended matter concentration was high (Peters, 2010). During the present investigation, ceramic UF membrane characterised by a tubular configuration consisting of 19 channels (CTI, France) with a molecular weight cut-off (MWCO) of about 150 kDa was used and the effective area for filtration was 0.245 m². The wastewater was placed in the feed tank with 100 L of capacity (Figure 2) and circulated through stainless steel membrane module by a centrifugal pump (type Salmson reference centrifugal pump). The valves placed before (V1) and after (V2) the membrane module were adjusted to obtain the required operating trans-membrane pressure of about 1.25 bars. The retentate was totally recycled to the feed tank at a constant recirculation flow-rate of about 3000 L·h⁻¹ while the permeate was collected and weighted during the experiments using electronic balance (Ohaus Corporation; CD11-EU). The permeate flux was initially high then reduced to a steady value during the treatment. Since temperature of water have a significant impact on flux, it is common practice to adjust the flux to a reference temperature (20°C) using the empirical Arrhenius law (Pellegrin et al., 2015). Using Darcy's law, the water permeability (L_p) (L·h⁻¹·m⁻²·bar⁻¹) was taken as the slope of the linear regression between TMP and *J*₂₀ values according to the following equations (1) and (2) :

$$LP (L h^{-1} m^{-2} bar^{-1}) = J_{(20^{\circ}c)} / TMP \quad (1)$$

$$J = Q / S \quad (2)$$

where,

- J: permeate flux ($L \cdot h^{-1} \cdot m^{-2}$),
- S: Membrane surface (m^2),
- Q: permeate flow rate ($L \cdot h^{-1}$).

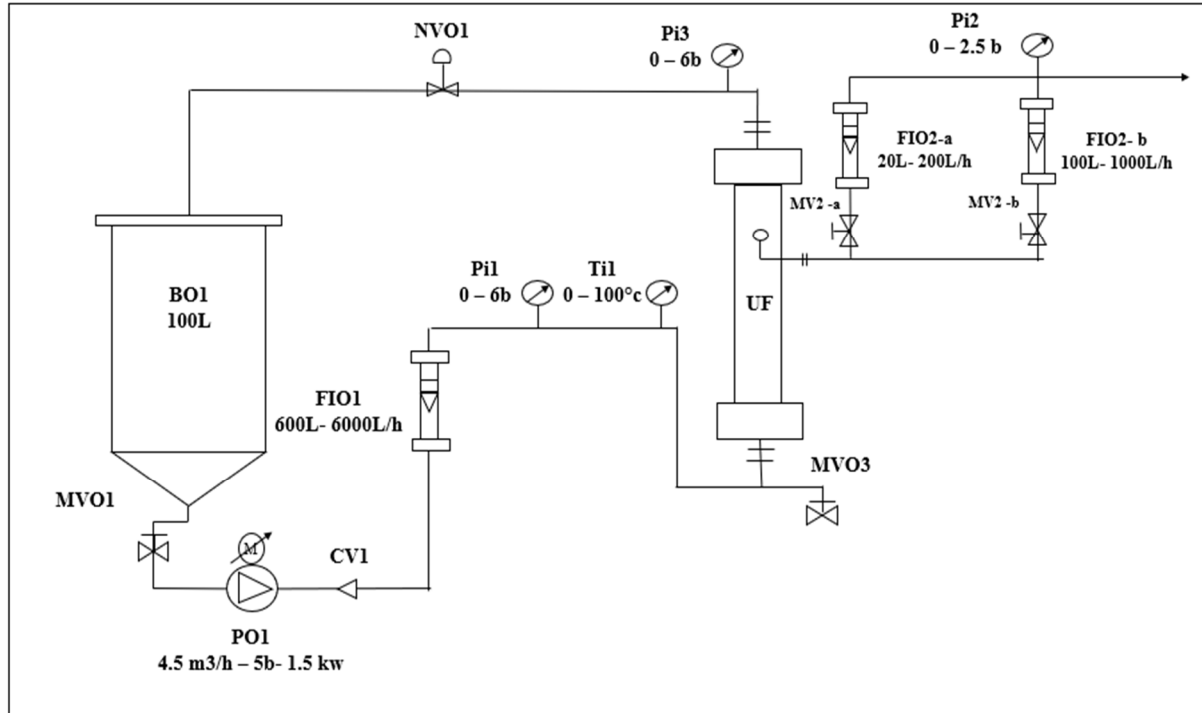


Fig. 2. Schematic design of cross flow membrane filtration pilot.

During UF experiments, samples of feed wastewater, retentate and permeate were taken for analysis to investigate the efficiency of the membrane in the retention of suspended matter in terms of turbidity and organic matter (COD and TOC); the passage of pollutants through the UF membrane is characterized by the retention rate noted TR and calculated as the following equation (3):

$$TR (\%) = \left[1 - \left(\frac{C_p}{C_c} \right) \right] \times 100 \quad (3)$$

where C_p and C_c indicate the concentration of pollutants in the permeate and in the retentate, respectively. In hybrid process using CF followed by UF (detailed procedure of CF experiment was mentioned in section 2.3), the wastewater treated by CF under optimal conditions was divided after sedimentation into supernatant and sediment, the supernatant was directly used for UF experiments. A schematic diagram of the different scenarios of the wastewater treatment is shown in Fig. 3 for 2 types of effluent (synthetic and real). For all these cases, the DEF is used to give an idea about the membrane performances as a function of the MWCO (Balannec et al., 2005).

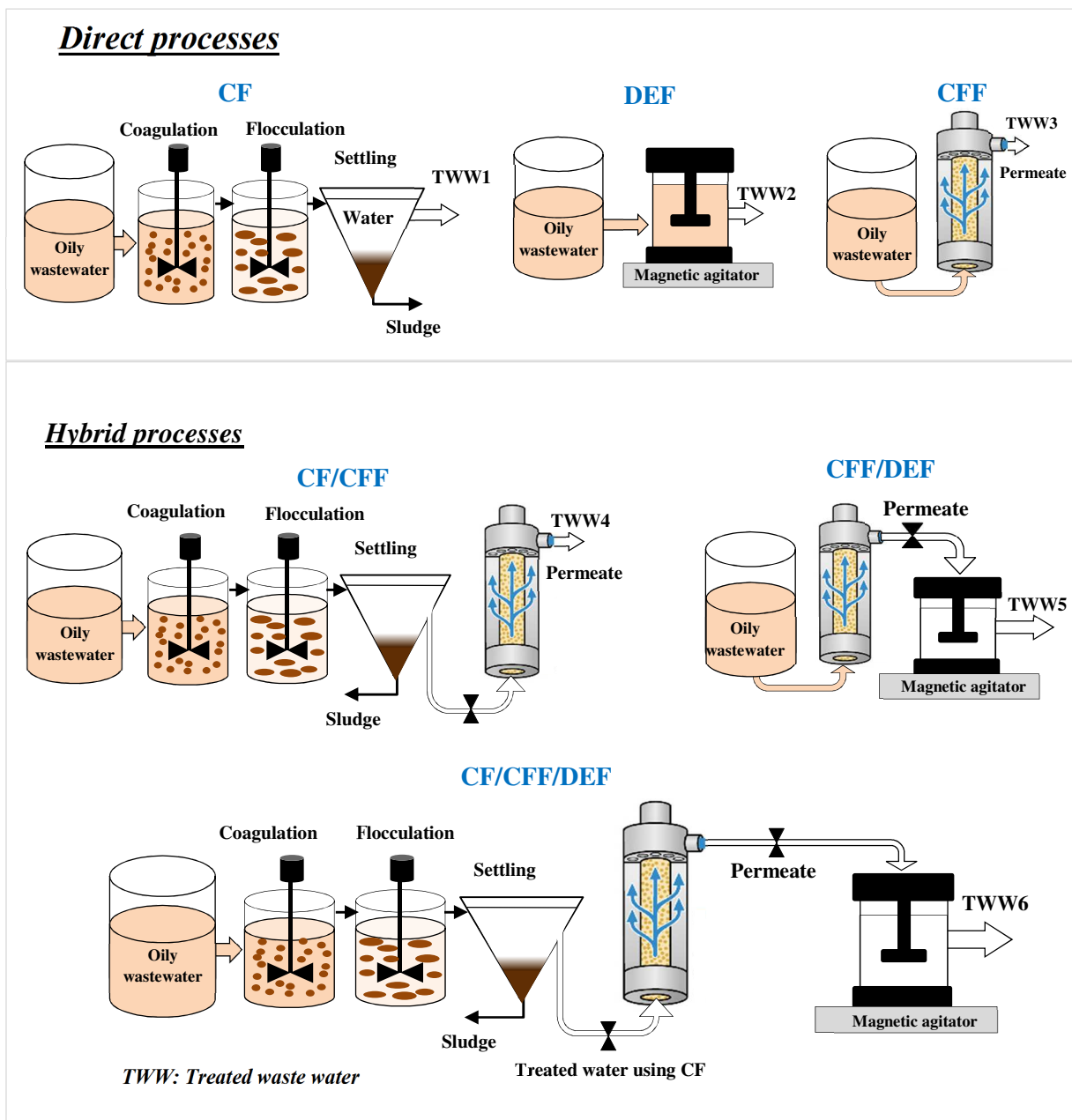


Fig. 3. Schematic diagram of direct (CF, CFF and DEF) and hybrid (CF/CFF, CFF/DEF and CF/CFF/DEF) processes carried out to treat VORW

2.4.3. Membrane fouling and washing

Membrane UF fouling in the case of Oil in Water filtration is caused by deposited solute or colloidal particles on the surface and/or into the membrane and/or strong physical or chemical sorption on the membrane. Flux decline in this case can be recovered by washing with alkaline and/or acid solutions. In the present study, chemical cleaning of the fouled membranes were conducted after each experiment, (i) rinsing, (ii) first washing with sodium hydroxide ($20 \text{ g}\cdot\text{L}^{-1}$) at a temperature of 80°C for 30 min, (iii) rinsing with distilled water, (iv) washing with nitric acid ($5 \text{ g}\cdot\text{L}^{-1}$) at a temperature of 50°C for 30 min,

(v) rinsing with distilled water (Lee et al., 2001). Cleaning efficiency was evaluated based on the analysis of easily measurable process parameters such as membrane permeability where its variation was investigated with time during several filtration and cleaning cycles. According to this classical method of fouling characterisation, the decrease of permeability during a filtration cycle is attributed to shortterm fouling phenomena, such as mainly the particle deposit at the membrane surface or pore blockage in the case of UF applications (Remize et al., 2010).

2.5. Analytical methods

Raw and treated wastewater were analysed for physicochemical characteristics to monitor the change in pollutant concentration throughout the different treatment processes. pH and turbidity were measured using a pH meter type HACH sensION⁺ pH3 and a Turbidimeter type WTW Turb 55Q IR. Conductivity (EC) was measured using WTW conductivity meter. Chemical Oxygen Demand (COD) was measured using the WTW[™] Chemical Oxygen Demand Test Kits. Total Organic Carbon (TOC) was measured using the TOC-L type Total Organic Carbon Analyzer type analyzer (TOC-VCPN, SHIMADZU Japan). Biochemical Oxygen Demand (BOD₅) was measured using the oxytop system (WTW) after incubation at 20°C during 5 days. Total Suspended Solids (TSS) and Total Volatil Silids (TVS) were measured using standard methods for water and wastewater analysis (APHA, 1999). The collected samples were filtered through a 0.45µm filter (mixed cellulose esters, Advantec, Japan) before the analysis of chemical parameters such as nitrite (NO₂⁻), nitrate (NO₃⁻), Total Phosphorus (TP), ammonium (NH₄⁺), chloride (Cl⁻), sodium (Na⁺), calcium (Ca₂⁺), sulfate (SO₄²⁻) and potassium (K) using the ion chromatography pekín Elemer C (Walkley and Black, 2003). Lipid content was measured gravimetrically using hexane as solvent, after the extraction, hexane was evaporated using a rotary evaporator at 70°C (Walkley and Black, 2003). Fatty acids were identified using Gas chromatography (GC) equipped with a split/splitless capillary injector and flame ionization detector (FID) (Touchstone, 1995).

2.6. Phytotoxicity test

Because there is a direct relationship between COD and toxicity of wastewater, it is important to use both bioassay toxicity and physicochemical tests to assess the risk that raw and treated wastewater discharges or reuse for irrigation present to the environment (Latif and Licek, 2004). Bioassay tests are considered a standard method to assess toxicity of substances or complex mixtures, such as found in industrial wastewater and represent useful tools to assess toxic effects of complex mixtures commonly found in industrial wastewater discharges (Schmittet al., 2005). In fact, physicochemical parameters are insufficient to describe the adverse effects of industrial wastewater on aquatic or terrestrial organisms (Dalzell et al., 2002). This is why bioassay tests are appropriate procedures to assess the toxicity of complex mixtures of substances present in industrial wastewater (Robidoux et al., 1998). On the other hand, toxicity tests are useful tools to demonstrate the efficiency of a wastewater treatment process to remove toxic substances (Isidori et al., 2004). *Daphnia pulex* is an aquatic organism. It represents one of the first levels of the trophic chain and is an excellent biomarker of aquatic toxicity. Many plant species have been recommended as biomarkers for terrestrial toxicity using root elongation of germinated seeds (Park et al., 2016) among which lettuce seed (*Lactuca sativa*) has been recommended by the U.S. Environmental Protection Agency (EPA) (1982). It is a good choice to demonstrate the possible adverse effect of using wastewater for irrigation. In our case of study, the phytotoxicity test using lettuce seeds (*Lactuca sativa*) is the most appropriate Bioassay test. To investigate the phytotoxicity of different samples of raw and treated oily wastewater, germination index (GI) of *Lactuca sativa* was calculated according to the methodology described by Tiquia (2000).

Ten seeds were uniformly placed in Petri dishes that contained a Whatman paper filter where 10 mL of water samples were then uniformly added to each dish. The dishes were capped and kept in a dark

incubator at a $20^{\circ}\text{C} \pm 2^{\circ}\text{C}$ temperature for 7 days. Distilled water was used for control tests. Phytotoxicity tests were performed in triplicates for each sample and the average values were recorded. After incubation, the number of germinated seeds was counted and expressed as the relative seed germination (RSG), relative root growth (RRG) and germination index (GI) of lettuce seeds based on the following equations (4), (5), and (6), respectively, described by Buchmann et al. (2015):

$$\text{RSG (\%)} = (\text{number of germinated seeds} / \text{number of seeds}) \times 100 \quad (4)$$

$$\text{RRG (\%)} = (\text{relative root length of the germinated seeds in the sample} / \text{relative root length of the germinated seeds in distilled water}). \quad (5)$$

$$\text{GI} = (\text{RSG} \times \text{RRG}) / 100 \quad (6)$$

3. Results and discussion

3.1. Treatment of Synthetic Vegetable Oil Refinery Wastewater (SVORW)

3.1.1. Preparation of vegetable oil/water stable emulsion

Oil-in-water (O/W) emulsions are thermodynamically unstable systems and they tend to separate over time. In this regard, the use of emulsifiers is required in order to stabilize the oil/water interface and maintain oil droplets dispersed in the aqueous phase under the application of mechanical forces. In the particular case of Soya oil / water emulsion, $2 \text{ g}\cdot\text{L}^{-1}$ of soya oil and $2 \text{ g}\cdot\text{L}^{-1}$ of Tween 80 as emulsifier under the homogenization period of 30 min were found sufficient for the preparation of emulsions. The water emulsions were stable on the basis of the absence of oil layer above the surface of the solution after 7 days. In our characterization study, synthetic soya oil refinery wastewater (SVORW) was prepared according to oil content in real oily wastewater ($2 \text{ g}\cdot\text{L}^{-1}$ of oil) with COD, TOC and turbidity values of about $11700 \text{ mgO}_2\cdot\text{L}^{-1}$, $4870 \text{ mg}\cdot\text{L}^{-1}$ and 2770 NTU , respectively ; whereas for real soya oil refinery wastewater (RVORW), COD, TOC and turbidity mean values were of about $12230 \text{ mgO}_2\cdot\text{L}^{-1}$, $3899 \text{ mg}\cdot\text{L}^{-1}$ and 3730 NTU , respectively. These results has pointed out that there is a slight difference in the characterization of synthetic and real wastewater: this difference can be explained by the presence of other minority compounds and/or impurities generated from the vegetable oil during the refining process in industrial site. The starting volume of feed mixtures for the cross-flow ultrafiltration was 100L, which is optimal for such a laboratory plant, given that this is the sufficient volume of feed mixture needed (Šereš et al., 2016). In order to prepare large volume, concentrated synthetic wastewater were prepared. Calibration curve gives a linear relationship of COD, TOC and turbidity vs. Oil content ($\text{g}\cdot\text{L}^{-1}$) which prove that this characteristic of effluent are proportional with the oil content (COD = $5839.8 [\text{oil}]$ with $R^2 = 0.97$, turbidity = $645.98 [\text{oil}]$ with $R^2 = 0.98$ and TOC = $1190.2 [\text{oil}]$ with $R^2 = 0.97$) in an oil concentration range of 0-100 $\text{g}\cdot\text{L}^{-1}$. Thus, concentrated effluent are suitable to prepare large volume needed for crossflow ultrafiltration treatment experiments.

3.1.2. Treatment of SVORW using Coagulation/Flocculation process

In order to assess the treatment efficiency of CF process, different coagulants and flocculants (coagulant aids) were used to determine the suitable chemical nature and dosing rate.

3.1.2.1. Influence of the nature and coagulant concentration

The operational conditions of CF were determined using ($\text{Al}_2 (\text{SO}_4)_3$) and (FeCl_3) widely used coagulants solutions in industrial sector. The effect of the concentration of each coagulant (ranged from 0 to $5 \text{ g}\cdot\text{L}^{-1}$) on the CF performances was analysed under initial pH of oil/water emulsion (SVORW) equal to 9 using a flocculant concentration (CHT Flocculant CV) of $60 \text{ mg}\cdot\text{L}^{-1}$.

Both the Al^{3+} and Fe^{3+} based coagulants dissociate in solution, the trivalent ions enhancing polymeric chain reactions to adsorb oil droplets onto their surfaces to form flocs (Tetteh et al., 2017).

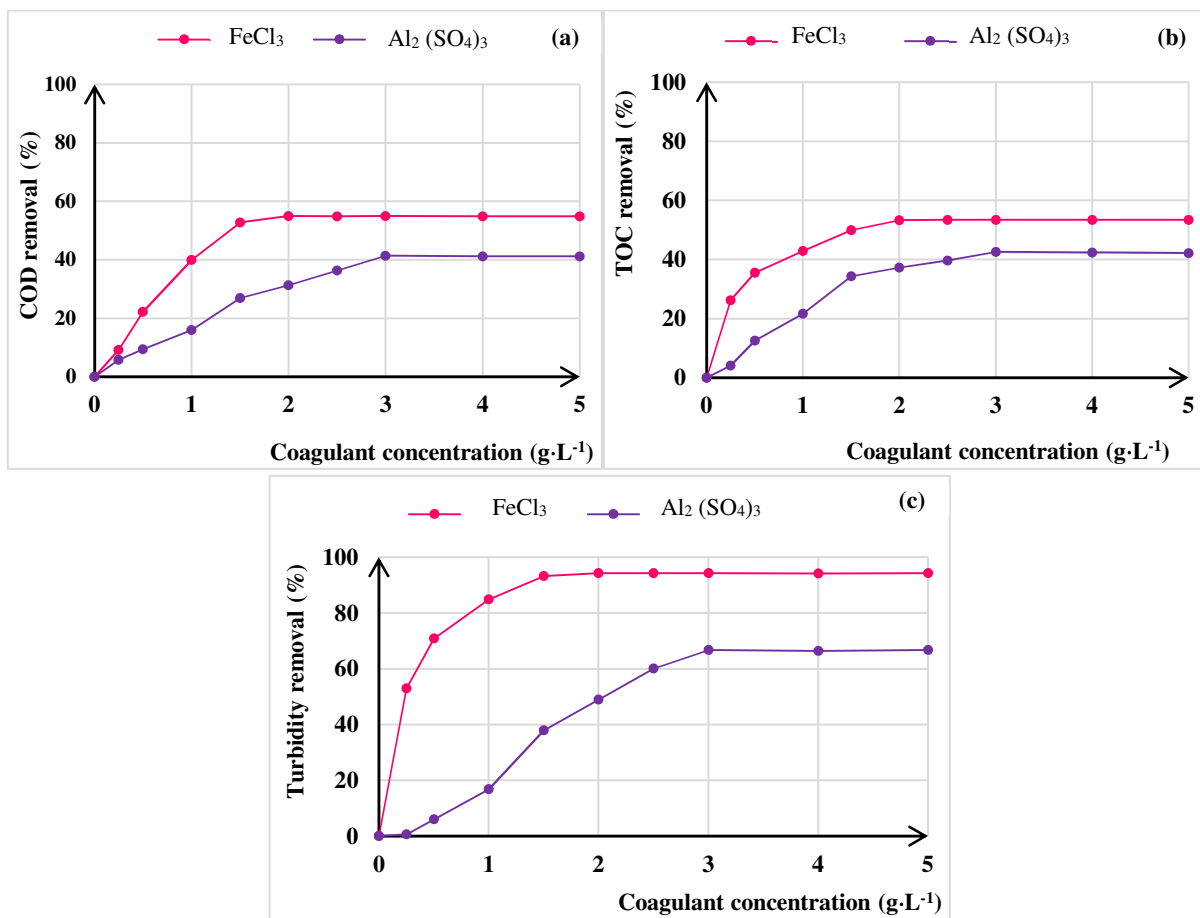


Fig. 4. Variation of the COD (a), TOC (b) and turbidity (c) removals from SVORW as a function of the coagulant concentration [Flocculant concentration CHT Flocculant CV of 60 mg·L⁻¹].

Based on Fig. 4, the removal rates of COD, TOC and turbidity all were improved with increased coagulant dosage in the range of 0-5 g·L⁻¹. Dissimilar to results previously found on real VORW which showed that $\text{Al}_2(\text{SO}_4)_3$ was the best coagulant experienced (Louhichi et al., 2019), results indicate that among the two coagulants used, FeCl_3 presented the best results with lower chemical consumption rate at initial oil/water emulsion (SVORW) pH value of 9 showing maximum COD, TOC and turbidity removals of about 54.95%, 53.35% and 94.23%, respectively, when it was used under a concentration of that 2 g·L⁻¹.

Whereas, at the same coagulant concentration, $\text{Al}_2(\text{SO}_4)_3$ was able to remove only 31.39% of COD, 37.34% of the TOC and 48.9% of turbidity. Figure 4 also shows that there was no significance effect on CF efficiency other than overdosing when FeCl_3 dosing rate was increased from 2 to 5 g·L⁻¹. In fact, coagulant overdosing can cause restabilization of oil droplets in aqueous solution, which decreases the effectiveness of the coagulant with increased costs of chemicals used (Daud et al., 2015). According to Zahrim et al. (2017), among all coagulants tested, CF treatment of highly polluted palm oil mill plant wastewater revealed the highest performances when FeCl_3 coagulant was used at a concentration of 8

$\text{g}\cdot\text{L}^{-1}$ under initial pH equal to 10, resulting in color removal up to 90% (Zahrim et al., 2017). Basibuyuk and Kalat (2004) also found that the performance of FeCl_3 was better than $\text{Al}_2(\text{SO}_4)_3$ where higher alum doses ($1250 \text{ mg}\cdot\text{L}^{-1}$) were needed in order to achieve similar COD removals with ferric chloride ($25\text{-}400 \text{ mg}\cdot\text{L}^{-1}$). To explain the organic matter removal phenomenon under coagulation using FeCl_3 , two main mechanisms: (1) neutralization / precipitation of the pollutants charge under acidic pH conditions, and (2) adsorption and/or sweep coagulation in the form of precipitated hydroxide under alkaline pH conditions.

3.1.2.2. Effect of flocculant concentration

To enhance the CF efficiency and to improve the performance of coagulant for pollutants removal from SVORW, high molecular weight polymers with a relatively low charge density (coagulant aids/flocculants) are commonly used by particle bridging and charge neutralization. In the present investigation, two flocculants (coagulant aids) : CHT-flocculant-CV (cationic) and MF55 (anionic), widely used in industrial sector, were selected for testing the coagulation efficiency using FeCl_3 under an optimal dosage of $2 \text{ g}\cdot\text{L}^{-1}$. Due to the fact that the flocculant dose is a highly important environmental factor in flocculation (Huang, et al., 2016), the impacts of adding different doses of flocculants was investigated in this study. Fig. 5 shows the impact of the combination of FeCl_3 with each coagulant aid on COD, TOC and turbidity removals. The results showed that by adding CHT-flocculant-CV during CF treatment, a more effective pollutants (in terms of COD, TOC and Turbidity) removal was achieved.

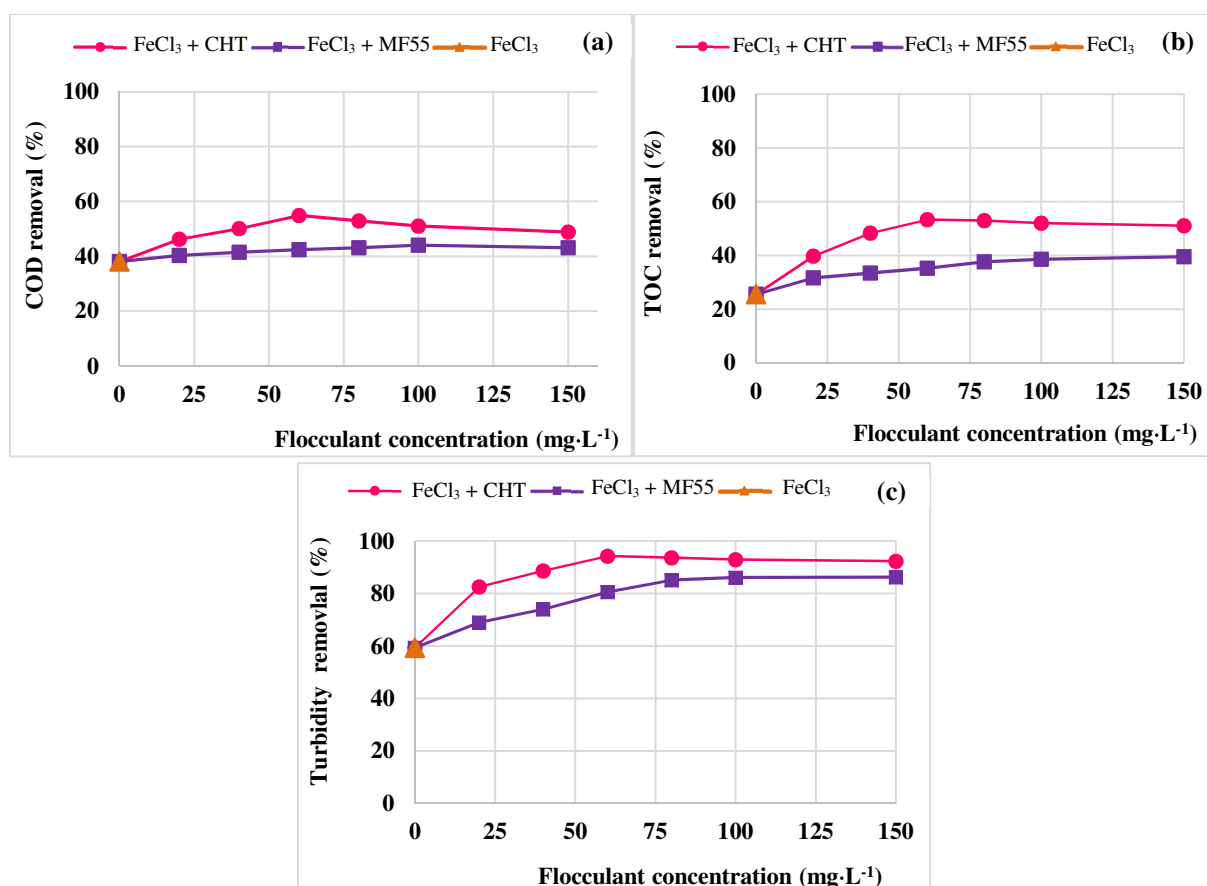


Fig. 5. Variation of the COD (a), TOC (b) and turbidity (c) removals from SVORW as a function of the flocculant concentration [Coagulant concentration of $2 \text{ g}\cdot\text{L}^{-1}$].

The CHT-flocculant-CV (cationic flocculant) was more efficient in the removal of COD, TOC and turbidity from SVORW at a lower concentration comparing to MF55 (anionic flocculant). The optimal dose of CHT flocculant CV was found to be $60 \text{ mg}\cdot\text{L}^{-1}$ resulting in COD, TOC and turbidity removals of about 55%, 52.6%, and 94.2%, respectively. Whereas, the optimal dose of MF55 was found to be $100 \text{ mg}\cdot\text{L}^{-1}$ resulting in COD, TOC and turbidity removals of about 44%, 38.6%, and 86.1%, respectively.

Furthermore, using the CHT flocculant CV flocculant at a concentration of about $60 \text{ mg}\cdot\text{L}^{-1}$ has enhanced the treatment efficiency of the CF showing an increase of COD, TOC and turbidity removals from 38%, 25.5% and 59.4%, respectively, (without using flocculant) to 55%, 52.6% and 94.2% when using $60 \text{ mg}\cdot\text{L}^{-1}$ of CHT flocculant CV flocculant which shows that the flocculation step markedly improved the performance of the CF during the treatment of SVORW.

Liang et al. (2009) also found that cationic flocculant can significantly enhance the settleability of flocs formed when it is used in combination with FeCl_3 whereas anionic flocculant showed little effect on the settling characteristics. Particle bridging is the predominant mechanism for polyelectrolyte flocculation (Mishra et al., 2005). The difference between cationic and anionic flocculant in improving coagulation performance may lie in their different reformation after polymer adsorption. It also appears that with an increase in the flocculant dose up to a certain level, the removal rates of COD, TOC and turbidity increases. Beyond recorded maximum value of each flocculant, the pollutants removal rates in terms of COD, TOC and turbidity tend to decrease with increasing the flocculant concentration. The upward then downward trend of the pollutants removal rates (Fig. 5) was explained by the fact that the optimal amount of flocculant in the suspension causes the aggregation and sedimentation of a larger quantity of particles while an excessive amount of flocculant would hamper the formation and sedimentation of flocs by increasing the repulsion energy between the flocculant and the particles in solution (Mishra et al., 2005). Results revealed that the optimal conditions for maximum turbidity, COD and TOC removal from SVORW under initial pH of 9 were of about $2 \text{ g}\cdot\text{L}^{-1}$ and $60 \text{ mg}\cdot\text{L}^{-1}$ of FeCl_3 and CHT flocculant CV, respectively. However, under these optimal conditions, residual turbidity, COD and TOC were of about 159.6 NTU, $5270 \text{ mgO}_2\cdot\text{L}^{-1}$ and $2271 \text{ mg}\cdot\text{L}^{-1}$. These values remained above the allowable limits for the discharge of water into the receiving environment required by the Tunisian standard NT 106-002. Hence, it is appropriate to consider a physical treatment such as membrane filtration to refine the final treated wastewater in order to comply with discharge limits or reuse.

3.1.3. Treatment of SORW using membrane filtration

3.1.3.1. Influence of MWCO

The impact of MWCO on the permeate quality, was analyzed to determine the performance and ability of each membrane to remove the contaminants (Salahi et al., 2010) in terms of COD, TOC and turbidity while their removal arises mainly from the removal of free and dispersed oil from the effluent. For these experiments Synthetic Vegetable Oil Refinery Wastewater (SORW) was used. It must be outlined that the oil/water feed emulsion (SORW) was highly loaded with Organic Matter (COD of $11700 \text{ mgO}_2\cdot\text{L}^{-1}$, TOC of $4870 \text{ mg}\cdot\text{L}^{-1}$ with initial turbidity of about 2770 NTU). For MF membranes with pore sizes of $0.22 \mu\text{m}$ and $1.2 \mu\text{m}$, pollution removal rates ranged from 16.9% to 48.2% for COD, from 15.2% to 41.34% for TOC and from 37.6% to 93.4% for turbidity. Permeate analysis showed residual COD, TOC and turbidity ranged from $6060 \text{ mgO}_2\cdot\text{L}^{-1}$ to $9725 \text{ mgO}_2\cdot\text{L}^{-1}$, from $2857 \text{ mg}\cdot\text{L}^{-1}$ to $4130 \text{ mg}\cdot\text{L}^{-1}$ and from 183 NTU to 1727 NTU. These values remain above the allowable limits for the discharge of water into the receiving environment required by the Tunisian standard NT 106-002. As expected, UF membranes was more efficient and for MWCO from 3 kDa to 100 kDa, the removal efficiency of the turbidity was around 100%, indicating the total removal of free oil droplets from the feed Oil/water emulsion

(SORW). It was also observed that the removal rates of COD (ranged from 78.7% to 91.6 %) and TOC (ranged from 80.1% to 89.6 %) all were improved with the decrease of the membrane molecular weight cut off from 100 to 3 kDa. In fact, when the MWCO decreases, the membrane surface charge and the charge density become more and more important in regards to its retention and selectivity (Moritz et al., 2001).

Using a 100 kDa MWCO, residual turbidity, COD and TOC were of about 4.7 NTU, 2495.6 mgO₂·L⁻¹ and 967.7 mg·L⁻¹, respectively. While the MWCO decreased to 3 kDa, residual turbidity, COD and TOC were of about 1.4 NTU, 982.8 mgO₂·L⁻¹ and 508.4 mg·L⁻¹ respectively. As expected, the filtration flux decreased with the decrease of the MWCO: Qu et al. (2014) demonstrate that the reversibility of fouling decreases progressively as pore size of the membrane decreases between 100 and 10 kDa. From these results, UF membrane of 100 kDa give sustainable efficiency with a good rejection (upto 99.8%, 78.7%, and 80.1% removal of turbidity, COD and TOC content, respectively) and the higher permeate flux. Padaki et al. (2015) also confirmed that 100 kDa was more efficient comparing to 20kDa, 30kDa and 100kDa membranes, achieving high rejection (upto 94.1%, 31.6%, 96.4%, and 97.2% removal of TSS, TDS, turbidity and oil and grease content, respectively) with a high permeation flux of 96.2 L·h⁻¹·m⁻².

3.1.3.2. Cross flow Filtration

The pilot-scale unit was operated in batch mode operation where the retentate is fully returned to the feed tank for recycling through the module to treat the SVORW. The contaminant concentration in the feed tank increases steadily with operation time. Because of the operational capability of the pilot plant unit, a volume concentration ratio (VCR) was fixed as the end of the batch experimental runs in agreement with the industrial objectives. The volume concentration ratio is described by Eq (7):

$$VCR = V_0 / V_r = 1 + V_p / V_r \quad (7)$$

where V₀ is the initial feed tank volume and V_r and V_p are the retentate and permeate volumes, respectively. Thus, we studied the influence of the volume concentration factor and of retention efficiency by performing concentration experiments on large volumes (100 L) at constant TMP equal to 1.25 bars (Fig.6).

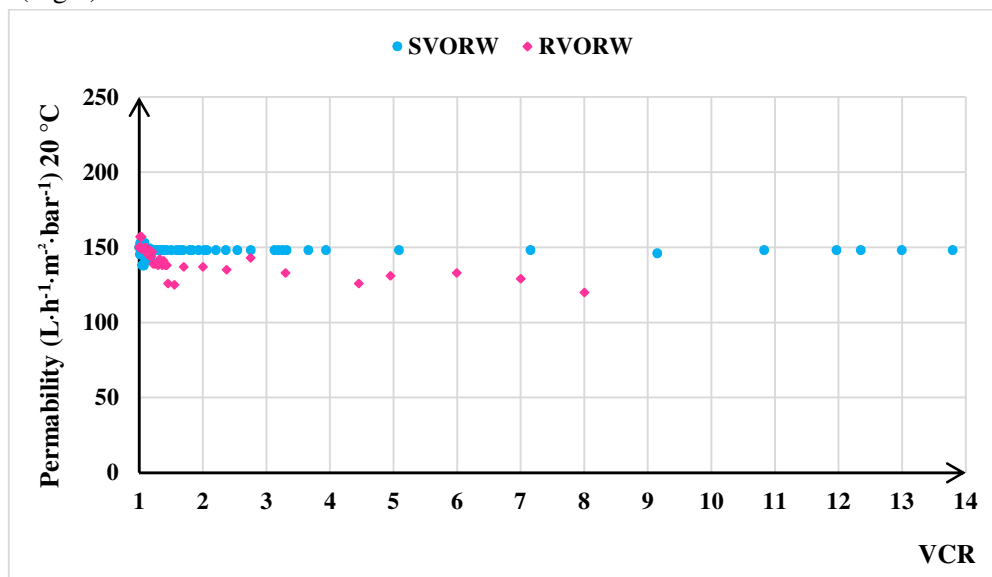


Fig. 6. Variation of membrane permeability as a function of volumetric concentration ratio (VCR) during the direct cross flow UF treatment of SVORW and RVORW.

When the membrane permeability was drawn as a function of the volumetric concentration ratio (VCR), results showed that during the UF treatment of oil-in-water emulsion (SVORW), the membrane permeability after an initial decrease was of about $150 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}\cdot\text{bar}^{-1}$ in the VCR studied, this value was 45% lower than the initial clean water membrane permeability which was of about $280 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}\cdot\text{bar}^{-1}$ (Fig. 6). This decrease was expected because the higher the pollution (suspended solids, COD, TOC, oil) of the initial solution the lower the permeation flux (Gésan-Guiziou et al., 2002).

During the UF process, membrane permeability was quasi-stable as a function of VCR, this was mainly attributed to the membrane fouling that exhibits dual functions while acting as a protective barrier for membrane fouling that it provides additional resistance to permeation (Formentini-Schmitt et al., 2013).

Table 1. Effect of feed concentration on COD, TOC and turbidity removals during cross flow UF treatment of SVORW

COD			TOC			Turbidity		
Feed concentration ($\text{mgO}_2\cdot\text{L}^{-1}$)	Permeate ($\text{mgO}_2\cdot\text{L}^{-1}$)	Removal (%)	Feed concentration ($\text{mg}\cdot\text{L}^{-1}$)	Permeate ($\text{mg}\cdot\text{L}^{-1}$)	Removal (%)	Feed Turbidity (NTU)	Permeate (NTU)	Removal (%)
Raw SVORW								
11700	971.1	91.7	4870	397.88	91.83	2770	7.2	99.74
11680	872.5	92.53	6655	385.99	94.2	3820	2.29	99.94
13420	708.58	94.72	10111	388.26	96.16	5840	1.17	99.98
50200	702.8	98.6	24436	410.52	98.32	10820	4.39	99.96
67400	1408.66	97.91	45536	473.57	98.96	31750	3.17	99.99
Pre-treated SVORW using CF process								
5270	882	85.05	2271	280.47	87.65	159	<1	99.98
8000	823	89.71	2997	420.48	85.97	450	<1	99.79
10500	658	93.73	4358	297.65	93.17	657	1.4	99.78
16380	992	93.94	7308	313.51	95.71	830	<1	99.99
31850	663	97.92	15791	277.92	98.24	880	<1	99.99

Considering turbidity removal efficiency, no significant difference was observed in the whole treatment process and the values were all larger than 99.7 %, while that permeate COD and TOC increased slightly, as the feed suspensions were concentrated, from 91.7% to 98.6% for COD removal and from 91.83% to 98.96% for TOC removal (Table 1). A possible explanation for this increase with concentration factor is that surfactants and other organics were released as droplets coalesced in the growing polarized layer. Low molecular weight organics released in this layer would have easily joined the permeate rather than diffused back into the bulk solution (Lipp et al., 1988). In summary, the cross flow UF treatment of soluble oil-in-water emulsion (SVORW) was able to recover 97% of treated water. In addition, high pollutants retention percentages were achieved, while the mean values of residual turbidity was of about 3.6 NTU (99.8 % removal of turbidity), of residual COD was of about $932.7 \text{ mgO}_2\cdot\text{L}^{-1}$ (92 % removal of COD) and of residual TOC was of about $411.2 \text{ mg}\cdot\text{L}^{-1}$ (91.5 % of TOC). However, COD values of treated SVORW remained well above the permissible limit of $90 \text{ mgO}_2\cdot\text{L}^{-1}$ according to Tunisian standards NT.106.002 (1989) for Public hydraulic discharge as well as for reuse for agricultural purposes (NT.106.003), while there is no requirement regarding Turbidity and TOC values. To improve the permeability or permeate quality after membrane process, it would be necessary to define: (a) a

pretreatment before UF process (such as by coagulation/flocculation) or (b) a permeate post treatment using a membrane filtration. These two proposals are discussed below.

3.1.4. Combination of Coagulation/Flocculation and Cross Flow filtration processes

In effect of CF as pretreatment when combined to UF process, on permeate flux and oil removal (in terms of COD, TOC and turbidity), efficiencies was investigated : permeate quality is increased and membrane fouling is reduced. CF was first carried out at the optimal conditions found (a dose of ferric chloride of $2\text{g}\cdot\text{L}^{-1}$, $60\text{ mg}\cdot\text{L}^{-1}$ of CHT flocculant CV and initial pH of 9). The supernatant was treated by UF. The permeate quality remains controlled by CF efficiency. After CF at optimal conditions found, residual turbidity, COD and TOC were equal to 159.6 NTU, $5270\text{ mgO}_2\cdot\text{L}^{-1}$ and $2271\text{ mg}\cdot\text{L}^{-1}$, respectively.

For UF process of coagulated effluents, the VCR has a little effect on membrane permeability which slowly decreased from $60\text{ L}\cdot\text{h}^{-1}\cdot\text{m}^2\cdot\text{bar}^{-1}$ to $40\text{ L}\cdot\text{h}^{-1}\cdot\text{m}^2\cdot\text{bar}^{-1}$ for VCR of about 3. However, it should be noted that during direct UF of SVORW, the permeability remained stable at a value of about $150\text{ L}\cdot\text{h}^{-1}\cdot\text{m}^2\cdot\text{bar}^{-1}$ which was higher than the permeability values obtained using hybrid process CF/CFF. This probably occurred due to the agglomeration of particles and the presence of very tiny flocs, which during the filtration tests may have accumulated in the membrane pores, causing a more expressive decrease of permeability (Arhin et al., 2017). Other authors also found or studied similar decrease of membrane permeability using hybrid CF/UF process, they explained this behavior by the disparate characteristics of flocs that involved in the feed waters of filtration (Barbot et al., 2008 ; Barbot et al., 2010 ; Listiarini et al., 2009). When oily-water emulsion was pre-treated using CF process, the feed treated water for ultrafiltration contained flocs with different sizes, even after the sedimentation step. Additionally, the flocs remained in the effluents after settling and the settled flocs were supposed to have different densities and fractal dimensions. These properties of flocs have been proved to have marked influences on membrane foulings. Judd and Hillis (2001) also observed the decrease of permeability using coagulation/flocculation as pre-treatment prior to membrane filtration process and explained it by the incomplete coagulation followed by intensive internal pore blockage. Furthermore, Ben-Sasson et al. (2013) suggested another explanation, that when pollutants particles aggregate because of the destabilization flocculation mechanism, the higher removal rate due to the increase in particle size is followed by an increase of the accumulated mass load on the membrane. This higher accumulation rate occurs without significant change to the properties of the components that form the cake. Therefore, while high removal rates will be observed, fouling intensity will increase. Other studies also focused on the relationship between additional coagulant dosage and floc properties on the subsequent membrane performances, which is necessary and of importance meaning (Feng et al., 2015). The percent of COD, TOC and turbidity rejections increased from 85% to 97.9%, 85.65% to 98.2% and 99.98% to 99.99%, respectively, when initial COD values increased from $5270\text{ mgO}_2\cdot\text{L}^{-1}$ to $31850\text{ mgO}_2\cdot\text{L}^{-1}$, TOC increased from $2271\text{ mg}\cdot\text{L}^{-1}$ to $15791\text{ mg}\cdot\text{L}^{-1}$ and Turbidity values increased from 159 NTU to 880 NTU (Table 1). The pretreatment of SVORW by CF process using ferric chloride at a concentration equal to $2\text{g}\cdot\text{L}^{-1}$, CHT flocculant CV at a dosage of $60\text{ mg}\cdot\text{L}^{-1}$ and under initial wastewater pH of 9, has enhanced the UF performances and has provided a good quality of the treated wastewater. COD, TOC and turbidity removals using hybrid process CF/CFF reached 93.13 %, 93.5% and 99.9%, respectively, with residual mean values of about $803.6\text{ mgO}_2\cdot\text{L}^{-1}$ and $318\text{ mg}\cdot\text{L}^{-1}$ for COD and TOC, respectively, as well as a residual turbidity $<1\text{ NTU}$. Other authors also found that UF in post-treatment to CF for wastewater treatment enhance the performances of the treatment (Ellouze et al., 2010).

In terms of pollutant retention, the quality of water samples treated by hybrid process CF/UF was sufficient for discharge, as the final COD value was below the permissible limits according to Tunisian standards. NT 106-002 for public canalization (COD of $1000 \text{ mgO}_2\cdot\text{L}^{-1}$), therefore, CF may be an effective pre-treatment process before using UF treatment.

3.1.5. Combination of membrane filtrations

The effect of membrane filtration as post filtration process during the reclamation of pre-treated SVORW using cross flow UF process was evaluated. Specifically, the permeate of SVORW treatment using a 150 kDa membrane cut-off (UF) has been submitted to a post filtration process in dead-end filtration mode (DEF) using different MWCO membranes : 3-5-10-30-100 kDa. Each membrane was tested based on its efficiency in COD, TOC and turbidity removals. Results are illustrated in Fig.7.

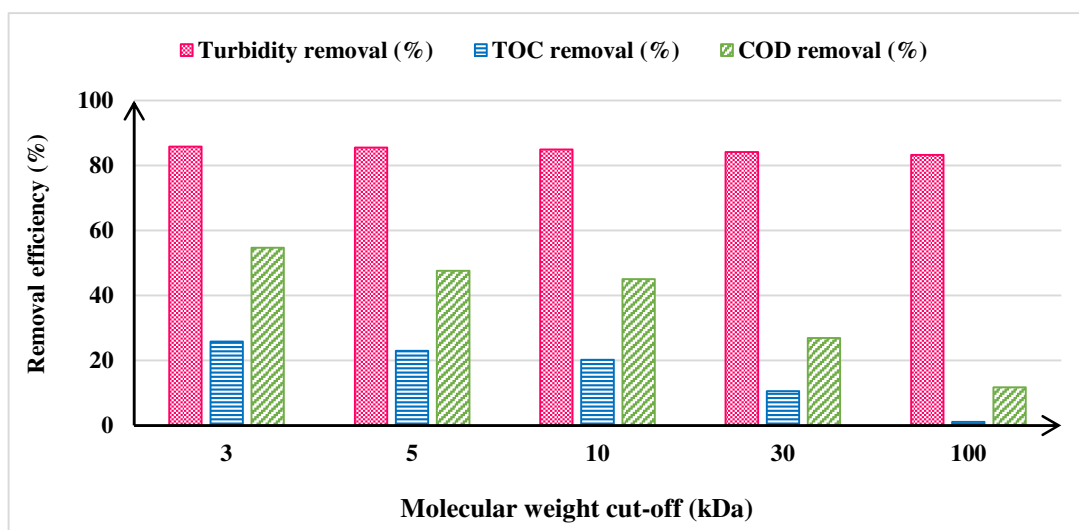


Fig. 7. Performances of DEF process in the retention of COD, TOC and Turbidity of pre-treated SVORW using CFF as function of membrane MWCO.

The effect of the membrane post treatment combined to CFF process was not apparent on COD (11.76 %) and TOC (1.1%) removal rates from SVORW when a membrane with MWCO of about 100 kDa was used. As expected the pollutants rejections increased with the decrease of MWCO of the membrane, COD removal/retention increased from 26.9% to 54.8% when membrane MWCO decreased from 30 kDa to 3 kDa for initial COD of about $932.7 \text{ mgO}_2\cdot\text{L}^{-1}$, similarly TOC retention also increased from 10.6% to 25.8% when membrane MWCO decreased from 30 kDa to 3 kDa for the initial TOC of about $411.2 \text{ mg}\cdot\text{L}^{-1}$. Besides, all the membranes tested achieved a very satisfactory retention of turbidity ranged from 83.3 to 85.8 % for a membrane MWCO of 100-3 kDa respectively generating a permeate with residual turbidity <1 NTU. As expected, membrane filtration applied as a post-treatment to the CFF process has improved the performance of the SVORW treatment compared to its treatment with direct CFF or DEF. Indeed, hybrid membrane filtration processes was able to achieve :

- COD removal rates ranged from 92.9% to 96.4% with residual COD ranged from $823 \text{ mgO}_2\cdot\text{L}^{-1}$ to $422 \text{ mgO}_2\cdot\text{L}^{-1}$. While, COD removal under individually CFF treatment was about 92.02 % with a residual COD of about $932.7 \text{ mgO}_2\cdot\text{L}^{-1}$, whereas, it was of about 55 % using CF with a residual COD of about $5270 \text{ mgO}_2\cdot\text{L}^{-1}$. However, hybrid CF/CFF treatment of SVORW leads to a COD removal of about 93.1% with a mean value of residual COD of about $803.6 \text{ mgO}_2\cdot\text{L}^{-1}$.

- TOC removal rates ranged from 92% (residual TOC of about 406.7 mg·L⁻¹) to 93.7% (residual TOC of about 305 mg·L⁻¹). Under direct CFF treatment, TOC removal reached 91.5 % (residual TOC of about 411.2 mg·L⁻¹), it was about 52.6% using CF process (residual TOC of about 2271 mg·L⁻¹), whereas, the hybrid CF/CFF process leads to a TOC removal of about 93.47% with a residual TOC equal to 318 mg·L⁻¹. Therewith, residual turbidity was of about 159.6 NTU (removal of about 94.2%) using CF process, 3.6 NTU (removal of about 99.9%) under CFF, and a value < 1NTU (removal of about 99.98%) whatever the hybrid process used.

However, regardless the process used (individual or hybrid), the residual COD of all the treated water samples remained above the limit fixed by Tunisian standards for Public hydraulic discharge (NT.106.002) as well as for reuse for agricultural purposes (NT.106.003). This results on synthetic oily wastewater can provide knowledge for choosing the most adhequat scenario and it is considered as preliminary work devoted to Real Vegetable Oil Refinery Wastewater (RVORW) treatment.

3.2. Treatment of Real Vegetable Oil Refinery Wastewater (RVORW)

3.2.1. RVORW characterization

The refinery (mentioned herein as ZOUILA) uses chemical and physical methods for the refining of soybean oil. Fifteen (15) RVORW samplings were collected during 2016–2019 from a local Tunisian edible oil refinery. The main physicochemical industrial influent characteristics are summarized in Table 2. The main pollution load in the RVORW are organic matters responsible for high biochemical and chemical oxygen demands (BOD₅ and COD), turbidity, total suspended solids (TSS) and other chemical parameters like Nitrate (NO₃⁻), ammonium (NH₄⁺), total phosphorus (P), etc. Except the Magnesium, the physicochemical analysis of RVORW revealed that all of the parameters exceed the Tunisian standards (NT.106.002) indicating that the RVORW is highly charged with organic and chemical pollutants and must be treated further before it can be discharged to any receiving water. Analyzed samples for COD in RVORW were characterized with values ranged between a minimum of 3083 mgO₂·L⁻¹ and a maximum of 16033 mgO₂·L⁻¹ with mean value of about 12230 mgO₂·L⁻¹. The estimation of COD is of great importance for water having unfavorable conditions for the growth of micro-organisms, such as presence of toxic chemicals.

Table 2. Vegetable oil refinery wastewater characterization during 2016–2019 (average values of fifteen samples)

Parameters	Min	Max	Mean value	Tunisian Standards	
				NT.106.002 (1989)	NT.106.003 (1989)
pH	12.5	8.22	11	[6.5- 8.5]	[6.5- 8.5]
Conductivity (mS·cm⁻¹)	2.4	4	3.3	-	-
Salinity (g·L⁻¹)	1.4	2.5	1.8	-	-
Turbidity (NTU)	1400	10150	3730	-	-
TSS (mg·L⁻¹)	256	1116	667	30	30
VSS (mg·L⁻¹)	113	903.2	510.8	-	-
COD mgO₂·L⁻¹)	3083	16033	12230	90	90
BDO₅ (mgO₂·L⁻¹)	400	1000	560	30	30
Ammonium (mg·L⁻¹)	20.2	89.5	59.5	1	-
Phosphorus (mg·L⁻¹)	22.7	65	22.5	0.05	-
Phosphate (mg·L⁻¹)	116	2160	662	0.05	-

Nitrogen (mg·L⁻¹)	21	72	32	1	-
Nitrate (mg·L⁻¹)	1.1	169.7	31	50	-
Nitrite (mg·L⁻¹)	0.2	79.5	9.1	0.5	-
Sulfate (mg·L⁻¹)	91.6	428.5	186	600	-
Chloride (mg·L⁻¹)	97.7	3072.35	645.3	600	2000
Oil & grease (mg·L⁻¹)	1430	3750	2420	20	-
Calcium (mg·L⁻¹)	136	212	177	500	-
Potassium (mg·L⁻¹)	34	107.1	79.3	50	-
Sodium (mg·L⁻¹)	436	1417	933	300	-
Magnesium (mg·L⁻¹)	29.5	103.4	80.4	200	-

(-): Not determined

Evaluating the ability of the RVORW to biodegrade has a vital interest to determine the choice of method of treatment (biological or physicochemical treatment). According to the data from Table 2, the COD/BOD₅ ratio is ranged between 7.7 and 49.5 with mean ratio of about 23.5, which is normally above 5 indicating the presence of poorly biodegradable substances that explained the aim of this study.

Total suspended solid (TSS) in vegetable oil refinery effluents may originate from emulsified fats and oils and soaps (Niewiadomski et al., 1995). The nature of these sources makes them predominantly organic. The RVORW samples studied in this investigation are highly loaded suspended solids with mean values ranged from 256 to 1116 mg·L⁻¹ and a very high turbidity ranged between 1400 and 10150 NTU with mean value of about 3730 NTU. The obtained results were compared with other studies and showed some similarities (Aslan et al., 2009 ; Ben-Sasson et al., 2013). According to the data from Table 1, residual Oil released from the refining process is the main responsible of the organic load, this latter was ranged from 1430 mg·L⁻¹ and 3750 mg·L⁻¹ with mean value of about 2420 mg·L⁻¹. Additionally, heavy metals (not mentioned in the table 1) (cadmium (Cd), Cobalt (Co), chromium (Cr), copper (Cu), manganese (Mn), nickel (Ni), plumb (Pb), and thallium (Tl)) were detected as trace metals in RVORW samples.

3.2.2. Coagulation/flocculation treatment of RVORW

In our previous work (Louhichi et al., 2019), the influence of pH, coagulant nature and concentration and flocculant dosage on removal of turbidity and COD from RVORW was studied. Further optimization of CF was investigated using Response Surface Methodology via Box Behnken Design. The results obtained from the regression equations revealed that the maximum removal of turbidity (100%) and COD (99%) were obtained for Al₂(SO₄)₃ concentration of 2.4 g·L⁻¹, flocculant (CHT) dosage of 60.05 mg·L⁻¹ and initial wastewater pH of 9.23. This approach was used to treat a large volume of RVORW in order to prepare a sufficient amount of CF-treated wastewater to undergo membrane post-treatment (100L). A detailed characterization of raw and treated RVORW under optimal conditions of CF process are illustrated in Table 3.

Table 3. Physico-chemical characterization of raw and treated RVORW under optimal conditions of CF treatment

Parameters	Raw RVORW	Treated RVORW using CF	Removal (%)	NT 106.002 (1989)	NT 106.003 (1989)
pH	10.2	7.5	-	[6.5 – 8.5]	[6.5 – 8.5]
Color	0.9	0	100	-	-
Salinity (g·L⁻¹)	2.7	3.5	-	-	-
Turbidity (NTU)	4090	10	99.75	-	-
TSS (mg·L⁻¹)	1720	17.98	98.95	30	30

COD (mgO₂·L⁻¹)	14200	524	96.31	90	90
BOD₅ (mgO₂·L⁻¹)	300	75	75	30	30
COD/ BOD₅	51	1.6	-	-	-
TOC (mg·L⁻¹)	2017	351	82.6	-	-
Ammonium (mg·L⁻¹)	89.5	35.7	60.1	1	-
Sodium (mg·L⁻¹)	1417.4	1183.4	16.51	300	-
Potassium (mg·L⁻¹)	107	32.5	69.6	50	-
Calcium (mg·L⁻¹)	136.5	72	47.2	500	-
Magnesium (mg·L⁻¹)	108	42	61.1	200	-
Nitrates (mg·L⁻¹)	1.02	0.71	30.4	50	-
Nitrogen particulate (mg·L⁻¹)	10	0	100	1	-
Phosphorus (mg·L⁻¹)	54	2.18	95.96	0.05	-
Chloride (mg·L⁻¹)	162	170	-	600	2000
Sulfate (mg·L⁻¹)	102	154	-	600	-
Aluminum (mg·L⁻¹)	0.8	0	100	5	-
Iron (mg·L⁻¹)	0.41	0	100	1	5
Zinc (mg·L⁻¹)	0.2	0	100	1	5

(-): Not determined

According to the data from Table 3, treatment of RVORW using CF process under the optimal conditions (Louhichi et al., 2019) was able to eliminate 96.3% of COD, 82.6% of TOC and 99.75 % of turbidity with an obtained volume of CF-treated RVORW of about 800 mL·L⁻¹; whereas, the volume and the wet mass of the obtained sludge were of about 200 mL·L⁻¹ and 41.9 g·L⁻¹: the pollutants removal rates found are consistent with the results obtained in our previous work. These results show that the CF process in use for RVORW treatment is inefficient, particularly in the removal of organic contaminants responsible for BOD₅ and COD. Typically, the oil droplets in wastewater can be divided into three forms: free oil, dispersed oil and emulsified oil. Free oil with droplet sizes larger than 100 mm and dispersed oil with a size range of 10-100 mm can be removed by conventional methods, such as CF (Coca et al, 2011). However, this method is inapplicable for separation of emulsified oil which is stabilized by surfactant resulting in a stable emulsion with a droplet size smaller than 10 mm. Based on size exclusion, membranes can retain almost all substances/ oil droplets larger than their pore sizes and thus possess desirable separation efficiency (Zhu et al., 2014). However, it is efficient for removal of suspended solids (98.95%), Potassium (69.6%), Nitrogen particulate (100%), Calcium (47.2%) and Phosphorus (95.96%). It is to highlight that the concentration of the most of physicochemical parameters measured was much beyond the permissible limits prescribed by Tunisian standards for Public hydraulic discharge for Public hydraulic discharge (TN.106.002) as well as for water reuse in agriculture (TN.106.003).

3.2.3. Treatment using membrane filtration

3.2.3.1. Effect of the MWCO

The effect of the MWCO for RVORW treatment under similar operating conditions was discussed using different membrane sizes, i.e. 1.22µm, 0.45µm, 0.22µm (MF membranes) and 500 kDa and 100 kDa (UF membranes). DEF was introduced to predict the most adequate membrane pore size in terms of removal of organic and suspended pollutants from RVORW (Bourgeois et al., 2001). According to Fig 8-A, all membranes used have shown a high efficiency in the removal of pollutants from the ROVRW. The turbidity removal efficiencies were between 97.4% when the MF membrane with 1.22 µm pore size was used and 99.9% when the UF membrane with MWCO of 100 kDa was investigated. Furthermore,

the removal of organic pollution from RVORW expressed in terms of COD and TOC ranged respectively from 87.7-96,7 % and 81-92% % for MF (1.2 μ m) and UF (100 kDa) membrane. In addition, the pore size of the membrane decreases, the efficiency of oil and pollutants removal increases in the permeate due to membrane pore blockage and formation of the more and more thicker cake layer (as a function of the decrease in pore size) on the membrane surfaces, where the oil drops and pollutants find it difficult to cross the surface of the membranes because they were picked up by this layer and they did not allow to pass through the sediment pores (Hua et al., 2007 ; Loh et al., 2015) (Figure 8). Padaki et al. (2015) also found that UF membranes having molecular weight cut-off ranged between 100 kDa and 200 kDa showed the best performance comparing to MF membranes for mineral oily wastewater treatment. These results are also in fairly good agreement with those previously reported study in the DEF essays of treatment of SVORW.

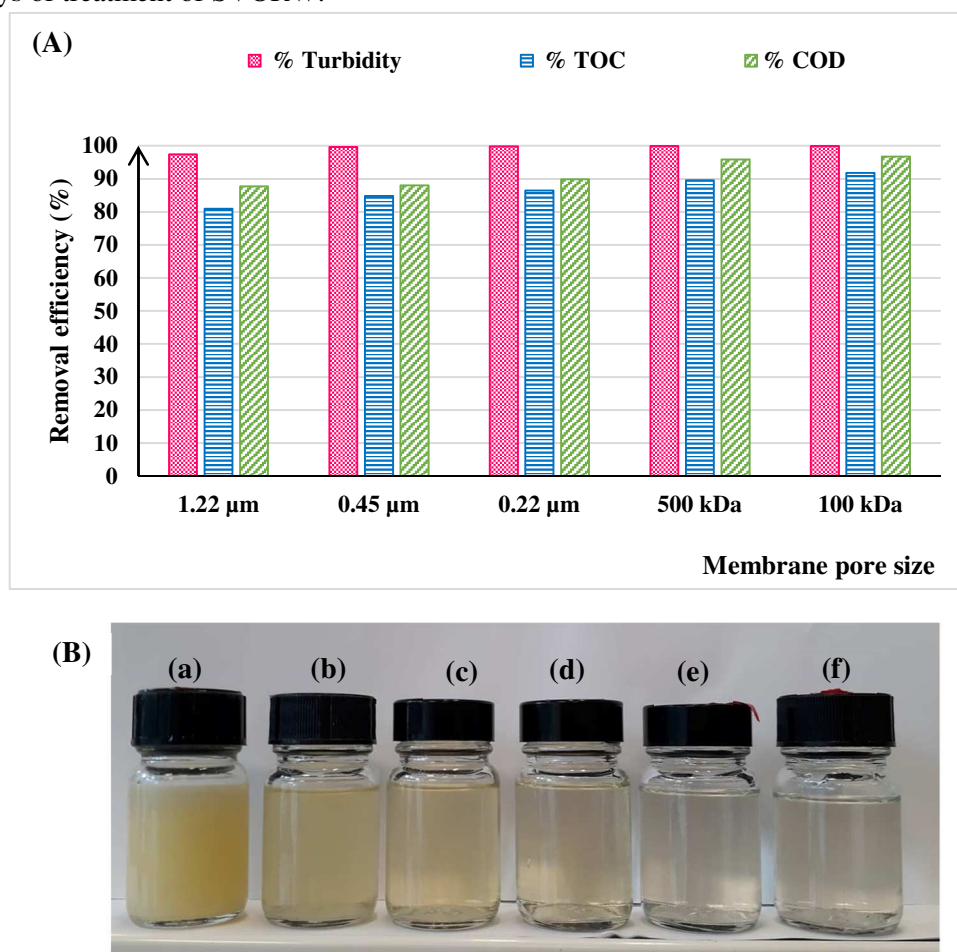


Fig. 8. (A) Performance of DEF in the treatment of RVORW (a) using different membrane sizes: (b) 1.22 μ m, (c) 0.45 μ m, (d) 0.22 μ m, (e) 500kDa and (f) 100kDa. (B) The picture for the permeate of each of the membranes used for RVORW under DEF mode.

3.2.3.2. Cross flow filtration (CFF)

In agreement with these results, in order to evaluate the efficiency of ultrafiltration for oil and pollutants removal from RVORW, a bench-scale experiment was carried out using 0.245 m² UF (150 kDa) module in cross-flow mode at a flow rate of 3000 L \cdot h⁻¹ and a trans-membrane pressure (TMP) of 1.2 bar. As indicated by Fig. 6, two trends were observed: initially, the permeability was decreased very sharply

then it stabilized. During first step, the permeability dropped from an initial value of $150 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}\cdot\text{bar}^{-1}$ to $120 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}\cdot\text{bar}^{-1}$ (VCR of about 3): in agreement with the SVORW results. This may be due to the blockage of the top portion of the UF membrane pores and to the cake formation over the membrane surface (Jönsson and Trägårdh, 1990). It is to highlight that when the initial colloidal layer was formed, it became a dominant factor of the permeability, in fact, the increase of the colloidal layer leads to permeability decline. For higher VCR values above 3, the UF membrane permeability was quasi-stable at a value of about $120 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}\cdot\text{bar}^{-1}$. The recorded pattern of permeability during the treatment of oily wastewater (RVORW) is typical for an UF process (Ghidossi et al., 2009), and it results from both fouling and concentration polarization (Jönsson and Trägårdh, 1990). High efficiency in the removal of pollutants from the ROVRW are obtained (Figure 9 a-b-c): the turbidity removal efficiency was equal to 99.9% whatever the VCR; COD and TOC removals efficiency ranged respectively from 95.3-98.6% and from 95.8-98.8%. The volume ratio is divided by a factor 25 and several studies showed that the concentrate may contain until 50% of oil (Gryta et al., 2001) and can be further separated and concentrated by centrifugation and either incinerated to recover energy or it could be collected and made into useful products such as soap production. In our case, the reuse of recovered oils for soap production will be adopted by ZOUILA company. The characterization of recovered oils in the UF retentate was performed and compared to that of refined soybean oil in order to determine if they have compositions allowing them to be recycled in the soap production process. Additional drying of the retentate was performed and the oil samples were subjected to GC analysis in order to determine whether the vegetable oil compositions has been changed after UF process. For this purpose, the retentate has been chosen for the GC analysis while the percentage values obtained for each sample were compared to the fatty acid percentage ranges defined for Soya oil in the codex (Table 4) (Uncu et al., 2017).

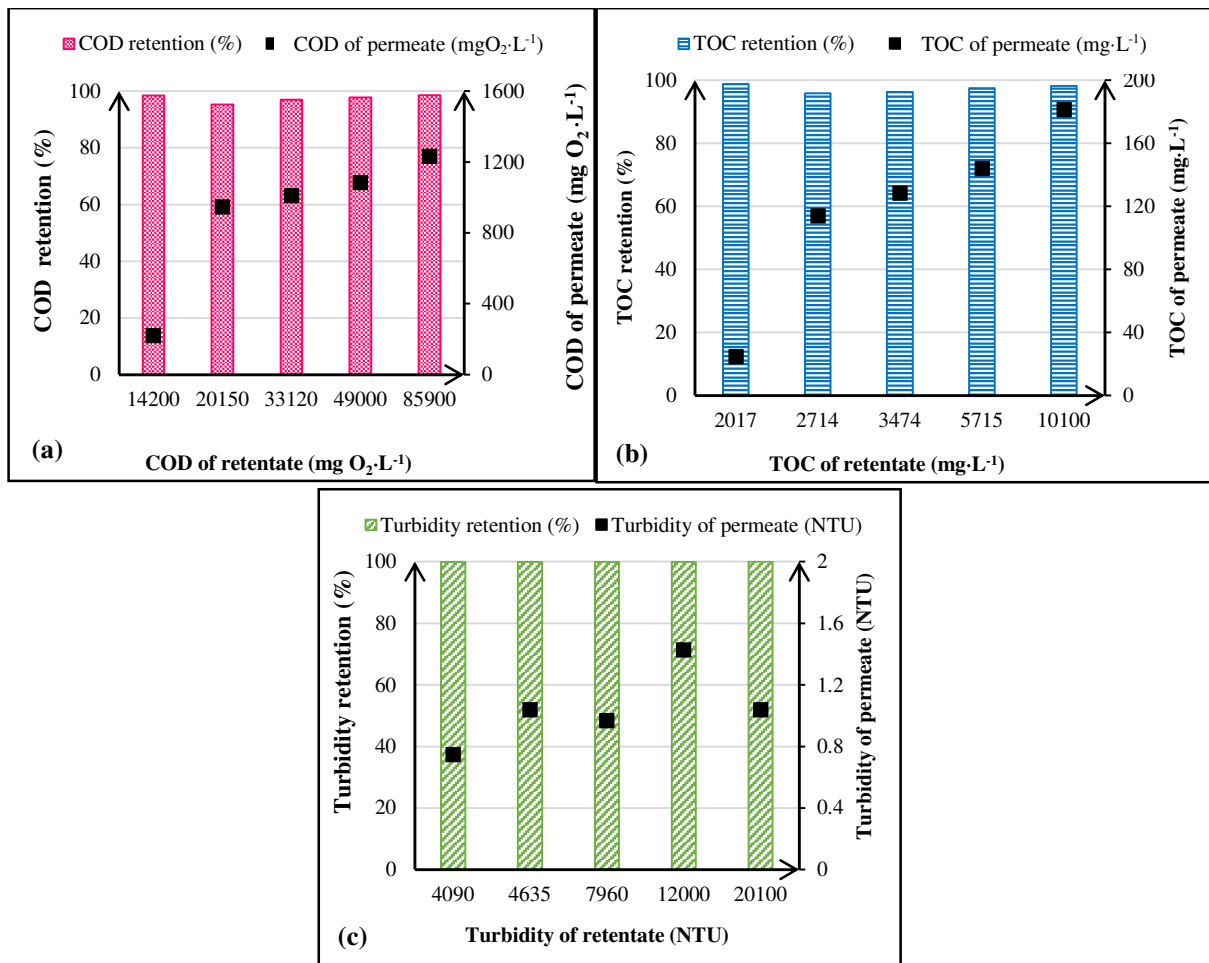


Fig. 9. Effect of feed concentration on COD (a), TOC (b) and turbidity (c) removals from RVORW treated using CFF process.

Soybean oil is a major source of the five essential fatty acids for humans (palmitic, stearic, oleic, linoleic, and linolenic acids). It is composed of approximately 16.6% saturated fatty acids (palmitic [C16:0] and stearic [C18:0]), 23.3% monounsaturated fatty acids (oleic [C18:1]), and 59.1% polyunsaturated fatty acids (linoleic [C18:2] and linolenic [C18:3]). Similar percentage of these major five fatty acids were obtained in the retentate obtained after CFF treatment of RVORW, which prove that direct cross flow UF treatment was efficient in successful oil-water separation without being destructive to the nature of oil. These results are consistent with those found by Firestone (1999). A part from treatment and purification of the oily wastewater (RVORW), the present investigation demonstrates the possibility of effective reuse of retentate as an additional value through ultrafiltration since the oil contained in the retentate has the same composition as the raw oil. Therefore, this study clearly shows that the oily fraction contained in the retentate is suitable for reuse in soap production at ZOUILA but the mean value of residual organic matter was equal to 898 mgO₂·L⁻¹ and remained above the permissible limit of 90 mgO₂·L⁻¹ of COD according to Tunisian standards NT.106.002 (1989) for Public hydraulic discharge. Therefore, maximum removal of organic pollutants from oily wastewater (such as from RVORW) in order to be in accordance with the standards may be achieved by the application of a pre-treatment process as upstream to UF (i.e. the hybrid CF/UF process).

Table 4. Major fatty acid and *trans* fats content in retentate oils recovered during UF treatment of RVORW.

Composition in fatty acid and trans fats (%)	Retentate (VCR=11)	Edible oil	Codex Norm
Myristic acid (C14:0)	0.1	0.081	ND-0.2
Palmitic acid (C16:0)	14.25	11.060	8-13.5
Palmitoleic acid (C16:1)	0.12	0.114	ND-0.2
Heptadecanoic acid (C17:0)	0.13	0.098	ND-0.1
Heptadecenoic acid (C17:1)	0.05	0.044	ND-0.1
Stearic acid (C18:0)	6.32	4.184	2.0-5.4
Trans fatty acid (C18:1)	0.02	0.025	-
Oleic acid (C18:1)	27.88	22.855	17-30
Trans fatty acid (C18:2) + (C18:3)	0.03	0.081	-
Linoleic acid (C18:2)	45.13	53.786	48.0-59.0
Arachidic acid (C20:0)	0.50	0.295	0.1-0.6
Linolenic acid (C18:3)	5.24	7.205	4.5-11.0
Gadoleic acid (C20:1)	0.22	0.170	ND-0.5

(-) : Not determined

3.2.4. Combination of Coagulation/Flocculation and cross flow filtration processes

During our previous study, the CF process used alone demonstrated an efficiency for the RVORW treatment under optimal conditions (Coagulant concentration of $2.4 \text{ g}\cdot\text{L}^{-1}$, flocculant dose of $60 \text{ mg}\cdot\text{L}^{-1}$ and initial RVORW pH of 9). However, when the RVORW was treated with CF process, results demonstrated that this process applied alone is insufficient to produce acceptable water, so advanced treatment, like membrane separation using UF process, is needed as post-process to reach good water quality (Gao et al., 2011). Treated CF- RVORW was ultrafiltered to the ceramic membrane filtration unit using a bench-scale experiment with 0.245m^2 UF (150 kDa) module in cross-flow mode and a trans-membrane pressure (TMP) of 1.25 bar in the mode of recycling retentate and removing permeate.

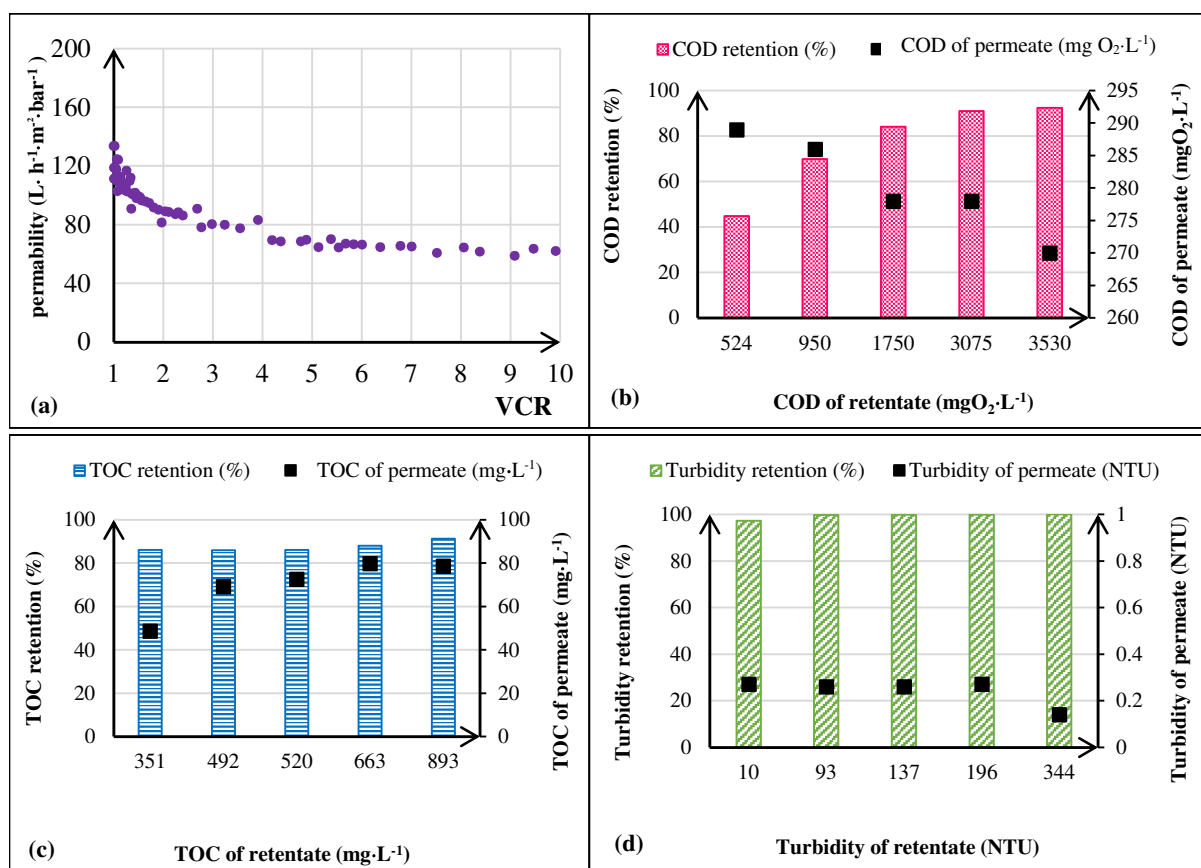


Fig. 10. Effect of feed concentration on membrane permeability (a) and on COD (b), TOC (c) and turbidity (d) removals from RVORW treated using hybrid CF/UF process.

Membrane permeability dropped sharply from initial value of $135 L \cdot h^{-1} \cdot m^{-2} \cdot bar^{-1}$ then stabilized at a value close to $60 L \cdot h^{-1} \cdot m^{-2} \cdot bar^{-1}$ with increasing feed concentration. In agreement with the results obtained for synthetic solution, it was found that CF of RVORW as pre-treatment application did not improve the membrane permeability comparing to direct ceramic UF membrane. In fact, for both cases, the permeability decreased to reach stabilised values which is lower for hybrid CF/UF process than for direct CFF. This could be due to the presence of some amount of aluminum sulfate (and/or CHT-flocculant-CV) in the pre-treated RVORW solution using CF process, these salts may concentrate near the UF membrane surface due to polarization effects triggering a secondary flocculation over and near the membrane surface which may affect the membrane permeability (Stoller et al., 2009). According to Fig 10 b-c-d, when UF was applied to RVORW pre-treat using CF process under optimal conditions, COD removal (compared to COD of coagulated RVORW solution) was ranged from 44.8 to 92.5%. This indicates that the COD removal efficiency by using UF as post-treatment to CF process was significantly increased with the increase of VCR. Moreover, UF when applied as post-treatment to CF process showed a significant TOC removal efficiency ranged from 85.9% to 91.2 with a very effective turbidity removal ranged from 97.3% to 99.9%. The CF/UF permeate was characterized by a neutral pH, a residual turbidity <1 NTU (conform to the permissible limit fixed by Tunisian standards), a mean value of residual COD of about $280 mg O_2 \cdot L^{-1}$ which remains above the permissible limit fixed by Tunisian standards ($90 mg O_2 \cdot L^{-1}$) and a mean value of residual TOC of about $69.7 mg \cdot L^{-1}$. As expected, the hybrid CF/UF process applied to treat RVORW showed that the permeate quality was increased when compared with individually CF and UF operated processes with a sustainable flux. Using the

hybrid CF/UF process, removal rates of over 97% were achieved for most of the parameters measured in the obtained permeate.

In deed, COD removal under individually CF treatment was about 96.3% with a residual COD of about 542 mgO₂·L⁻¹, whereas it was in the order of 93.67% only using direct UF with a residual COD of about 898 mgO₂·L⁻¹. However, hybrid CF/UF treatment of RVORW leads to a COD removal of about 98% with a residual COD of about 280 mgO₂·L⁻¹. Similarly, TOC removal under individually CF treatment was about 82.6% (residual TOC of about 351 mg·L⁻¹), it was about 94% using direct UF (residual TOC of about 118.4 mg·L⁻¹), whereas, the hybrid CF/UF process leads to a TOC removal of about 97% (residual TOC equal to 69 mg·L⁻¹). Likewise, mean values of residual turbidity were of about 10 NTU using CF treatment (removal rate of about 99.75%), value of turbidity of about 1.05 NTU using direct UF (removal rate of about 99.98%) and < 1 NTU using hybrid CF/UF process (removal rate of about 100%). The performance evaluation of the coupling of CF to UF showed that the hybrid CF/UF process has improved dramatically the treated effluent water quality when compared to that obtained when CF and UF were individually operated. These finding were also raised by Vuppala et al., (2017) during the treatment of olive oil mill wastewater (OMW). They revealed that the hybrid CF/UF process provided better results regarding the removal of organic compounds (73% and 58% removals of COD and TOC, respectively) when compared to direct CF treatment of OMW (35% and 28% removals of COD and TOC, respectively). These findings are also consistent with those found by Almojjly et al. (2019) which proved that the CF as pre-treatment process enhance the performance of membrane filtration applied for the treatment of oily wastewater (Almojjly et al., 2019).

Furthermore, the hybrid CF/UF process performance levels recorded in our study (COD removal of about 98% with a residual COD of about 280 mgO₂·L⁻¹) were more important than those found by Azbar and Yonar (2004) during the VORW treatment who registered only 88% of COD removal with a residual COD of about 1650 mgO₂·L⁻¹ (COD of raw VORW of about 13750 mgO₂·L⁻¹) using a hybrid lab-scale CF/DAF process. These findings show that UF process combined with CF as pretreatment is more efficient than the use of DAF coupled with the CF technique for better organic matter removing during the treatment of VORW.

3.2.5. Combination with membrane filtrations

Despite the efficiency of ultrafiltration treatment coupled or not with a CF process, pollutants contents of treated effluent remained above the values fixed by Tunisian standards for water discharge into receiving environment NT 106.002. So a post membrane was investigated on permeate using Dead End Filtration (DEF) with flat membrane with MWCO of about 1-10-30- 100 kDa. The proposed hybrid CFF/DEF process was employed for treatment of the industrial wastewater (RVORW). The treated wastewater by the integrated membrane processes has the same quality than the permeate of a single CFF process. Indeed, the removal of COD (ranged from 93.7% to 97.2%) and TOC (ranged from 94.1% to 95.4%) as well as turbidity (99.97%) of the hybrid CFF/DEF permeate are compared to those obtained with direct CFF process (permeate COD, TOC and turbidity removals of about 93.7%, 94.1% and 99.97%, respectively). These findings reveal that the COD, TOC and Turbidity retentions took place mainly during the treatment of RVORW using direct CFF process where the major suspended matter and organic load were removed prior to DEF process regardless the MWCO used.

In the case of coupling CFF with the post-treatment using membrane (DEF) and/or pretreatment using CF makes it possible to obtain the results tabulated in Table 5. This table makes it possible also to compare all the treatments. Based on table 5, results showed that when the RVORW has been treated

by CF process used alone or combined with the membrane processes (hybrid CF/CFF process and hybrid CF/CFF/DEF process) the pH values were in accordance with the Tunisian standards for Public hydraulic discharge (NT.106.002) than those for reuse in irrigation (NT.106.003). So, we can conclude that membrane processes did not significantly influence the pH values of the treated RVORW which is in agreement with the results of Di Lecce et al. (2014). Furthermore, when the CF Process was combined with membrane filtration, the hybrid processes (CF/CFF and CF/CFF/DEF) applied to the treatment of RVORW were able to remove the wastewater turbidity with final values <1 NTU. According to table 5, results reveal that the treated wastewater by the integrated CF/CFF and CF/CFF/DEF have the better quality than those obtained using the other single CF, CFF and DEF processes as well as the hybrid CFF/DEF process. Thus, the significant effect of CF prior to membrane filtration was observed through this study. The treated RVORW has final COD and TOC of about 250 mgO₂·L⁻¹ and 40.2 mg·L⁻¹, respectively, under hybrid CF/CFF/DEF process and about 280 mgO₂·L⁻¹ and 69.7 mg·L⁻¹, respectively, under hybrid CF/CFF process. Hybrid CF/CFF process is efficient in term of the removal of the total amounts of organic and chemical pollutants. A post filtration is not necessary or perhaps can be used with a small MWCO but in this case the operational costs will strongly increases. Nevertheless, COD of permeates remained non-compliant with the Tunisian standards for Public hydraulic discharge (NT.106.002) as well as for reuse for agricultural purposes (NT.106.003).

Table 5. Physico-chemical characterization of raw and treated VORW using direct CF, DEF and CFF processes as well as hybrid CF/CFF, CFF/DEF and CF/CFF/DEF processes.

	Raw RVORW	CF	DEF (100 kDa)	CFF	CF / CFF	CFF/ DEF	CF /CFF/ DEF	NT 106.002 (1989)	NT 106.003 (1989)
pH	10.2	7.5	9.62	10.1	7.3	10	7.15	[6.5–8.5]	[6.5 - 8.5]
Turbidity (NTU)	4090	10	2.08	1.05	<1	<1	<1	-	-
COD (mgO ₂ ·L ⁻¹)	14200	524	467	898	280	466	250	90	90
TOC (mg·L ⁻¹)	2017	351	166	118	69.7	100.3	40.22	-	-
Ammonia (mg·L ⁻¹)	89.5	35.7	1.8	0.98	0.94	0.95	0.87	1	-
Sodium (mg·L ⁻¹)	1417.4	118 3.4	373.3 2	372.5	321.35	329.4	316.87	300	-
Potassium (mg·L ⁻¹)	107	32.5	24.03	29.4	16.26	18.53	15.23	50	-

(-): Not determined

3.3. Evaluation of the phytotoxicity of treated Real Vegetable Oil Refinery Wastewater (RVORW)

Even after integrated treatment, RVORW can be still toxic for environment. One of the ways to assess the degree of toxicity of wastewater, apart from the determination of the physical and chemical indicators is the toxicity test (da Costa Filho et al., 2016). Currently, tests based on plant bioindicators are often recommended as an effective and affordable method of assessing the toxicity (Placek et al., 2016) with a sensitivity similar to tests using mammalian cells (Obidoska et al., 2015). Seed germination of lettuce (*Lactuca sativa*) was used to evaluate the feasibility reuse of treated wastewater in irrigation. The seed germination index (GI) is a good indicator for phytotoxicity (Brewer et al., 2003). The

phytotoxicity of the raw and treated RVORW after treatment using the CF, CFF, hybrid CF/CFF and hybrid CF/CFF/DEF processes was evaluated during this investigation by measuring and calculating the relative seed germination (RSG), relative root growth (RRG) and germination index (GI) of lettuce seeds within 7 days (Fig.11).

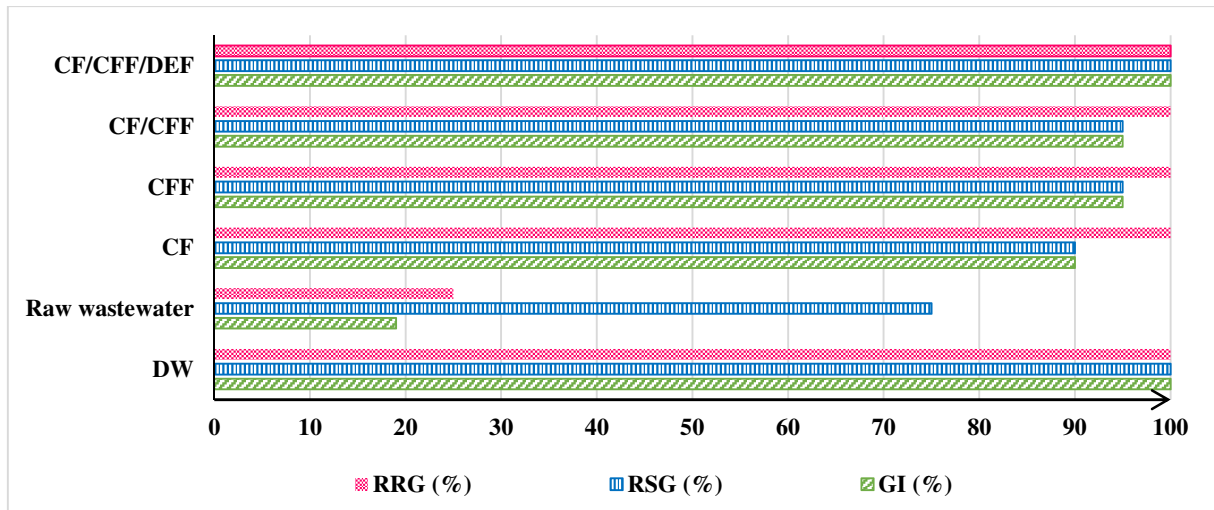


Fig.11. Germination indices of *Lactuca sativa* seeds under raw and treated RVORW using direct (CF and CFF) and hybrid (CF/CFF and CF/CFF/DEF) processes.

According to Fig.11, results showed that the germination index (GI) for raw RVORW was 19% while seed germination of the treated wastewater was 90%, 95%, 95% and 100%, respectively, for CF, CFF, hybrid CF/CFF and hybrid CF/CFF/DEF treatment. According to Abdullahi et al. (2008), a seed GI greater than 70% is considered non-phytotoxic, while a GI of less than 70% is considered phytotoxic. Hence, the results indicate strong phytotoxicity to plants of the raw (Al-Qahtani et al., 2011). However, seeds irrigated with treated RVORW using the CF, CFF, hybrid CF/CFF and hybrid CF/CFF/DEF treatments has higher germination rates than raw wastewater. Our results demonstrate clearly the beneficial effect of the physical and chemical RVORW treatments on seed germination of *Lactuca sativa* (GI>70%). Based on the GI, hybrid CF/CFF/DEF was the most effective process in the removal of all of the toxicity of the RVORW (similar that distilled water (DW)). Furthermore, in addition to GI, we analyzed the relative seed germination (RSG) and relative root growth (RRG) to see the effect of the raw and treated RVORW on seed germination and root growth of lettuce. Both RSG and RRG were improved to reach 100% for treated RVORW using the hybrid CF/CFF/DEF process compared to the low levels in the raw RVORW (75% and 25%, respectively). The RSG in RVORW treated using CFF and hybrid CF/CFF were similar (95%). It was equal to 100% in RVORW treated using hybrid CF/CFF/DEF and comparable to the RSG in the control (Distilled water). The RRG in all treated RVORW were equal to 100% and were also comparable to the RRG in the control. On the basis of these findings, phytotoxicity assessment of oily wastewater reported that raw RVORW has an inhibitory effect on the seed germination and growth parameters of *L. sativa*; therefore, its direct application in the agricultural field is not recommended and treatment using CF, CFF, hybrid CF/CFF and especially the hybrid CF/CFF/DEF process were suitable for application to agriculture without taking precautions.

4. Conclusion

The adverse impact of highly polluted oily wastewater as well as scarcity of water resources in many regions around the world has driven many researchers and scientists toward developing useful techniques and approaches to produce treated waters of a quality suitable for reuse and recycling. The present study highlights the efficiency of a hybrid process for suitable VORW treatment through which contaminants such as oil, grease, organic and inorganic pollutants can be removed for safe applications. Comparative performance evaluation of direct (CF,UF and DEF) and hybrid (CF/UF,UF/DEF and CF/UF/DEF) treatment processes was performed on SVORW to identify the best conditions to perform with RVORW treatment. The screening of membranes with different MWCO performed on DEF mode revealed that the best treatment performance in terms of turbidity (99.95%), COD (91.8%) and TOC (96.7%) removals were obtained using dead-end UF membrane with MWCO of 100 kDa. The bench-scale experiment carried out using a commercial ceramic 0.245 m² UF membrane (150 kDa) in CFF mode at a flow rate of 3000 L·h⁻¹ and a transmembrane pressure (TMP) of 1.2 bars, demonstrated that the UF was able to remove 99.97%, 93.7% and 94.1% of turbidity, COD and TOC respectively. Whereas, mean residual COD, TOC and turbidity values were of about 898 mgO₂·L⁻¹, 118 mg·L⁻¹ and 1.05 NTU, respectively. These values remained above the allowable limits for the discharge of water into the receiving environment (NT 106.002) as well as for water reuse in agriculture (NT 106.003). Otherwise, permeability remained stable at a value close to 150 L·h⁻¹·m⁻²·bar⁻¹ as a function of the VCR, suitable for application in industrial scale membrane process. To enhance the UF performances, CF was used as pre-treatment prior to UF under optimal conditions (2.4 g·L⁻¹ of aluminium sulfate, CHT flocculant CV= 60.05 mg·L⁻¹ at pH = 9.23). The hybrid CF/UF process has improved the treated VORW water quality by significantly enhancing turbidity, COD and TOC removals reaching 100%, 98% and 97%, respectively, compared to direct CF and UF used separately. However, the CF pre-treatment was useless from the standpoint in reducing membrane fouling and did not improve the membrane permeability (135 L·h⁻¹·m⁻²·bar⁻¹) compared to that achieved with direct UF (150 L·h⁻¹·m⁻²·bar⁻¹). Nevertheless, for both cases (direct UF and hybrid CF/UF), the membrane permeability was in agreement with an industrial application and the decrease can be explained by the flux structure (barbot et al., 2010). Moreover, further DEF as post treatment (hybrid CF/UF/DEF process) did not improve the final quality of the treated VORW water. These findings on treated VORW water quality and membrane performance strongly suggest that the hybrid CF/UF process is the promising option to realize water resource recovery and pollution removal even though it does not offer the advantage for vegetable oil recovery and valorization.

Overall, the obtained results can be useful for the development and performance optimization of industrial installation to treat and reuse vegetable oil refinery wastewater using a hybrid CF/UF process as feasible, safer and more environmentally friendly alternative to other available treatment options.

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SVORW



Soya oil

RVORW



Direct DEF



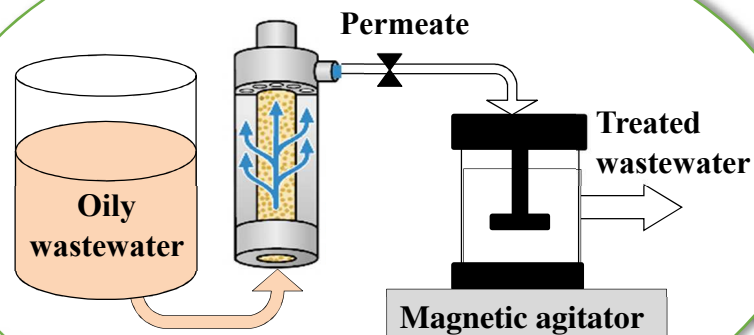
Direct CFF



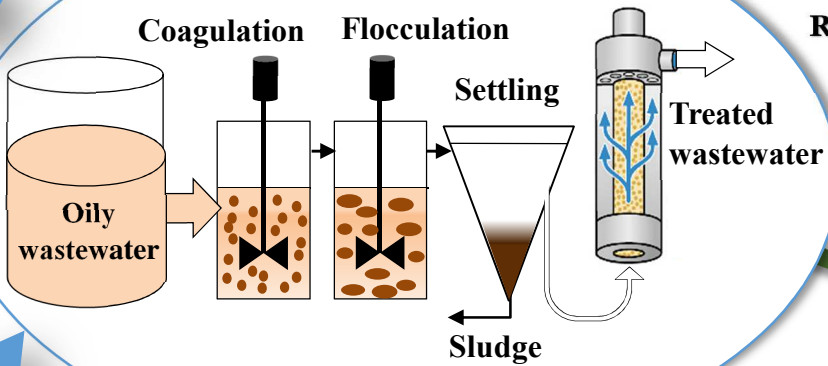
Direct CF



Hybrid CFF/DEF



Hybrid CF/CFF



Oil recovery



Water Reuse/Recycle



Environmental Protection