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MEMBRANE TECHNOLOGY AND ITS SUITABILITY FOR TREATMENT OF TEXTILE WASTE WATER IN PAKISTAN

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Abstract
Membrane technology has wide range of applications in the textile industry. Various types of dyes and chemicals can be recovered from the textile effluent using this technology and a large proportion of wastewater can be reused. Since textile is one of the major industries in Pakistan and it utilizes a huge volume of water, membrane technology can be an efficient and cost-effective method for treating textile effluents. The problem of membrane fouling is also discussed. The suitability of the technology has been assessed. The approach of employing primary treatment methods followed by Coagulation and Reverse Osmosis through Membranes is being recommended. The effectiveness of various types of membranes available in the world needs to be demonstrated for a specific plant. The results of initial studies performed by Aslam *et al*. have also been included.

Keywords: Coagulation, Dyes, Membrane Technology, Waste water.

INTRODUCTION
The textile industry uses a large quantity of chemicals and huge quantities of water. Detergents and caustic are used to remove dirt, grit, oils, and waxes. Bleach is used to improve whiteness and brightness. Dyes, fixing agents, and many in-organics are used to provide the brilliant array of colors the market demands. Sizing agents are added to improve weaving. Oils are added to improve spinning and knitting. Latex and glues are used as binders. A wide variety of specialty chemicals are used such as softeners, stain release agents, and wetting agents. Many of these chemicals become part of the final product whereas the rest are removed from the fabric and are purged in the effluent stream. The local authorities have begun to target the textile industry to clean up the wastewater that is being discharged. Regulators are looking for toxicity due to high salt content, high salt Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD), heavy metals, and color of the effluent.
The textile industry in Pakistan comprises of 670 textile units. It is estimated that 65% of export revenue is generated by the textile sector and 38% of workforce is employed by the textile industry. The overall share of the textile industry in the

GNP is 9% [Aslam *et al*.]. Fig. 1 indicates the share of cloth production of various continents. More than 70% of the world cloth production is done in Asia/Oceania countries [Visvanathan and Kumar 2000]. The value added share to total value added by textile industry in developing countries is shown in Fig. 2.

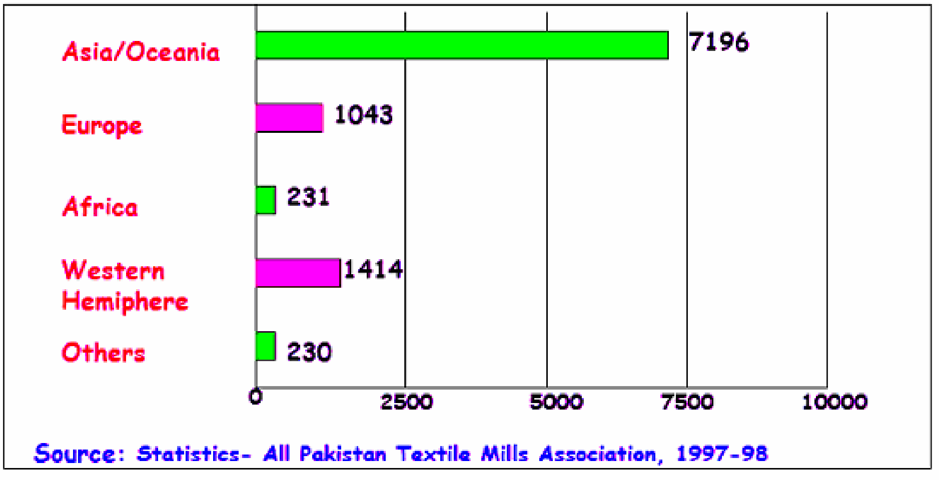

Fig. 1: World cloth production in '000 metric tonnes (1997-1998)

The conventional technologies for textile wastewater treatment are categorized as:

- Biological Treatments (e.g. aerobic/ anaerobic digestion, plant absorption, bio-scrubbers, bio-filtration etc.).
- Chemical Treatment (e.g. neutralization, oxidation, reduction, catalytic oxidation, ion exchange etc).
- Physical Treatments (e.g. filtration, sedimentation, adsorption, and membrane etc)

Coagulation followed by Membranes Technology is being considered to be the best combination for the waste treatment of textile effluent. A typical reverse osmosis membrane separate dissolved solutes from water via a semi-permeable surface that allows water to pass in preference to the solute. The membrane is made using a long chain organic molecule, called a polymer. This polymer must be hydrophilic i.e. water is attracted to its chemical structure [Saeed Gul *et al*. 2005]. Ferrous Sulphate, alum, lime, and polyelectrolyte magnofloc have been reported to give good results to reduce micro organisms [Wagner 2001]. Membrane processes for water treatment are pressure-driven processes. This is a new technology which can restrict maximum micro-organisms present in waste water. It can be helpful in areas such as: color removal, BOD reduction, salt reduction, Polyvinyl Acetate (PVA) recovery, and latex recovery. Membrane technology is unique in that it can provide a return on investment and can contribute towards pollution abatement. Also, capital investment in this technology is competitive with conventional techniques. The common membrane types are:

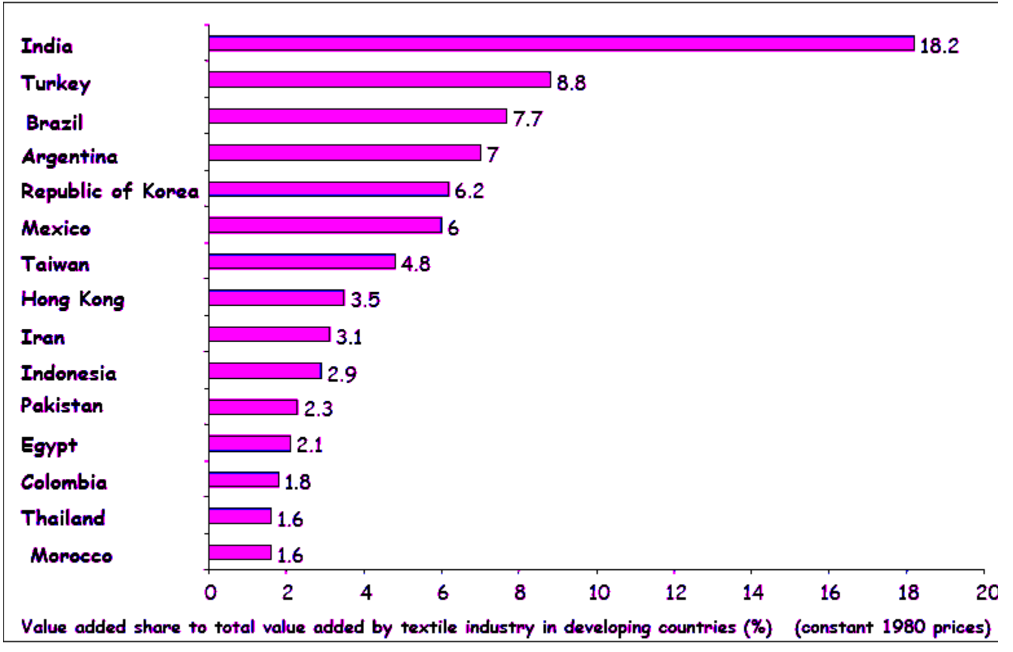

Fig. 2: Value added share to total value added by textile industry in developing countries.

- Micro-Filtration (MF)
- Ultra-Filtration (UF)
- Nano-Filtration (NF)
- Reverse Osmosis (RO)

Micro-filtration is used to separate colloids from polymers with pores of 0.1 to 1 micron. MF will typically show 90+% reductions in turbidity or silt density index. Typical applications are clarification of juices and clarification of sugar solution. Micro-filtration membranes are made of several polymers including Poly (Ether Sulfone), Poly (Vinylidiene Fluoride) and Poly (Sulfone). Ceramic, carbon and sintered metal membranes have been employed where extraordinary chemical resistance or where high temperature operation is necessary.

Ultra-filtration is used to separate polymers from salts and low molecular weight materials, with pores of 0.001 to 0.1 micron. Turbidity is sharply reduced by 99+%. Polymers are retained for reduced TOD (Total Oxygen Demand), BOD_5 (Biological Oxygen Demand) and COD (Combined Oxygen Demand). A wide range of molecular weight cutoffs are available from 1000 to 500,000 Daltons. Typical applications are haze stability in juices, concentration of E-coat paint, whey protein concentration and concentrating stable oily water emulsions. UF is an excellent mean to remove metal hydroxides, reducing the heavy metal content to 1 ppm or less.

Nano-Filtration is used to separate sugars and divalent salts from water and monovalent salts. NF has found wide application for water softening. It also is demonstrating ability to decolorized solutions. However, NF modules are extremely sensitive to fouling by colloidal material and polymers. For this reason extensive pretreatment is required. UF makes an excellent pretreatment substitute by eliminating the polymer addition, chlorine disinfectant and mixed media per-filtration. Virtually all NF and RO membranes are thin film composite membranes.

Reverse Osmosis is used to remove almost every thing from water. Like NF, RO is very sensitive to fouling and the influent stream must be carefully pretreated. As a rule of thumb, the smaller the pore the higher the operating pressure, the capital investment and the operating cost. MF and UF operate at 20 to 100 psi transmembrane pressures (P_{tm}) and velocities of 20 to 100 cm s^{-1}. Typical NF flux rates are 5 to 30 GFD (Gross Flow per Day). The (P_{tm}) in RO is typically 500 to 1000 psi, with cross flows of 20 to 100 cm s^{-1}. The range of typical RO fluxes is 5 to 15 GFD.

The choice of a membrane material is determined by the specific application objective i.e. removal of particulate or dissolved solids, hardness reduction or ultra-pure water production, removal of specific chemicals etc.

MEMBRANE MATERIALS

Membranes are made of different polymeric materials, depending upon membrane type and application. RO membranes and NF membranes are generally made of cellulose acetate and aromatic polyamides. UF membranes are made of polymeric materials, i.e., polysulfone, polypropylene, nylon-6, polytetrafluoroethylene (PTFE), Polyvinyl Chlorides (PVC), acrylic copolymer etc. Inorganic materials such as ceramics, carbon based membranes, zirconia etc are also used in manufacturing RO and NF membranes. The MF membranes are made from natural or synthetic polymers such as cellulose acetate, polyvinylidene difluoride (PVDF), polyamides, polysulfone, polycarbonate, polypropylene, PTFE etc. The inorganic materials such as metal oxides (alumina), glass, zirconia coated carbon etc. are also used for manufacturing the MF membranes.

WASTEWATER ANALYSIS OF TEXTILE INDUSTRY

A typical textile unit is expected to generate various types of waste water differing in magnitude and quality at the stages shown in Table 1.

Table 1: Wet processes producing waste water.

Process	Effluent
Singering Desizing	High BOD, high TS (Total Solids), neutral pH
Scouring	High BOD, high TS, high alkalinity, high temperature
Bleaching	High BOD, high TS, alkaline wastewater
Mercerizing	
Heat-setting	Low BOD, low solids, alkaline wastewater
Dying, Printing & Finishing	Wasted dyes, high BOD, COD, solids neutral to alkaline wastewater

Table 2 shows typical wastewater analysis of the textile industry in Pakistan [Markovska et al., Ara 1998, Anonymous 1999]. The analyses were performed on seven different industries in Pakistan.

Table 2: Waste Water Analysis of Textile Industry in Pakistan.

Sr. No.	Industry	pH	BOD mg l^{-1}	COD mg l^{-1}	TDS mg l^{-1}	TSS mg l^{-1}	Cl ppm	SO_4 ppm	S ppm
1.	Sitara Textile Mill	9.9	480	1230	4810	970	2400	370	1.3
2.	Ihsan Yousuf Textile Mill	11.8	201	900	5250	1620	1050	750	3.5
3.	Al-karim Dying & Printing	8.0	210	810	3460	930	1100	660	0.5
4.	Al-Rafiq Dying	7.7	1100	2600	4790	370	1150	710	0.5
5.	Chenab Fabrics	8.2	190	380	4200	130	1050	500	0.5
6.	Hilal Corporation Dying Unit	6.7	540	2460	5560	470	1600	580	12
7.	Hilal Corporation Printing Unit	8.8	480	2300	5280	200	1010	800	0.2

The National Environmental Quality Standards for Municipal and Liquid Effluents in Pakistan [Ara 1998] are as presented in Table 3.

Table 3: National Environmental Quality Standards.

Parameters	Standards mg l^{-1}
pH	6-9
BOD_5	80
COD	150
TDS	3500
TSS	200
Cl	1000
SO_4	600
S	1.0
Others (Oil & Grease)	1.0

APPLICATIONS

Membrane technology offers several applications at various stages of textile processing. These applications are unique because they provide a return on investment while abating the water pollution problem. The main stages of textile processing where membrane technology can be helpful are printing, scouring operations, dyes bath, latex recovery, sizing, and indigo recovery.

PRINTING

The printing operation uses large quantities of water for washing the continuous rubber belt as shown in Fig. 3. The wastewater is laden with fine pigments and polymeric binders giving the stream high color and BOD. UF membranes can be used to remove the color and the binder. The clean permeate has a 90% reduction in BOD and 100% reduction in color. The water can be recycled back to the print machine for reuse. One of the recommended membranes for this application is the one inch FEG (Fluid Extracting Gauze) tube used in a modified batch mode. It readily handles the high viscosity fluid at the end of the run. It can be mechanically cleaned with a sponge ball or pig and it has a long membrane life. Economics are based on the reuse of the water and the reduction of BOD. Lower water costs are realized through reduced volumes to be purchased and treated and the lower BOD level can reduce fines and surcharges.

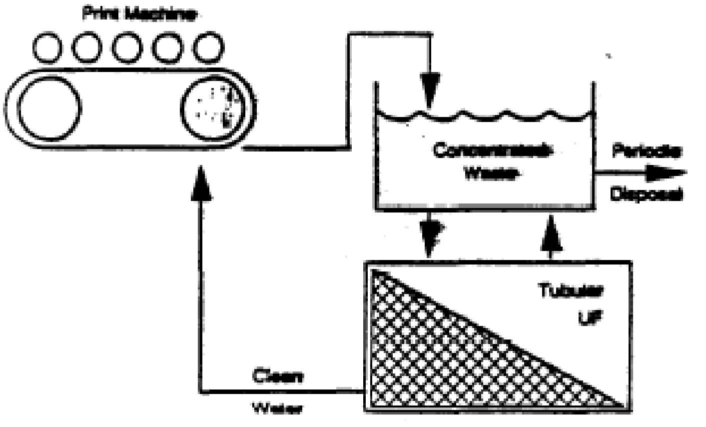

Fig. 3: Schematic diagram of wastewater generated from printing process.

SCOURING OPERATION

Scouring operations (Fig. 4) generates large BOD, oil and grease loadings on the sewer system. Heavy metals in cotton greige goods sometimes cause a problem also. Typically, these emulsions are stable and hard to treat by traditional means. UF membranes retain and concentrate the emulsion to 30-50% oil which can be economically hauled away. At these concentrations the O/W (Oil-in-water) emulsion supports combustion and can be used as fuel. Heavy metals are reduced to their solubility limit, usually less than 1ppm. Scouring operations are best achieved with ceramic or hollow fiber membranes.

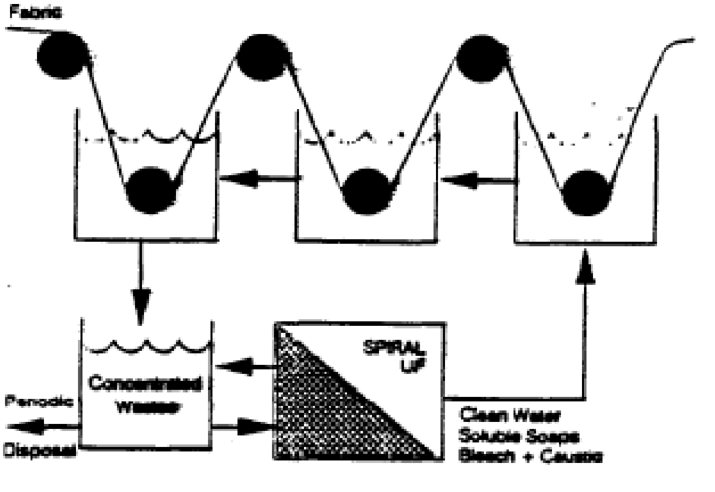

Fig. 4: Wastewater generation from scouring operations.

DYE BATH

Most dye baths (Fig. 5) have three major pollutants: the dye which presents an aesthetics problem in waters used for recreation, heavy metals incorporated in the dye, and the salt which can present a toxicity problem when discharged to small streams. UF is capable of completely separating many dyes such as vat, acid, and pre-metallized dispersed and direct dyes from the brine. Some dye manufacturers use UF to wash excess salt out of the dyes. NF can be used to separate fiber reactive dyes and cationic dyes from the salt. Cost savings are generated from the reuse *of* water, recovery of heat from water and the value of the dyes if the dye is reused. Also, salt recovery from the dye offers good return on investment.

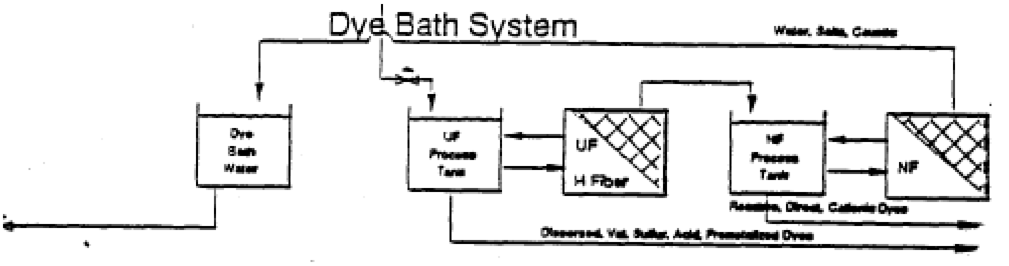

Fig. 5: Dye Bath System.

LATEX RECOVERY

Latex is an expensive material used as the binder in carpet manufacturing. In general, latex is mixed with an extender such as calcium carbonate. The waste stream is too dilute to be reused and is discarded causing aesthetics and BOD/COD problem. Latex recovery by UF is a standard operation for the many latex manufacturers and users. Latex has two benefits, decreased purchase of latex and BOD reduction. The hot permeate is laden with surfactant, making excellent process for cleaning water.

SIZE RECOVERY

PVA size recovery has been used in large, integrated weaving plants to recover and concentrate the size from the desizing bath as shown in Fig. 6. Size recovery can be used economically on small stream to remove the size from the desizing baths. The size can be reused in-house or sold to a nearby weaving company. As a last resort, the size can be hauled off as waste. The hot permeate can be recycled back to the desizing bath. Poly (Acrylic Acid) and polyester sizes can also be recovered through this way. Cost saving are achieved from lower PVA purchases, lower BOD surcharges, heat recovery and water reuse.

INDIGO DYE RECOVERY

Indigo dye is only 80% fixed onto the fabric with the remainder being washed away. The Quinine from it is highly insoluble in water and can readily be recovered by UF. The concentrate can be blended with fresh Indigo, reduced with hydrosulfite and caustic and reused. One of the recommended sufficient arrangements for this application is to use a 1 feet tube to blend the material. The high cross flow velocity gives highly stable fluxes while keeping system and operating cost to minimum.

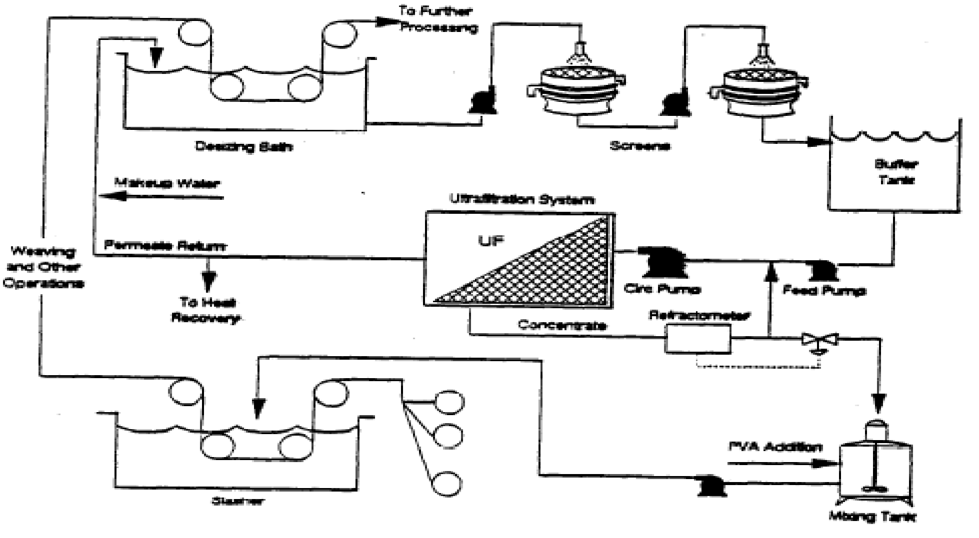

Fig. 6: Overall PVA Recovery System.

WATER SOFTENING

Nano-filtration is an excellent alternative to ion exchange or green sand water softening. NF is popular to soften, decolorize, and eliminate bacteria and viruses from the drinking water supply. The principal advantages are low maintenance, no regeneration costs, and low discharge volume.

DISCUSSION

Combining membrane technology with physio-chemical treatment has advantages over the other processes. Membrane processes have many cost-effective applications in textile industry. The cost competitiveness results from the ability to recover materials with valuable recycle water, reducing fresh water consumption and waste water treatment costs, small disposal volumes which minimizes waste disposal costs reduction of regulatory pressure and fine [Markovska *et al*.]. Generally, cellulose acetate and aromatic polyamide membranes are employed during treatment of textile water through membrane process [Mark *et al*.]. The membrane processes are getting popular for waste water treatment and millions of US dollar membranes are sold annually. The relative cost and advantages [Stephen *et al*. 2002] of various membranes are presented in Table 4.

The textile industry is becoming more need of a closed operation. Hence, strategically placed membrane system can play an important role in recovering chemicals which are presently being lost as well as high quality water can be produced [Pala *et al*. 2003].

Table 4: Membrane configuration cost analysis and advantages.

Configuration	Area to Volume Ratio m^2/m^3	Cost	Advantages
Pleated Cartridge	800-1000	Low	Robust construction, compact design.
Plate and frame	400-600	High	Can be dismantled for cleaning
Spiral Wound	800-1000	Low	Low energy cost, robust and compact
Tubular	20-30	Very High	Easy mechanical cleaning, high TSS tolerant.
Capillary tube	600-1200	Low	Characteristics between tubular and hollow-fiber membrane
Hollow-Fiber	5000-40,000	Very Low	Compact design, tolerates high, colloidal level

CONCLUSIONS

Membrane processes have many cost effective applications in the textile industry. The ability to recover materials of value, recycle water, hence reducing water consumption, reduction of regulatory pressures, fines and improved heat recovery systems are of significant importance. Since textile industry is a major sector in Pakistan and huge volumes are used for processing, the use of membrane technology can be beneficial. As the environmental regulation and conservation of water resource issue are becoming hot in the country, the recovery of water from textile industry has gained significance. The survey presented indicates the suitability and large scope of RO membrane in Pakistan.

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