

Treatment of Reverse Osmosis Reject Water from Industries

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Abstract

Reverse Osmosis (RO) process is a water purification technology which purifies drinking water, desalinate the seawater and treatment of effluents from various domestic and industries to yield potable water in the form of permeate and waste in the form of RO reject or retentate or concentrate. RO reject however cannot be further purified due to the presence of high concentration of organic pollutants and high osmotic pressure must be treated before discharging. This paper review about the treatment of RO reject from the effluent of textile, pharmaceutical and leather industry to reduce the environmental impacts on further disposal of RO concentrate.

Keywords: Organic Pollutants, RO Concentrate, RO reject.

I. INTRODUCTION

Reverse osmosis (RO) is a method for the reclamation of wastewater / industrial effluent by removal of wide range of organic pollutants, bacteria and viruses, dissolved organic matter, and inorganic salts [1-5]. It is economical and ecofriendly process of purifying water. By this process, 50–80% of water for drinkable or dischargeable quality is produced as permeate [6] and the balance 20 to 30% formed as RO reject or retentate or concentrate. Generally retentate is formed by membrane fouling, coagulation and flocculation process as it cannot be further purified due to

high osmotic pressure. The application of membrane separation processes comprising ultrafiltration and reverse osmosis units includes disposal of reverse osmosis (RO) rejects through evaporator.

Reverse Osmosis Membrane rejection is influenced by interaction between effluent composition and membrane properties [7, 8]. The smoother surfaces with irregular ambiguous nodules lead to higher water fluxes and lower rejections, whereas rough surfaces with uniform distinct nodule structures contributed to higher rejections [9]. The electrostatic interactions and molecular sieving were important rejection mechanisms for membranes [10]. RO reject disposal without treating leads to environmental impacts. In this paper, an overview of Treatment of RO reject from three industries – Textile, Pharmaceutical and Leather industry were studied. The industries are chosen due to high concentration of RO reject in comparison with others.

II. RO RETENTATE OF TEXTILE INDUSTRIES:

The textile industry is one of the largest consumers of water and chemicals for wet processing of textiles [11]. Textile processing is complex and includes sizing where various types of water soluble polymers, also called textile sizing agents, such as starch, polyvinyl alcohol, carboxy methyl cellulose and acrylates are used to increase the strength of the yarn for weaving, scouring (e.g., detergent treatment), bleaching, mercerizing (where sodium hydroxide is added to provide lustrous appearance and strength to cotton), carbonizing (adding acid followed by baking and thereby removing (carbonized) impurities from wool, dyeing and finishing).

Textile wastewater treatment deals with pollutants spanning a wide range of non-biodegradable highly persistent organics and pesticides used in such insect-proof fabrics. When dyeing / printing textiles, water serves two purposes: First, the transmission of the colour onto the fibre; second, it washes out excess amounts of dyes from the treated fabrics. This class of the effluents produced are heavily coloured and contain high concentrations of salt and exhibit high biochemical oxygen demand (BOD) and chemical oxygen demand (COD) values [12].

The polluting effluents of textile and dyeing industries which is of major environmental issues are treated by physico-chemical and biological process. The physico chemical process contains membrane technologies like Reverse Osmosis / Nano filtration and ultra-filtration. Mainly the effluent treatments goes effective with RO producing 50-80% of useable permeate. But the rest 30-50% retentate out of Reverse osmosis contains high concentration of total dissolved solids and organics as reject.

The TDS of RO rejects from textile can be further treated with various process listed in Table 1: like electrodialysis, solar and wind evaporators, nano filtration, capacitive dionization(CDI).

A. Electrodialysis (ED) RO reject

ED has been found to be an economically promising method for concentrating RO reject of textile industrial effluent from 4.35% to nearly 24% inorganic constituents [13]. The application is especially useful for RO rejects containing low concentrations of COD. ED exhibits potential for large scale application to save energy by reducing the volume of textile effluent reject being sent to the evaporator enormously.

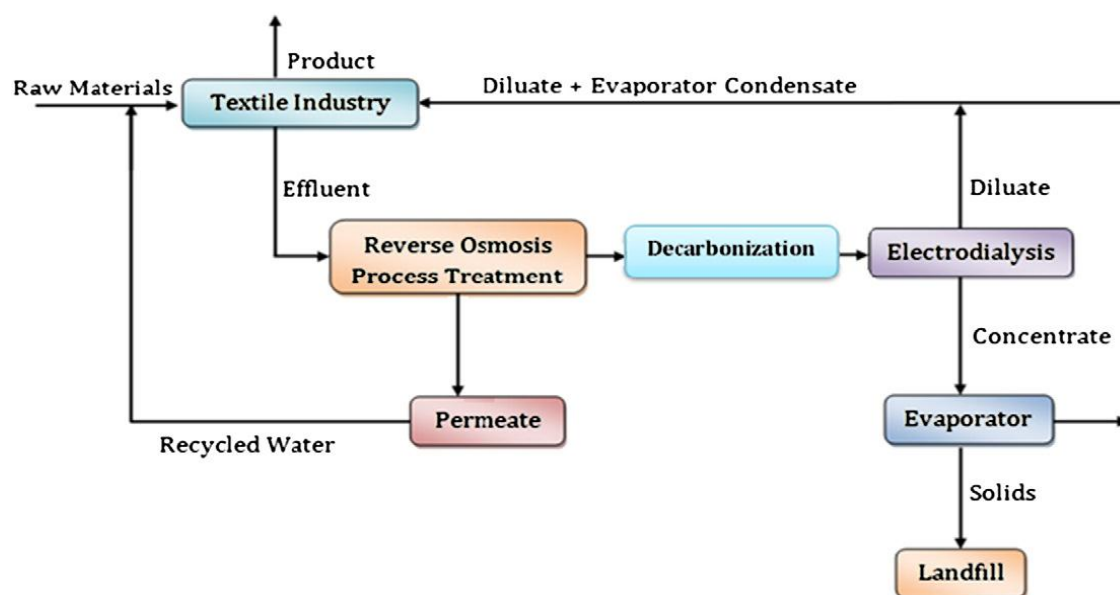


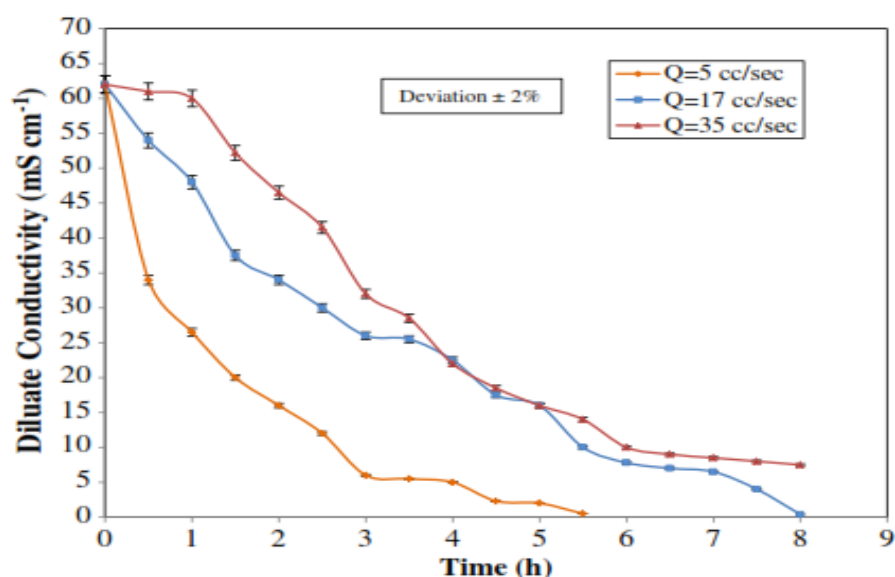
Figure 1: ED coupled reverse osmosis

RO reject of textile effluent of KNIT Textiles, Tiruppur

RO system working at KNIT Textiles, Tiruppur, Tamil Nadu, India was analyzed [13]. The TDS after RO process was found to be more than 4% with chlorides comprising nearly 1.65% w/v of the reject stream. From Table 1 comprises characteristics values of RO reject. Due to the high scaling potential caused by the high concentration of calcium and magnesium ions present in the RO reject, it was necessary to decarbonize the RO reject by aeration under constant pH condition prior to its treatment as shown in Fig. 1. For decarbonization, concentrated HCl (28% w/w) was added to the aerated RO reject, keeping the pH steady at 5.5.

Table 1 : Characteristics of RO reject of effluent from KNIT Textiles, Tiruppur

Component	RO reject	Post decarbonization (Feed to ED)
Conductivity (mS/cm)	62.6 (± 2)	59.9 (± 2)
TDS (mg/L)	47,000 (± 900)	43,500 (± 800)
COD (mg/L)	6700 (± 100)	6700 (± 100)
BOD (mg/L)	2500 (± 50)	2500 (± 50)
pH	8.8 (± 1)	5.5
Cl ⁻ (mg/L)	16,500 (± 300)	16,500 (± 300)
SO ₄ ²⁻ (mg/L)	2750 (± 50)	2750 (± 50)
K ⁺ (mg/L)	1085 (± 20)	1085 (± 20)
Ca ²⁺ (mg/L)	1195 (± 20)	520 (± 10)
Mg ²⁺ (mg/L)	1650 (± 20)	640 (± 10)

**Figure 2:** Effect of flow rate on diluate specific conductivity and time of operation

The flow rate of feed (diluate) and concentrate liquids was varied from 18 L/h to 126 L/h. Fig. 2 clearly shows the effect of flow velocity on the rate of separation. The time of operation required to attain final concentration for a flow rate of 126 L/h was 12 h and this value decreased to 8 h for 61.2 L/h. At 18 L/h, the separation was very rapid and attained within 5.5 h. The higher flow rates and removal of inorganics and organics was due to high polarization. Thus 90% efficiency of reject treatment is achieved using ED.

B. Capacitive De Ionization

The CDI process has about 3 times lower energy requirement than the Electro dialysis Reversal (EDR) process [14] and more than 3 times lower production cost as compared with as low-pressure RO desalination facility [15]. The CDI process cycle consists of three phases, namely, purification, regeneration and purge. During purification phase, an electrical field with a potential difference of about 1.2–1.5 V (direct current) between the two electrodes remove the dissolved ions from the water as its passes through the electric field. The anions and cations will attracted to the opposite charge, through the ion exchange membranes and directed to the respective electrode until saturation occurs. Product with lower conductivity will be generated during purification phase. Regeneration then takes place by reversing the potential. Hence, the ions are expelled into the rinse water and eventually purge out from the into a concentrate stream. In practice, more than 80% of water can be recovered with the CDI process [16].

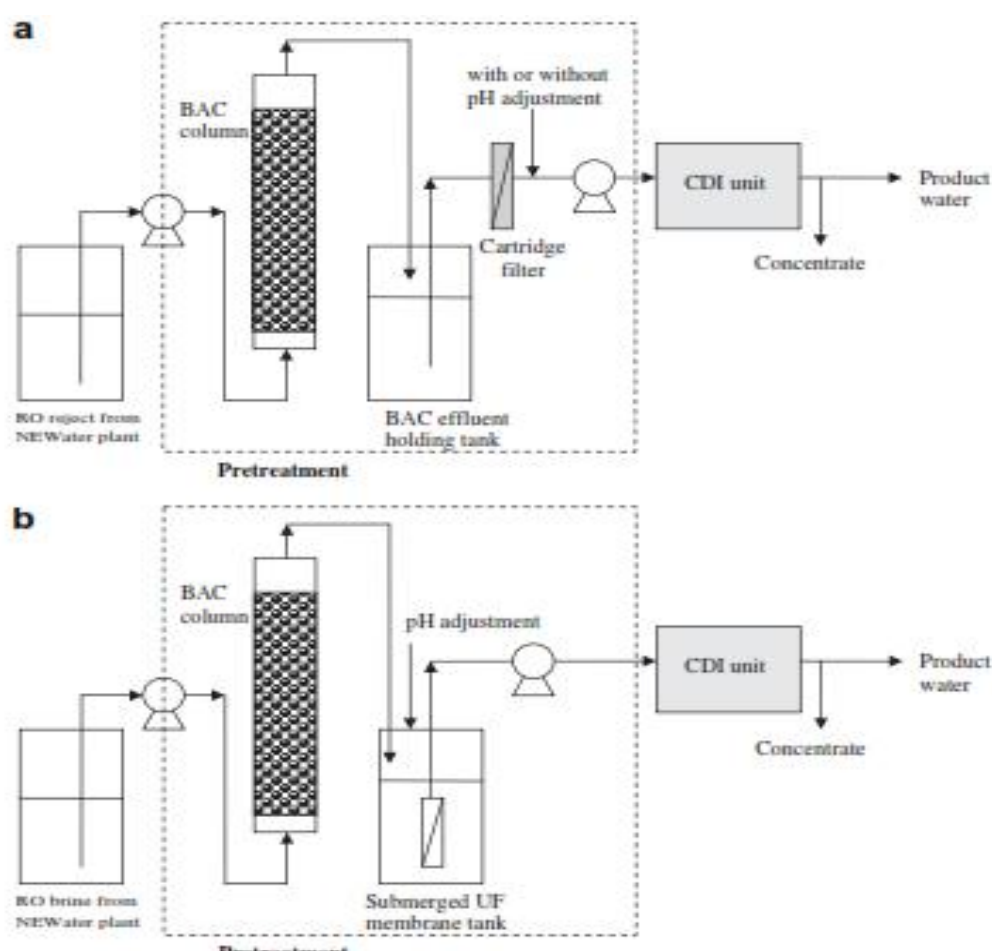


Figure 3. Schematic diagram of the experimental set-up to treat RO reject (a) P1 and P2; (b) P3.

The average water qualities of the CDI product and the removal efficiencies of the CDI process treating different pretreated effluents are summarized in Table 2. The average pH in the CDI product for P1, P2 and P3 were 7.1, 5.7 and 6.0, respectively. The average divalent ion removals were only marginally higher than the monovalent ions in the CDI product from P1 feed while there were almost insignificant differences in the removal of monovalent and divalent ions in the CDI product from P2 and P3 feed. Despite high molecular weight of the SO_4^{2-} ion, the smaller hydrated radii of this ion [17] could have contributed to the high removal efficiency (more than 87%).

Table 2: Water quality of RO feed, CDI product and their removal efficiencies

Parameters	RO feed water (mg L^{-1})	CDI product quality (mg L^{-1})			Removal efficiency (%)		
		P1	P2	P3	P1	P2	P3
TDS	484	150	142	129	88.2	90.2	90.5
TOC	6.7	9.9	7.0	6.6	53.8	63.4	50.3
Na^+	109.0	34.1	25.6	19.1	86.9	90.4	91.3
K^+	22.0	6.1	3.5	3.2	87.0	90.8	91.6
Mg^{2+}	9.0	0.7	1.6	1.3	93.6	91.4	88.3
Ca^{2+}	21.0	3.7	3.8	4.5	94.6	93.8	92.7
Cl	176.0	36.0	43.8	43.2	90.3	88.6	90.7
NO_3^-	27.0	3.3	3.1	4.6	92.8	92.9	93.0
PO_4^{3-}	17.0	14.5	6.7	5.6	52.6	65.8	80.5
SO_4^{2-}	69.0	20.5	10.4	12.2	90.2	91.9	92.8

More than 88 and 87% TDS and ion removals were achieved using CDI process from the pretreated RO reject, except for PO_4 and TOC removals of which only ranged from 52 to 81% and 50 to 63%, respectively. The product water from the integrated pretreatment with CDI process was comparable or of better quality than the RO feed water to the water reclamation plant [18].

III. RO REJECT PROCESSING OF PHARMACEUTICAL EFFLUENT

Pharmaceutical effluents contain aqua toxic substances while manufacturing process. They can be treated effectively when it is not mixed with any other sources of waste water before it gets diluted. Most common available treatment methods are discussed below [19, 20].

A. Advanced oxidation process of osmosis retentate

Advanced oxidation processes (AOPs) are an effective treatment technology for removal of variety of organic pollutants in wastewater treatment [21]. Reduction of Pharmaceutical and Personal Care Products (PPCPs) concentrations in the RO retentate through Advanced oxidation processes (AOPs) for destroying the high concentration of effluent organic matter (EfOM) and other inorganic constituents by high radiation was studied [22].

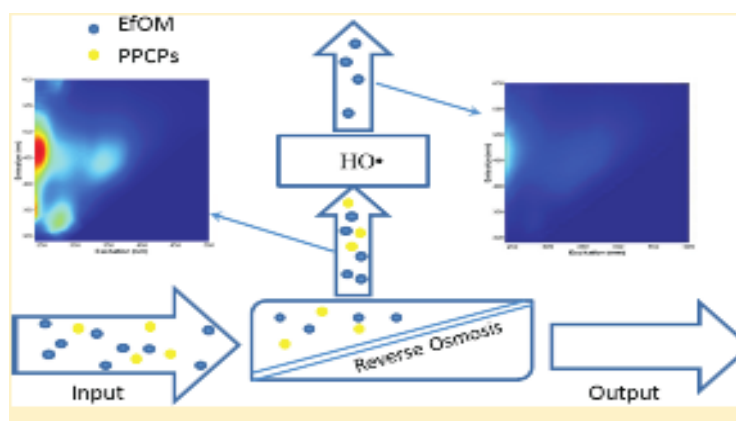
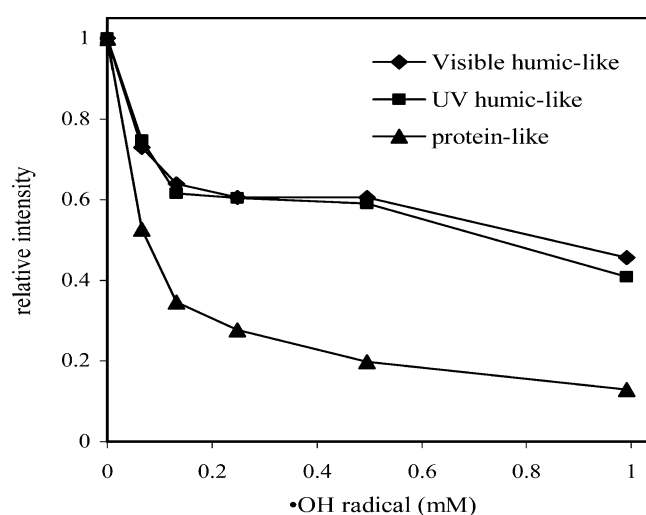


Figure 4: AOP

Based on the absolute hydroxyl radical ($\text{HO}\cdot$) reaction rate constants for individual pharmaceutical compounds, and that of the RO retentate (EfOM and inorganic constituents), it was possible to model their destruction. Using excitation-emission matrix (EEM) fluorescence spectroscopy, the $\text{HO}\cdot$ oxidation of the EfOM could be observed through decreases in the retentate fluorescence. The decrease in the peak normally associated with proteins correlated well with the removal of the pharmaceutical compounds.



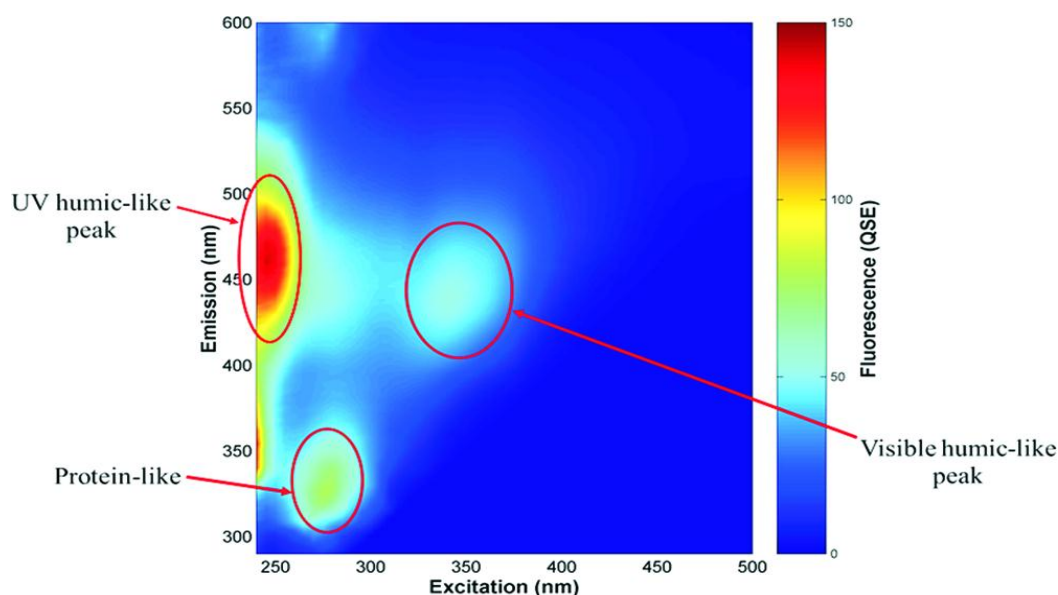


Figure 5: Relative intensity of the fluorescence peaks as a function of HO• oxidation. (9 UV humic-like peak: $\lambda = 459$ nm, (visible humic-like peak: $\lambda = 345$ nm, $\lambda = 245$ nm, $\lambda = 445$ nm, protein-like peak: $\lambda = 276$ nm, $\lambda = 329$ nm).

The removal of PPCPs approached 80 to 100%, while there was a 40 to 50% reduction of UV and visible humic-like peaks (as illustrated in Figure 5). At the same time, the protein-like peak showed good correlation with individual PPCP removal up to 80%. This result suggests that monitoring the protein-like peak may be a suitable indicator for evaluating the HO• radical loss of PPCPs in RO retentate. The decrease in the peak normally associated with proteins correlated well with the removal of the pharmaceutical compounds. These results suggest that fluorescence may be a suitable parameter for monitoring the degradation of PPCPs by AOPs in RO retentate.

B. Electrochemical oxidation

In addition to conventional technologies, such as coagulation and activated carbon adsorption [23], advanced oxidation technologies, including ozonation, photocatalysis, sonolysis, and electrochemical oxidation have been proposed for eliminating contaminants from the concentrate stream [24-30]. Electrochemical oxidation, in particular has several advantages. For example, it can be used to treat RO concentrate streams with moderate to high salinity [31], which ensures excellent electric conductivity and reduces the energy consumption, and with moderate chloride concentrations, which promote indirect oxidation and disinfection pathways [32].

Several composite samples were obtained from points 1 (7) and 2 (8) and analyzed for 77 compounds; Two grab samples were obtained from points 3, 4 and 5 and analyzed for 12 compounds. The concentrations of 10 compounds were measured in 6 grab samples obtained from point 6. The electro oxidation of the reverse osmosis concentrate was performed in a commercial DiaCell system (two 70 cm UF, Permeate 2 circular electrodes, boron doped diamond on silicon anode and stainless steel cathode, separated by an electrode gap of 5 mm) using a power supplier (Agilent 6654 A, maximum output of 9 A and 60 V), feed tank with a cooling jacket and recirculation pump. The feed temperature was maintained at 20 °C. All the experiments were performed in batch mode, with a recirculation flow-rate of 10 L/min, and working volume of 2 L. The applied current (J) ranged from 20 to 100 A/m. Composite water samples were taken from the WWTP influent and effluent, while grab samples were withdrawn from the outlet streams of the tertiary treatment units.

Electro oxidation is a promising technology for removing emerging contaminants from the RO concentrate streams as shown in Fig.7. High removal percentages were obtained for most of the selected compounds. The removal values by this method are comparable to those reported by Menapace et al. [33] who proposed combining electro oxidation and ozonation treatments to achieve elimination values of up to 99% for the group of studied pharmaceuticals.

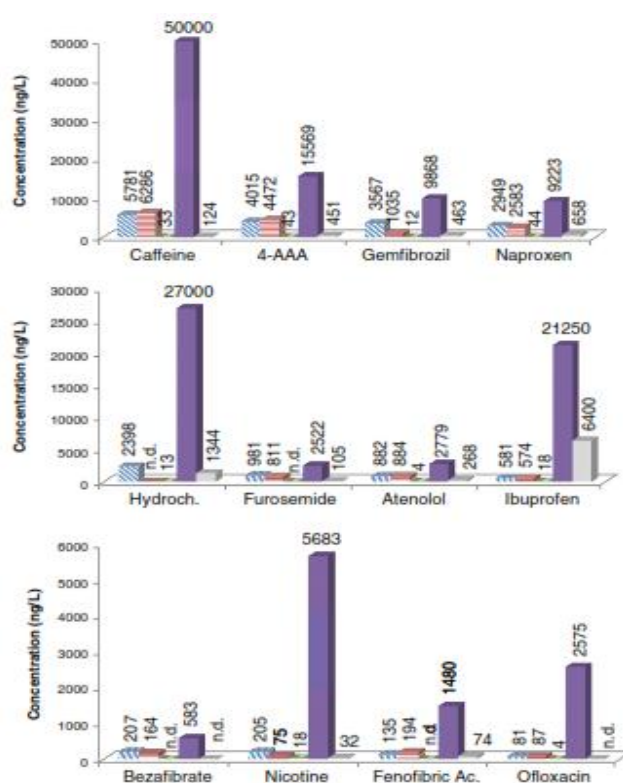


Figure 6: Concentrations (ng/L) of emerging pollutants at different stages of the advanced treatment at the Vuelta Ostrera WWTP. ... WWTP effluent; UF permeate; RO Permeate; RO Concentrate; ELOX effluent. n.d.: not detected.

IV. RO REJECT PROCESSING OF TANNERY EFFLUENTS

The Indian leather industry is the sixth largest tanning industry in world (Council for Leather Exports, 2010). It almost satisfies 10% of worldwide requirement for leather. With about 3000 tanneries dealing 700,000 tonnes of hides and skins per annum, generates about 100,000 m³ of wastewater per day [34]. Various chemicals generally used in tanning industry due to the process of soaking, liming, pickling, tanning, splitting, trimming and dyeing are sodium chloride, lime, sodium sulphide, ammonium, sulphuric acid, formic acid, chromic acid, anionic dyes, acid dyes, basic dyes etc. Volume of wastewater generated and its characteristics vary from tannery to tannery. They may also vary within the same tannery from time to time. The waste discharges from each sectional operation are rich in TDS, BOD, COD. Table 3 comprises the different technologies used for RO reject of tannery effluent by different authors. The major problem regarding Indian leather industry is the treatment of waste and safe disposal of concentrate while permeate can be reused in many industries since.

Table 3 : Summary of RO reject treatment technologies and authors

RO Reject Treatment Technologies	References
Electro coagulation	Espinoza- Quiñones et al., 2009;
Fenton Oxidation	Schrank et al., 2005; Módenes et al., 2012
Ozonation	Preethi et al. 2009; Westerhoff et al. (2009)
Photo catalysis	Dialynas et al., 2008; Zhou et al., 2011

A. RO reject of tannery using solar evaporator

Reverse Osmosis (RO), the membrane separation process, is widely being used on the fresh water supply to industrial and domestic sectors with the generation of reject streams containing huge concentrations of cations and anions besides organic impurities. Hence, the reject stream is advised to evaporate in solar pans/multiple effect evaporators to reduce the volume of disposal. The evaporated residue consists of a high concentration of chloride and sulfate ions along with organic impurities.

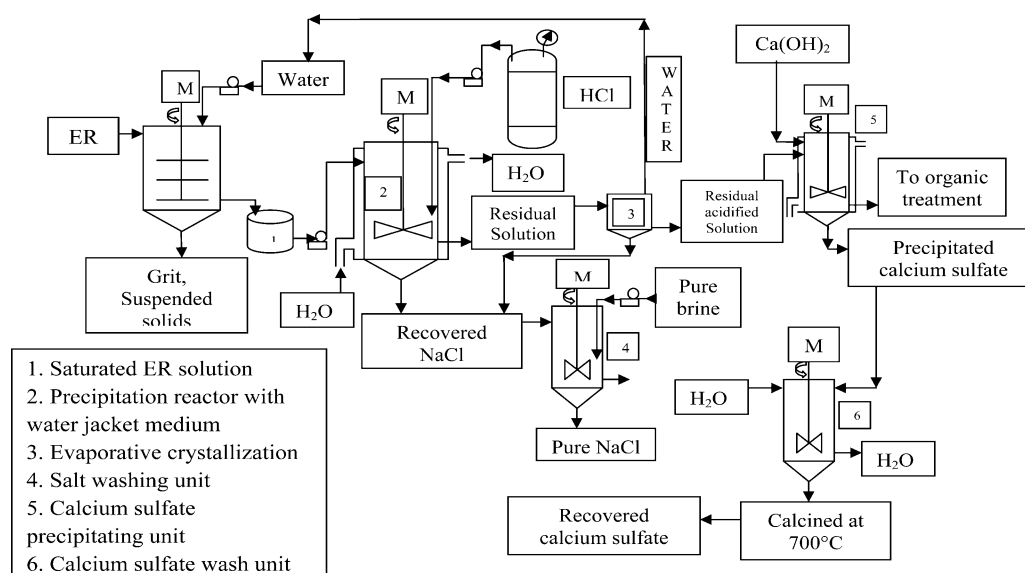


Figure 7: Schematic flow diagram for the separation of chloride and sulfate ions from ER generated from the leather industry.

The separation of sodium chloride from ER was selectively removed by reactive precipitation technique using hydrogen chloride gas. The reactive chemical precipitation technique removed NaCl by 27g/100 mL from ER solution. In order to increase the NaCl recovery, the residual solution was subjected to concentrate by evaporation of water molecules at 120 °C. Figure 9 shows that the increase in evaporation of water increased the crystallization of NaCl [35].

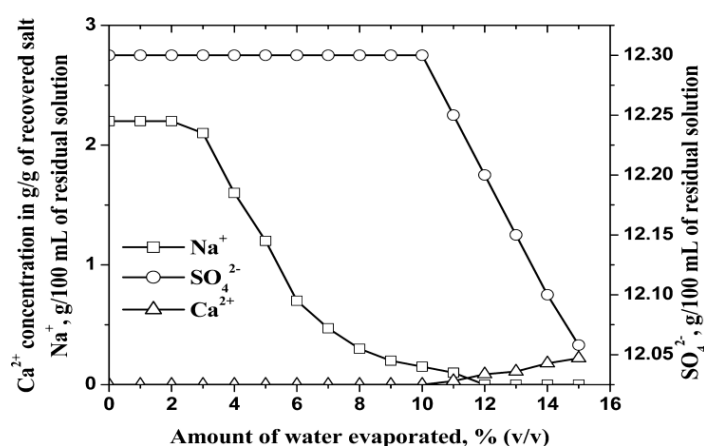


Figure 8: Effect of water evaporation on NaCl recovery from residual ER solution by evaporative crystallization

In order to study the effect of pH on sulfate ion separation, the pH of residual acidified ER solution was varied from 0.0 to 7.0 by the effect addition of calcium hydroxide solution. Figure 10 shows that the increase in solution pH from negative pH to 7.0 increased the separation of sulfate ions as calcium sulfate significantly. This was due to the precipitation of sulfate ions as calcium sulfate by exceeding the solubility product of Calcium sulphate in the solution. The integration of evaporative crystallization along with the reactive precipitation using HCl gas significantly enhanced the percentage recovery of NaCl from 84% to 99.5%. Further, the sulfate ion in the ER solution was separated by the addition of various neutralizing agents. Among the neutralizing agents Ca(OH)_2 and MgO , the Ca(OH) was effective on the separation of sulfate ions from the acidified ER solution. [36].

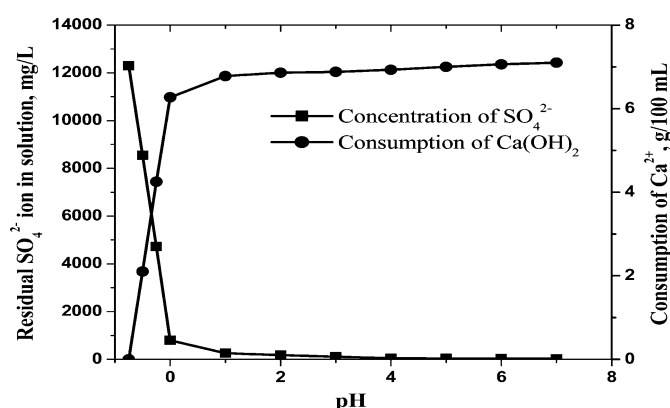


Figure 9: Profile of solution pH and consumption of calcium hydroxide as Ca^{2+} during the precipitation of sulfate ion from residual acidified ER solution.

V. CONCLUSION

In RO reject processing, the maximum efficiency of alternate treatment depends on the nature of industries and effluent. The maximum efficiency was achieved by oxidation processes in majority of industrial effluents. Hence the future studies are carried out in deeper to understand the process in better and utilize it in most efficient way.

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