

# Treatment of Textile Industry Wastewater by Sequential Hybrid Processes Photo-Fenton, Ultrafiltration (UF), Reverse Osmosis (RO) and Recovery of some Dyes, Salt and Perfluoroalkyl Sulfonate from the Retentate

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## ABSTRACT

Textile industry waste water should be treated by best available and economical hybrid treatment techniques (BAT) to achieve the discharge limits (ELV) set by European Union, and reuse them as process or irrigation waters. Recovery of some valuable materials/chemicals and reuse of treated waste water is a European Union Directive (European Commission). When the industrial wastewaters are not treated by the best available techniques, it is not possible to reuse the water and recover some valuable chemicals. Therefore, in this study a sequential photo-Fenton/UF/RO process was used to treat the COD, COD-dis, DOC, colour salt and reuse of treated textile wastewater and recovery of some economical merits from the retentate of the RO (dyes, salt and perfluoroalkyl sulfonate). The photo-Fenton experiments were carried out in a cylindrical pyrex thermostatic module with a volume of 2,5 L, 1,8 L textile wastewater and 2 mg/l, 6 mg/l, 12 mg/l Fenton was stirred with a magnetic bar. Five 25 W UV lamps, located vertically around the reactor, at powers varying between 15 w /m<sup>-2</sup>, 60 w /m<sup>-2</sup> and 90 w/m<sup>-2</sup> was applied to the photo-Fenton process. The yield in the photo-Fenton process is low. The maximum yields for COD, COD dis BOD5 were around 38%-45% at a sunlight power of 67 w/m<sup>2</sup>, at 4 mg/L FE(II), with 50 mg/l H<sub>2</sub>O<sub>2</sub> at 30°C temperature after 30 min contacting time. In the UF; poly (vinylidene fluoride) membrane was used with aporosity of 32% containing a pore radius of 9,56 nm. The RO membrane volume was 2L, 8L with a pre poly propylene yarn wound filter to remove the suspended solids and has a Thin Film Composite (TFC) material as membrane containing pore sizes of 0.0002 micron. The effects of trans-membrane flux (J=3 L m<sup>-2</sup>h<sup>-1</sup>, 5 L m<sup>-2</sup>h<sup>-1</sup>, 12 L m<sup>-2</sup>h<sup>-1</sup>) on the yields of pollutant parameters were studied in the last two membrane reactors. The COD, COD-dis, DOC, color, and TSS yields in photo- Fenton and UF were 34%, 39%, 42%, 38% and 41%; and 89%, 92%, 89%, 92% 90%, respectively. The maximum COD, COD-dis, DOC, color, and TSS yields were 99,99% for all parameters in the permeate of the RO while methyl red dye, salt and perfluoroalkyl sulfonate were recovered at a flux of 12 L m<sup>-2</sup> h<sup>-1</sup>. 6700 mg/l methyl red dye, 8300 mg/l NaCl salt and 7860 mg/l perfluoroalkyl sulfonate was recovered from the retentates of UF and RO by using 1m<sup>3</sup> raw textile wastewater while the permeate of RO can be used as irrigation water.

**Keywords:** Photo-Fenton; Ultrafiltration (UF); Reverse Osmosis (RO); Recovery; Reuse; Dyes; Salt; Perfluoroalkyl sulfonate; Retentate introduction

## INTRODUCTION

The textile industry contains large quantities of organic compounds which are not easily removed with chemical or biological treatment [1]. The treatment cost of textile wastewaters are high and these wastewaters high levels of COD, and organic chlorine due to the bleaching textile products. During heterogeneous photocatalytic oxidation high electrical energy demand are common problems among all the AOPs. The textile industries may face a shortage

of available water sources due to water scarcity and limitations of ground water use. In the near future, many textile companies will have to reuse dyeing effluent to achieve environmental and economic benefits [1] The production of photons with artificial light sources require an important energy cost. The photo-Fenton reactions can use photons with wavelength close to 400 nm. The mixtures Fe(III)+H<sub>2</sub>O<sub>2</sub> (known as Fenton-like reactions have shown photon absorption up to 550 nm [2]. In presence of Fenton

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reagent, photochemical reactions can be driven with photons of low energy, photons that belong to the visible part of the spectrum. Thus, photo-fenton processes are a potential cost-reduced AOP that can be run under solar irradiation [3]. In the irradiation of Fe(III)+H<sub>2</sub>O<sub>2</sub>, also called photo-fenton reaction, enhances the reaction rate of oxidant production, through the involvement of high valence Fe intermediates responsible for the direct attack to organic matter [4]. Ultrafiltration is a membrane separation process, mostly used in the separation of macromolecules and colloids from a solution; solutes retained usually have molecular weights of a few thousand Daltons [5]. The ultrafiltration membrane process has limited applications in the textile industry; this is mainly because the molecular weights of the dyes present in the highly colored textile discharge are much lower than the Molecular Weight Cut-off (MWCO) of the ultrafiltration membranes [6]. Ultrafiltration (UF) is usually applied as a pre-treatment step in systems demanding a high degree of process stream purification; it is followed by processes such as Ultrafiltration (UF), or Reverse Osmosis (RO) stages, which satisfy the demands on process water quality [7]. Due to low water conductivity requirement for reuse purpose, Reverse Osmosis (RO) technology can be an optimal process for reuse of dyeing effluents [8]. Although RO has become a viable technology for wastewater reclamation, high concentrations of Dissolved Organic Matter (DOM) in the dyeing secondary effluent may cause severe fouling of RO membrane and lead to a great loss of membrane permeate flux and deterioration of treated water quality [9]. Therefore, RO membrane fouling is still a major challenge in the reuse of some merits chemicals and proper pretreatment should be preceded as the first line of defense in controlling membrane fouling [10].

Hence, advanced treatment of dyeing secondary effluent is necessary to not only meet the stringent discharge limit but also reduce RO membrane fouling in reuse [11]. Advanced treatment methods, such as UF/MF have been studied widely to remove refractory compounds. The Advanced Oxidation Processes (AOPs) generally give good results, but are expensive. UF/MF are effective pretreatment technology to RO membrane [12].

Over recent years, water consumption, wastewater treatment, and the effluent reuse potential have become crucial factors for sustainable production. In this study a sequential photo-fenton/UF/RO process was used to treat the COD, COD-dis, DOC, colour and turbidity and reuse of treated textile wastewater and recovery of some economical merits from the retentate of the RO (dyes, salt and perfluoroalkyl sulfonate). The effects of some operational conditions on the performance of sequential photo-fenton process, UF and RO were studied. Some economical substances were recovered from the retentates while the permeate of RO was used as irrigation water.

## MATERIALS AND METHODS

### Reactor configurations and operational conditions

The photo-fenton sunlight reactors, UF and RO processes were sequentially used. The effluent of the first reactor should be used as feed in the second reactor.

All experiments, were performed under solar irradiation, were conducted in a hemostatic cylindrical glass reactor of 1,5 liter of volume. The reaction mixture in the glass reactors 1, certain amounts of Fe (II) and H<sub>2</sub>O<sub>2</sub> concentrations were added and they was continuously stirred with a magnetic bar. The experiments were conducted at five different temperatures (21°C, 30°C, 35°C, 40°C and 50°C). Five different Solar light powers were used according

to the hours placed of the glass reactors to the atmosphere. The sunlight power were 45 W/m<sup>2</sup>, 65 W/m<sup>2</sup>; 50 W/m<sup>2</sup>, 40 W/m<sup>2</sup> and 36 W/m<sup>2</sup> for the hours between 10.30 am-12.30 am, 12.30 pm-14.30 pm, 14.30 pm-16.30 pm 16.30 pm-18.30 pm and at between 18.30 pm-20.30 pm during a day at temperatures 21°C, 30°C, 35°C, 40°C and 50°C. The effects of increasing FE(II) (1 g/L, 2 g/L, 4 g/L, 6 g/L, 10 g/L), H<sub>2</sub>O<sub>2</sub> concentrations ( 20 mg/l, 50 mg/l, 70 mg/l, 80 mg/l and 90 mg/l), temperatures (21°C, 30°C, 35°C, 40°C and 50°C), contacting times (15 min, 30 min, 45 min, 60 min and 75 min) and sunlight powers (21°C, 30°C, 35°C, 40°C and 50°C). On the removal efficiencies of the pollutants in the used textile industry wastewater were studied.

The UF volume was 2 liters. The UF process was made from poly (vinylidene fluoride) membrane with a porosity of 32% containing a pore radius of 9,56 nm. Experiments were carried out under three different temperatures (25°C, 35°C, and 45°C) in order to observe membrane performances at each temperature. The effects of eight pressures (between 0,3 bar and 4,42 bar) temperatures on the permeate fluxes were researched. The effects of increasing temperatures at constant pressure (4 bar) and constant permeate flux 400 L/h.m<sup>2</sup> were studied on the on the cumulative permeate volumes were studied in UF. The effects of increasing temperatures at constant CFV (4 m/s) and constant TMP (4 bar) on the adsorption resistance of UF was studied.

The permeate flux is calculated according to  $J_p = VAt$

Where  $J_p$  is the permeate flux (L/m<sup>2</sup>h),  $V$  is the permeate volume (L),  $A$  is the effective membrane area (m<sup>2</sup>) and  $t$  is the sampling time (h). At the same time, permeate samples were collected for water quality analysis. The rejection coefficient (R) is calculated as a percentage)  $R\% = 1 - C_p/C_f \times 100$

Where  $C_f$  is the concentration in the feed stream and  $C_p$  is the concentration in the permeate stream.

RO membrane volume was 2,8 L with a pre poly propylene yarn wound filter to remove the suspended solids and has a Thin Film Composite (TFC) material as membrane containing pore sizes of 0.0002 micron. The operating pressure and operating temperature varied between 15 bar, 25 bar and 35 bar and d 20°C, 30°C and 40°C while the feed flowrate (12 L/min), corresponding to crossflow velocity from 1,5 m/s to 3,06 m/s) to detect the effects of increasing ro pressure and temperature on the OR membrane performance. Observed rejection of solutes (COD, conductivity and ions) was calculated with the Ri Equation 1.

$$Ri\% = 1 - \frac{C_{p,i}}{C_{f,i}} 100 \quad (1)$$

Where  $C_{p,i}$  is the concentration of the solute  $i$  in the permeate stream, and  $C_{f,i}$  is the concentration of the solute  $i$  in the feed water.

The osmotic pressure ( $\Pi_f$ ) of the textile wastewater was calculated by using the following Van't Hoff equation (Equation 2).

$$\Pi_f = \sum :: C_i f R T, \quad (2)$$

where  $C_i, f$  is the feed molar concentration of ion  $i$  (mol/L),  $R$  is the ideal gas constant (0,0821 atm L/K mol) and  $T$  is the absolute temperature (K). Estimated osmotic pressure values of the feed were equal to 1,89 bar, 2,22 bar and 2,85 bar for temperature values of 20°C, 30°C and 40°C, respectively.

The RO Membrane specifications was summarized in Table 1.

## Analytical procedures

Colour determination of the initial sample was carried out in a spectrophotometer at a wavelength of 465 nm, using 10 mm light path cells, according to standard methods [13]. COD, COD dis, DOC, TSS, turbidity, salt and BOD5, total polyphenols were measured according to Standard Methods [13]. Identifications of Benzene acetic acid, 3-Methyl benzoic acid, Decanoic acid, Undecanoic acid in textile wastewater was performed with GC-MS Agilent gas chromatograph equipped with a quadrupole HP mass selective detector was used. Samples were reconstituted to 100  $\mu\text{L}$  in dichloromethane and 1  $\mu\text{L}$  was injected in the GC. Identifications were carried out with the aid of the data base library WILEY. A capillary column HP-5MS (5% Phenyl Methyl Siloxane) with dimensions of 30 m, 250  $\mu\text{m}$ , 0,25  $\mu\text{m}$  was used. The carrier gas flow rate in the GC was 1,3  $\text{mL min}^{-1}$ . The sample injection was carried out with a 0,6 min of splitless time, at 250°C. The temperature program used during the GC-MS and lysis ramped as follows: 70°C (3 min), 5°C  $\text{min}^{-1}$  until 270°C (30 min). The retention times of Benzene acetic acid, 3-Methyl benzoic acid, Decanoic acid and Undecanoic acid were 10,80 min, 12,90 m,n, 16,26 min and 20,68 min, respectively with recoveries of 97-98,60%. Perfluoroalkyl sulfonate Recovered from the retentates of UF and RO was measured in HP-LC/MS by using methanol and acetone/acetonitrile (80:20, v/v) solvents. The characterization of textile industry wastewater is illustrated in Table 2.

## RESULT AND DISCUSSION

Effect of sunlight power on pollutant removals in photo-fenton process at five different sunlight powers was studied. For hours between 10 hr-12,30 hr (45  $\text{W/m}^2$ ), between 12,30 hr-14,30 hr (65  $\text{W/m}^2$ ), between 14,30 hr-16,30 hr (50  $\text{W/m}^2$ ), between 16,30 hr-18,30 hr (40  $\text{W/m}^2$ ) and at between 18,30 hr-20,30 hr (36  $\text{W/m}^2$ ) were studied at constant Fe(II), and  $\text{H}_2\text{O}_2$  concentrations of 50 mg/l and 250 mg/l at 21°C temperature after 30 min contacting time. The concentrations were chosen from the references in the recent literatures [1-4].

The maximum COD, COD dis, DOC, colour, TSS and BOD5 yields were detected at 65  $\text{W/m}^2$  sunlight power which is the maximum power of sunlight after 30 min contacting time (Table 3). The sun light manages the photo-fenton reactions, produces additional hydroxyl radicals and provides the recovery of Fe(II) needed in the Fenton reaction. The photo-fenton process can be contained the direct photolysis of ferric ion or photolysis of Fe(III)-peroxy complexes [4]. The ligands can be managed to substance

Table 1: Membrane specifications in RO.

Parameters	Parametric value
Manufacturer	Water and process technologies
Membrane model	SC* (RO)
Nominal salt rejection, %	99.9
Effective surface area, $\text{m}^2$	0.09
Permeability, $\text{L/h m}^2$	1,5 $\pm$ 0,1
Configuration	Flat
Module dimensions, cm	1,9 $\times$ 30,5 $\times$ 10,2
Chemical composition	TFC aromatic polyamide/ polysulfone
Surface nature	Hydrophilic
Maximum pressure, bar	70
Maximum temperature, °C	70
pH range	1-9
Maximum silk density index (SDI)	3

Table 2: Characterization of raw textile industry wastewater.

Parameter	Unit (mg/l)
COD	18,000
COD dis	14,000
BOD5	7600
TSS	12,000
Colour	8 $\text{m}^{-1}$
pH	5-8 (unitless)
Turbidity	12,000 mhos
Salt	8760
Total polyphenols	890
Benzene acetic acid	300
3-Methyl benzoic acid	590
Total Linear acids	560
Decanoic acid	250
Undecanoic acid	270
Dye (methyl red)	680
Perfluoroalkyl sulfonate	1230

charge transfer in the photolabile complexes formed by Fe(III) and organic compounds.

The studies performed only with Fe, sunlight power did not remove the pollutants given above. Only 1,10% removals were detected (data not shown).

Effects of increasing  $\text{Fe}^{+2}$  concentrations on the yields of pollutant parameters at constant sunlight power and  $\text{H}_2\text{O}_2$  concentration

Increasing initial quantities of iron in solution produce increasing removals in the pollutants for 30 min contact time. Although with 2 mg/l Fe(II) concentration the removals of all pollutants increased significantly the maximum pollutant yields was detected with 4 mg/l Fe(II) concentration (Table 4). The reaction with more Fe(II) proceeds at a faster rate, produces pollutant decays with an optimum Fe(II) concentration of 4 mg/l. After these Fe(II) concentrations the pollutant yields decreased. This can be explained by taking into account that Fenton reaction, is completed with 4 mg/l Fe(II) between 30 min. Furthermore, larger Fe(II) load, were detrimental in the photo-fenton reactions due to the low concentration of OH, need more time to manifest, and their effects appear only for long enough reaction times.

Effects of increasing  $\text{H}_2\text{O}_2$  concentrations on the yields of pollutant parameters at constant sunlight power and Fe(II) concentration and temperature.

The maximum pollutant yields were detected at a  $\text{H}_2\text{O}_2$  concentration of 50 mg/l (Table 5). The presence of both  $\text{H}_2\text{O}_2$  and Fe(II) under 50  $\text{W/m}^2$  sun light irradiation The COD, COD dis, DOC yields were around 67% while the colour, TSS and BOD5 reductions were low after 30 min contacting time.

Effects of increasing temperature on the yields of pollutant parameters at constant sunlight power, Fe (II) and  $\text{H}_2\text{O}_2$  concentrations.

The beneficial effect of temperature was tested in a set of experiments at five different temperatures (20°C, 30°C, 35°C, 40°C and 50°C). The maximum pollutant yields were detected at 35°C (Table 6). The increase of temperature elevated the COD, COD dis, DOC, colour, and BOD5 yields from 47%, 47%, 46%, 34%, 36% to 55%, 56%, 52%, 39% and 43%, respectively. Further

**Table 3:** The effect of sunlight power on the removals of pollutants at constant Fe(II) (2 mg/l) and H<sub>2</sub>O<sub>2</sub> (50 mg/l) concentrations and 30 min contacting time.

Hours/Sunlight power (W/m <sup>2</sup> )	Removal efficiency (%)					
	COD	COD DIS	DOC	Colour (m <sup>-1</sup> )	TSS	BOD5
10,30-12,30 (45)	21	27	28	23	12	18
12,30-14,30 (65)	42	44	45	29	13	32
14,30-16,30 (50)	40	41	40	26	14	30
16,30-18,30 (40)	32	33	34	20	10	28
18,30-20,30 (36)	31	32	30	20	9	25

increase of temperature did not affect positively the pollutant yields. No significant effect of temperature increase on the yields of TSS was detected.

When the experiment was carried out at high temperatures more than 35°C the levels of pollutant removal yields remained constant as are at 35°C or increased slightly. Under optimum operational conditions enough OH radicals through the photo-fenton reaction accelerated with temperature. The temperature seems to be assisting alternative ways of H<sub>2</sub>O<sub>2</sub> cleavage and OH formation, or Fe(II) recovery. Temperature is a key parameter that has to be taken into account, specially for the maximum removal yields of pollutants. This can be increased the optimum temperatures (in this study 30°C). Therefore, the yields can be increased by using low cost heating.

Effects of increasing contact times on the yields of pollutant parameters at constant sunlight power, Fe(II) and H<sub>2</sub>O<sub>2</sub> concentrations. The effect of increasing contact times on the yields of pollutant parameters was tested at four different contact times (15 min, 30 min, 45 min, 60 min). The maximum pollutant yields were detected at 30 min (Table 7). The increase of contacting time did not increase the COD, COD DIS, DOC, colour, TSS and BOD5 yields.

The initial COD, COD dis, DOC, color, TSS and BOD5 decrease due to photo-fenton reactions. Fe(II) is a limiting chemical since as long as Fe(II) is available the same initial reaction rate is expected. Under the experimental conditions tested here, Fe(II) consumption takes place in few seconds, producing the majority of pollutants decrease after 15 min of reaction and reached to a maximum after 30 min contacting time. This showed that why at short contacting-reaction times; the maximum removals was detected. This can be explained by taking into account that the photo-fenton reactions completed with 4 mg/l Fe(II) between 30 min. Furthermore, larger Fe(II) load were detrimental in the reactions due to the low concentration of OH generation. Although increasing contacting times gives the larger ratio of pollutant removals up to an optimum contact time. The high contact times exhausts the H<sub>2</sub>O<sub>2</sub> through non-efficient photochemical reactions. Excess of H<sub>2</sub>O<sub>2</sub> or Fe(II) might be detrimental, since these species can react with some of the intermediates like OH, responsible for the direct oxidation of the organic load. Thus, in order to check the effect that different reagent ratios on the reactions, experiments with several ratios of H<sub>2</sub>O<sub>2</sub>/Fe(II) were also conducted. H<sub>2</sub>O<sub>2</sub>/Fe(II) ratio there is a clear reduction in the initial amount of Fe(II) used, and an important role played in the photo-fenton treatment processes. The use of large quantities of Fe has a negative effect on the pollutant yields since it implies the need of an additional treatment step for Fe removal. The optimum H<sub>2</sub>O<sub>2</sub>/Fe(II) ratio for this study was 12:1.

### Treatability studies with UF

**Effect of TMP on the variations of permeate fluxes at increasing temperatures:** The water membrane permeability was determined by measuring the permeate flux of textile wastewater and deionized water (Tables 8 and 9) at a different temperature and the CFV was adjusted to 4 m/s. The temperature effect on the UF process was investigated at increasing temperatures. The values of water permeability obtained at 25°C, 35°C and 45°C were 160 L/h m<sup>2</sup> bar, 56 L/h m<sup>2</sup> bar, 195 L/h m<sup>2</sup> bar, 56 L/h m<sup>2</sup> bar, and 204 L/h m<sup>2</sup> bar, 78 L/h m<sup>2</sup> bar, respectively. It was found that the temperature increase leads to higher deionized water and textile wastewater permeate fluxes due to an increase of the mass-transfer coefficient [14,15].

The values of J<sub>p</sub> for textile wastewater conditions were not lower than J<sub>p</sub> initial values for deionized water at operational conditions given in materials and methods. This indicated that there was not a significant decrease in permeate flux during the experiments in textile wastewater compared to deionized water. The permeate flux was not declined due to membrane fouling in the textile wastewater since an adsorption of organic pollutants onto the membrane surface and into the pores or a concentration polarization and a cake formation were not detected. As the temperature increased, the J<sub>p</sub> values also increased. No differences between deionized water and textile wastewater J<sub>p</sub> values were detected at higher TMP. This can be attributed to the convection of particles toward the membrane surface was not enhanced in the textile wastewater and the accumulation of organic pollutants were not deposited onto the membrane surface and into the pores. As a result, the permeate flux was not decreased in the textile wastewater since no membrane fouling was detected. Initially, the permeate flux increased with an increase in operating pressure. At TMP higher than 3 bar, 4 bar, no accumulation of solute particles near the membrane surface and the formation of a cake layer was not detected. In this study, when feed pressure increases, a thicker and compacted cake layer was obtained at the equilibrium state. As shown in Tables 8 and 9, the increasing of TMP up to 4 bar, 2 bar increases the permeate flux.

**Variations of cumulative permeate volumes (V<sub>p</sub>) at 4 bar pressure and at 400 L.h<sup>-1</sup>.m<sup>-2</sup> permeate flux at increasing temperatures versus times in deionized water and textile wastewater:** In this study, in the textile wastewaters it was found that the permeate flux was not declined significantly at higher temperatures versus time (Table 10). At 30°C temperature, for a fixed TMP of 4 bar, permeate flux decreased by 0,9% from its initial value when the operating temperature was set at 30°C. The permeate flux increased as temperature increases from 30°C up to 50°C. This showed that the membrane fouling was not occurred via concentration polarization at higher temperature. In other words, at higher temperatures the formation of cake layer was not detected and permeate flux is increased. At increasing temperatures, the permeate flux increases. Increasing of temperature decreases the viscosity, as a result of increasing of permeation flux [14]. The increasing of temperature

**Table 4:** The effect Fe(II) concentrations on the yields of pollutant parameters at constant sunlight power (50 w/m<sup>2</sup>) and H<sub>2</sub>O<sub>2</sub> (50 mg/l) concentrations at hours between 12.30 hr-14.30 hr at a sunlight power of 65 W/m<sup>2</sup> after 30 min contacting.

Fe <sup>+2</sup> concentrations (mg/l)	Removal efficiency (%)					
	COD	COD DİS	DOC	Colour (m <sup>-1</sup> )	TSS	BOD5
1	21	27	28	23	12	18
2	42	44	45	29	13	32
4	48	46	48	33	16	42
6	32	33	34	20	10	28
10	31	32	30	20	9	25

**Table 5:** The effect of increasing H<sub>2</sub>O<sub>2</sub> concentrations on the yields of pollutant parameters at constant sunlight power (50 W/m<sup>2</sup>) and Fe(II) (4 mg/l) concentrations at hours between 12.30-14.30 at a sunlight power of 65 W/m<sup>2</sup> after 30 min contacting time.

H <sub>2</sub> O <sub>2</sub> concentrations (mg/l)	Removal efficiency (%)					
	COD	COD DIS	DOC	Colour (m <sup>-1</sup> )	TSS	BOD5
20	21	27	28	23	11	18
50	47	47	46	34	19	36
70	41	41	40	26	15	30
80	30	33	30	20	12	26
90	29	32	30	20	9	22

**Table 6:** The effect increasing temperatures on the yields of pollutant parameters at constant sunlight power (50 W/m<sup>2</sup>) and Fe (II) (4 mg/l) concentrations at hours between between 12.30-14.30 at a sunlight power of 65 W/m<sup>2</sup> after 30 min contacting time.

Temperature (°C)	Removal efficiency (%)					
	COD	COD DİS	DOC	Colour (m <sup>-1</sup> )	TSS	BOD5
21	47	47	46	34	19	36
30	50	51	49	37	20	39
35	55	56	52	39	21	43
40	51	52	50	38	20	42
50	51	51	50	38	20	42

**Table 7:** The effect increasing contact times on the yields of pollutant parameters at constant sunlight power (50 W/m<sup>2</sup>) and Fe (II) (4 mg/l) concentrations at hours between 12.30-4.30 at a sunlight power of 65 W/m<sup>2</sup> after 30 min contacting time.

Contact times (min)	Removal efficiency (%)					
	COD	COD DİS	DOC	Colour (m <sup>-1</sup> )	TSS	BOD5
15	47	47	46	34	19	36
30	50	51	49	37	20	39
45	55	56	52	39	21	43
60	51	52	50	38	20	42
75	51	51	50	38	20	42

increases the osmotic pressure and this increases the permeate flux by decreasing the permeation flux. It should be noted that the elevation of temperature increases the energy cost and the membranes in the UF were destroyed at high temperatures. Therefore, the membranes should be changed. In this study the utilized UF membrane was made from poly (vinylidene fluoride) and exhibited thermal stability compared to the other polymeric membranes [15].

The cumulative permeate volume V<sub>p</sub> obtained as a function of time for the poly (vinylidene fluoride) UF membrane at different temperature and with constant CFV= 4m/s was illustrated in Table 11 for deionized water.

The cumulative volumes increased with time, and at increasing

**Table 8:** Variation of permeate fluxes at increasing temperatures in textile wastewater.

Tem- perature (°C)	Pres- sure (bar)	J (L.h <sup>-1</sup> .m <sup>-2</sup> )	Tem- perature (°C)	Pres- sure (bar)	J (L.h <sup>-1</sup> .m <sup>-2</sup> )	Tem- perature (°C)	Pres- sure (bar)	J (L.h <sup>-1</sup> .m <sup>-2</sup> )
	0,3	89		0,6	92		0,69	96
	0,9	117		1,2	127		1,45	147
25	1,2	135	35	1,8	142	45	1,91	169
	1,6	200		2,3	220		2,45	235
	2,7	280		3,4	292		3,47	365
	3,9	450		4,2	470		4,42	560

**Table 9:** Effect of TMP on the variation of permeate fluxes at increasing temperatures in deionized waster.

Tempera- ture (°C)	Pres- sure (bar)	J (L.h <sup>-1</sup> .m <sup>-2</sup> )	Tem- perature (°C)	Pres- sure (bar)	J (L.h <sup>-1</sup> .m <sup>-2</sup> )	Tem- perature (°C)	Pres- sure (bar)	J (L.h <sup>-1</sup> .m <sup>-2</sup> )
	0,4	93		0,7	95		0,8	98
	1,0	127		1,3	130		1,49	149
25	1,3	142	35	1,9	147	45	1,99	172
	1,7	220		2,4	223		2,7	238
	2,8	300		3,5	297		3,7	369
	4,0	470		4,3	476		4,7	569

temperatures however, a significant decrease was not occurred in the permeate rate. The volumes increased with increased temperature. The ANOVA statistical and lysis showed there was a linear relationship between the permeate volumes of pure water and textile wastewater with time and increasing temperature at constant J<sub>p</sub> of 400 L.h<sup>-1</sup>.m<sup>-2</sup>. The slightly lower values of V<sub>p</sub> obtained from the textile wastewater in the comparison to distilled water were not due to the fouling of the poly (vinylidene fluoride) UF membrane used in this study.

**Effect of temperature on permeate flux versus volume retention factor (CVF=4 m/s, pressure 4 bar):** Table 12 shows the effect of temperature on permeate flux decline versus volume retention factor. The permeate flux ( $400 \text{ L.h}^{-1}.\text{m}^2$ ) was not decreased significantly with VRF increases since no significant fouling was observed in this study. The results of this study showed that shows constant permeate fluxes at 360, 392 and  $443 \text{ L.h}^{-1}.\text{m}^2$  of VRF=0,4-0,85 at increasing temperatures of  $^{\circ}\text{C}$  and  $94.59 \text{ L/h m}^2$  of VRF=2-30 and operating temperatures of  $25^{\circ}\text{C}$ ,  $35^{\circ}\text{C}$  and  $45^{\circ}\text{C}$ , respectively. No significant decreases on the permeate flux was noticed at decreasing temperature and VRFs.

The adsorption resistance of the UF membrane at different temperatures viruses increasing times: Table 13 indicated the non-significant the membrane fouling in poly (vinylidene fluoride) membrane during UF processing at a CFV of  $4 \text{ m/s}$  and  $\text{TMP}=4 \text{ bar}$  at increasing temperatures of  $25^{\circ}\text{C}$ ,  $35^{\circ}\text{C}$  and  $45^{\circ}\text{C}$ . The adsorption resistance ( $R_m$ ) not significantly decreased with increasing temperature, due to higher values of the viscosity of the textile wastewater. This can be attributed to the low mass-transfer coefficient in poly (vinylidene fluoride) membrane on UF. In this study, the increasing of temperature did not cause to fouling on the membrane surface. During ultrafiltration the adsorption resistance ( $R_a$ ) was increased insufficiently due to low turbulence.

**Removal of textile pollutants in UF:** The UF membrane process was studied at two J in order to detect the pollutant removals. It was found that the pollutant yields were slightly higher at  $470 \text{ L.h}^{-1}.\text{m}^2$  permeate flux than at  $200 \text{ L.h}^{-1}.\text{m}^2$  permeate flux (Table 14). High removal yields was detected for COD, CODdis, TOC, DOC, turbidity, color, total polyphenols, individual polyphenols namely Benzene acetic acid and 3-Methyl benzoic acid (87%-90%). The individual linear acid yields (Decanoic acid and Undecanoic acid) removals were also high (89%-91%). However low removal yields were detected for salt, dye, TSS and Perfluoroalkyl Sulfonate (60%-65%) (Table 14).

## Studies performed by RO

**Variation of permeate flux in deionized water and textile industry wastewater:** The operating pressure and operating temperature varied between 15 bar, 25 bar and 35 bar and  $20^{\circ}\text{C}$ ,  $30^{\circ}\text{C}$  and  $40^{\circ}\text{C}$ , respectively, while the feed flowrate was maintained constant as  $12 \text{ L/min}$ . The corresponding crossflow velocity changed from  $1,5 \text{ m/s}$  to  $3,06 \text{ m/s}$  in order to detect the effects of increasing to pressure and temperature on the RO membrane performance. A linear relationship between permeate flux and osmotic pressure for both pure water and textile wastewater (Tables 15 and 16) was detected. As the temperature was increased from  $20^{\circ}\text{C}$  up to  $30^{\circ}\text{C}$  and  $40^{\circ}\text{C}$  the osmotic pressure was increased. No significant differences between deionized water and textile wastewater of osmotic pressures were detected.

**Treatment of pollutants in RO:** Complete rejection of phenols, COD, CODdis and the other parameters were successfully achieved during RO experiments (Table 18). The rejection coefficients and removal yields (%) of the pollutants in the permeate are given in Table 16. Due to the organic content of the solutes concentration in the bulk was low a concentration gradient increase was not detected across the membrane. Reduced hydrodynamic shear near the valley regions of the membrane used in RO prohibits the suspended and colloidal organic matter adsorption and deposition. As a result, a resistance occurred to the fouling. This hinder the transport of pollutants on the pore of the membranes.

**Extraction of dye (methyl red), salt and perfluoroalkyl sulfonate from the retentates of UF ana RO**

**Recovery of sodium chloride from evaporated residue of RO rejects:** The retentate samples were evaporated and precipitated. The residue of RO rejects has been dissolved in water to prepare saturated NaCl solution. The increase in ionic concentration in the saturated solution shifts the reaction to backward direction by common ion effect. In this study, hydrogen chloride gas was prepared and purged to increase the concentration of  $\text{Cl}^-$  ions in the NaCl solution. The incremental increase in  $\text{Cl}^-$  ion concentration shifted dynamic equilibrium by increasing the ionic product of  $\text{Na}^+$  and  $\text{Cl}^-$ . The ionic product of  $\text{Na}^+$  and  $\text{Cl}^-$  exceeded the solubility product of sodium chloride [solubility product of NaCl, ( $K_{sp}$ ) is

**Table 10:** Variation of cumulative permeate volumes ( $V_p$ ) at 4 bar pressure and at  $400 \text{ L.h}^{-1}.\text{m}^2$  permeate flux at increasing temperature versus times in textile wastewater.

Temperature ( $^{\circ}\text{C}$ )	Cumulative volume (L)	Time (min)	Temperature ( $^{\circ}\text{C}$ )	Cumulative volume (L)	Time (min)	Temperature ( $^{\circ}\text{C}$ )	Cumulative volume (L)	Time (min)
25	0	30	35	0	30	45	0	30
	0,4	40		0,45	40		0,55	40
	0,6	50		0,68	50		0,70	50
	1,0	60		1,09	60		1,28	60
	2,0	70		2,18	70		2,29	70
	2,9	80		2,94	80		3,21	80

**Table 11:** Variation of cumulative permeate volumes ( $V_p$ ) AT 4 bar pressure and at  $400 \text{ L.h}^{-1}.\text{m}^2$  permeate flux at increasing temperature's versus times in deionized water.

Temperature ( $^{\circ}\text{C}$ )	Cumulative volume (L)	Time (min)	Temperature ( $^{\circ}\text{C}$ )	Cumulative volume (L)	Time (min)	Temperature ( $^{\circ}\text{C}$ )	Cumulative volume (L)	Time (min)
25	0	30	35	0	30	45	0	30
	0,8	40		0,98	40		1	40
	0,9	50		1,22	50		1,43	50
	1,4	60		1,55	60		1,68	60
	2,6	70		2,79	70		2,99	70
	3,4	80		3,90	80		4,19	80

**Table 12:** Effect of temperature on permeate flux decline versus volume retention factor.

Temperature (°C)	J (L.h <sup>-1</sup> m <sup>2</sup> )	VRF ratio	Temperature (°C)	J (L.h <sup>-1</sup> m <sup>2</sup> )	VRF ratio	Temperature (°C)	J (L.h <sup>-1</sup> m <sup>2</sup> )	VRF ratio
25	400	0	35	405	0,32	45	409	0,43
	390	0,2		396	0,31		418	0,49
	380	0,3		392	0,41		427	0,51
	370	0,4		381	0,55		437	0,69
	360	0,45		392	0,56		443	0,75
	360	0,55		392	0,75		443	0,85

**Table 13:** Variation of adsorption resistance versus time at increasing temperatures (CFV=4 m/s, TMP=4 bar).

Temperature (°C)	R (10 <sup>-12</sup> m <sup>-1</sup> )	Time (min)	Temperature (°C)	R (10 <sup>-12</sup> m <sup>-1</sup> )	Time (min)	Temperature (°C)	R (10 <sup>-12</sup> m <sup>-1</sup> )	Time (min)
25	4	30	35	4,3	30	45	4,5	30
	4,6	60		4,8	60		4,9	60
	5,2	90		5,6	90		5,8	90
	6	120		6,4	120		6,8	120
	7	180		7,4	180		7,7	180
	8	200		8,3	200		8,8	200

**Table 14:** Removal efficiencies of pollutants in textile industry versus permeate fluxes.

Parameters	J=200 (L.h <sup>-1</sup> m <sup>2</sup> )	J=470 (L.h <sup>-1</sup> m <sup>2</sup> )
	Removal efficiency %	Removal efficiency %
COD	0,88	0,92
COD dis	0,89	0,9
TOC	0,85	0,87
DOC	0,87	0,89
Colour	0,88	0,89
Total polyphenol	0,86	0,89
Turbidity	86	89
Salt	0,56	0,59
TSS	56	60
Individual polyphenols		
Benzene acetic acid	0,87	0,89
3-Methyl benzoic acid	88	90
Individual Linear acids		
Decanoic acid	87	89
Undecanoic acid	89	91
Dye (methyl red)	56	62
Perfluoroalkyl Sulfonate	63	65

**Table 15:** Relations between Permeate flux and osmotic pressure for RO membrane in textile wastewater for increasing temperatures.

Temperature (°C)	Permeate flux (L.h <sup>-1</sup> m <sup>2</sup> )	Π (osmotic pressure, bar)	Temperature (°C)	Permeate flux (L.h <sup>-1</sup> m <sup>2</sup> )	Π (osmotic pressure, bar)	Temperature (°C)	Permeate flux (L.h <sup>-1</sup> m <sup>2</sup> )	Π (osmotic pressure, bar)
20	5	4	30	7	5	40	9	7
	10	6		12	8		14	16
	15	12		18	14		20	22
	20	15		22	17		24	26
	30	20		32	25		34	37
	38	22		40	25		43	28

36 (mol/L)<sup>2</sup>] and thus the precipitation of sodium chloride was achieved from the saturated solution of NaCl. The supernatant solution was taken in reactive precipitation reactor and HCl gas

has been purged continuously for the reactive precipitation of sodium chloride. The required HCl is being prepared and used spontaneously. After successful purging of HCl gas the sodium

**Table 16:** Relations between Permeate flux and osmotic pressure for RO membrane in deionised water for increasing temperatures.

Temperature (°C)	Permeate flux (L.h <sup>-1</sup> .m <sup>-2</sup> )	IIf (osmotic pressure, bar)	Temperature (°C)	Permeate flux (L.h <sup>-1</sup> .m <sup>-2</sup> )	IIf (osmotic pressure, bar)	Temperature (°C)	Permeate flux (L.h <sup>-1</sup> .m <sup>-2</sup> )	IIf (osmotic pressure, bar)
20	8	6	30	9	8	40	12	10
	12	8		14	10		17	13
	18	14		20	17		24	19
	22	17		26	19		29	26
	34	23		38	27		42	37
	43	25		47	29		51	34

**Table 17:** Variation of permeate fluxes versus increasing temperature, pressures flow rates and cross flow velocities in RO.

Temperature (°C)	Time (min)	Permeate flux (L/h.m <sup>2</sup> )	Crossflow velocity (m/s)	Temperature (°C)	Crossflow velocity (m/s)	Permeate flux (L/h.m <sup>2</sup> )	Temperature (°C)	Permeate flux (L/h.m <sup>2</sup> )	Crossflow velocity (m/s)
20	10	15	1,5	30	3,06	25	40	35	5,09
	30	14				24		35	
	60	13				23		34,9	
	90	12				22		34,8	
	120	11				21		34,7	
	150	11				21		34,7	

**Table 18:** Removals and rejection percentages of pollutants in RO.

	Removal efficiency (%)	Rejection efficiency (%)
COD	99,99%	99,99
COD dis	100	99,99
TOC	100	99,99
DOC	100	99,99
Colour	100	99,99
Total polyphenol	99,99	99,99
Salt	99,99	99,99
TSS	100	99,90
Individual polyphenols	99,99	99,99
3-Methyl benzoic acid		
Benzeneacetic acid	99,99	99,99
Linear acids	99,99	99,99
Decanoic acid	99,99	99,99
Undecanoic acid	99,99	99,99
Dye (methyl red)	99,99	99,99
Perfluoroalkyl Sulfonate	99,99	99,99

**Table 19:** MR mass concentrations.

MR mass in the retentate (1× 10 <sup>3</sup> g)	Time (mn)	MR mass (g)
0,4	100	0,3
0,8	200	0,8
1	300	1
2	400	1,2
3	500	2,8
4	600	3,9

chloride salt is separated out from the solution by reactive precipitation. From 800 mg/l NaCl total 8300 mg/l salt recovered from the retentates of UF and RO from 1 m<sup>3</sup> textile wastewater.

**Recovery of sodium chloride from evaporated residue of RO rejects:** The retentate samples were evaporated and precipitated. The residue of RO rejects has been dissolved in water to prepare

saturated NaCl solution. The increase in ionic concentration in the saturated solution shifts the reaction to backward direction by common ion effect. In this study, hydrogen chloride gas was prepared and purged to increase the concentration of Cl<sup>-</sup> ions in the NaCl solution. The incremental increase in Cl<sup>-</sup> ion concentration shifted dynamic equilibrium by increasing the ionic product of Na<sup>+</sup>



Table 20: MR dye recovered from the retentate.

MR mass in the retentate (1× 10 <sup>3</sup> g)	Time (min)	MR concentration (g/l)	Calculated MR concentration (g/l)	Actual dye concentration (g/l)	Concentration factor
0,4	200	2	2,1	2,15	3
0,8	400	4	4,1	4,18	4
1	600	6	6,1	6,20	8
2	800	8	8,1	8,19	12
3	1000	10	10,1	10,2	18
4	1200	12	12,1	12,9	20

and Cl<sup>-</sup>. The ionic product of Na<sup>+</sup> and Cl<sup>-</sup> exceeded the solubility product of sodium chloride [solubility product of NaCl, (K<sub>sp</sub>) is 36 (mol/L)<sup>2</sup>] and thus the precipitation of sodium chloride was achieved from the saturated solution of NaCl. The supernatant solution was taken in reactive precipitation reactor and HCl gas has been purged continuously for the reactive precipitation of sodium chloride. The required HCl is being prepared and used spontaneously. After successful purging of HCl gas the sodium chloride salt is separated out from the solution by reactive precipitation. From 800 mg/l NaCl total 8300 mg/l salt recovered from the retentates of UF and RO from 1 m<sup>3</sup> textile wastewater.

**Recovery of Methyl red (MR) dye from the retentate of UF and RO:** The MR concentration in the feed and in the concentrate was measured. The calculated MR concentration in the retentate was obtained by the total mass balance of MR in the feed and in the draw solution, assuming no adsorption of dye to the membrane surface and is correlated with actual MR concentration by taken into consideration the concentration factor (Tables 19 and 20).

**Recovery of perfluoroalkyl sulfonate from the retentates of UF and RO**

100 g retentate samples containing perfluoroalkyl sulfonate was mixed with 5 ml distilled water and 70 ml methanol during 1 h. Then it was dried at 40°C under N<sub>2</sub> gas purging. The extracted mixture was placed to the methanol/ water liquid. It was centrifuged at 3000 rpm<sup>de</sup> and the extract was placed to the 0,3 ml vials. It was measured in HPLC-MS. From 1430 mg/l perfluoroalkyl sulfonate 7860 mg/l perfluoroalkyl sulfonate recovered from the retentates of UF and RO from 1 m<sup>3</sup> textile wastewater.

## CONCLUSION

The degradation of the organic content of a textile bleaching effluent has been successfully carried out by the simultaneous use of Fenton reagent under sunlight radiation. Solar light irradiation was found to be highly effective, opening the possibility of extended low cost applications. Temperature was a key parameter, markedly increasing reaction rates. The maximum COD, COD<sub>dis</sub>, DOC, Total polyphenol, TSS yields was detected at a permeate flux of 400 L/h.m<sup>2</sup> at constant CFV of 4 m/s) and a constant pressure of 4 bar. The results of the RO operation showed that RO has great effects on the removals of residual color and remaining salt from the RO at pressures between 0,4 and 4,7 bar and permeate fluxes between 93 L/h<sup>1</sup>m<sup>2</sup>-563 L/h<sup>1</sup>m<sup>2</sup>. RO water quality indexes for RO effluent all satisfied the reuse standards of recycled water. Color, COD<sub>cr</sub>, hardness, Cl<sup>-</sup> and SO<sub>4</sub><sup>-2</sup> all satisfied the standards of domestic drinking water (data not shown). Furthermore, NH<sup>3</sup>N, TN, TP, Hardness, Total alkalinity, Conductivity, Turbidity is not detectable in the permeate of RO. Overall Efficiency showed good performance in water reuse treatment. The RO system achieved

the highest removal rate of pollutants. The combined processes showed good performance in water reuse treatment. Salt, methyl red dye and perfluoroalkyl sulfonate were successively recovered from the retentates of UF and RO.

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