CHAPTER 2 : LITERATURE REVIEW

2.0 WATER USE AND FUTURE DEMANDS

Demand for water is rising at a faster rate today than at any previous moment in history. A world water crisis seems likely to emerge during the 21st century as this demand is accelerated by population growth, greater affluence and the mounting needs of agriculture, industry and other users (Rhoda,1995) to a level beyond the available water resources over widening areas of the globe. The changing global climatic trend is also a cause for concern, as there is the danger of reduced water resources in some areas while other areas may suffer an increase in severe storms.

Human use of water has increased more than 35 fold over the past three centuries and four-fold since 1940. Easter & Hearne, (1995) reported that recently, water withdrawals have been increasing 4-8 percent per year, with the bulk of the demand arising in the developing world. 60 percent is used for agriculture, 23 percent for industry and 8 percent for domestic uses. In Asia and Africa, over 85 percent of the water is used for agriculture. Average consumption rates vary widely, with per capita consumption in North and Central America being over twice that of Europe's, three times that of in Asia and seven times that of in Africa.

With the worlds' population growing to at least eight billion by 2025, and assuming steadily rising living standards, the demand for water will increase dramatically. Shortage of fresh water, deteriorating water quality, environmental pressures, increasing water and effluent treatment cost have all continued to raise the importance of water and waste water in industry. As water availability becomes more critical, the reuse of water will become environmentally and economically necessary.

2.1 INDUSTRIAL WATER POLLUTION

Industries discharge a broad spectrum of pollutants into our waterways. In the aggregate, they form the largest and most toxic of all concentrated sources of pollution. On the average, it has been reported that in the United States, industries discharge about three times the amount of waste that is discharged by all the sewered private residences, and the volume is increasing several times as fast as that of sanitary sewage. (Hunt, 1975)

Industries consume large quantities of water and are the major factor in the continuing rise in water pollution. Besides high BOD loads, industrial effluents contain enormous quantities of mineral and chemical wastes, which steadily become more complex and varied. These mineral and chemical wastes include metals such as iron, chromium, mercury and copper; salts such as compounds of sodium, calcium and magnesium; acids such as sulphuric and hydrochloric; petroleum wastes and brines; phenols, cyanides, ammonia, toluene; blast furnace wastes; greases; all varieties of suspended and dissolved solids; and numerous other wastes compounds. These wastes degrade the quality of the receiving waters by affecting tastes, odour and colour, excess mineralisation, salinity, hardness and corrosion. Many of these substances are toxic to plant, animal and human life.

The variety and complexity of inorganic and organic components and metals contained in industrial effluents present a difficult pollution control problem. Industrial pollution control technology must be adequate to achieve effective yet economical control of pollution from industrial sources. Generally, there are two basic options to pollutant discharges, these being :

1. The treatment of effluents resulting in harmless discharges into the environment.

2. The management of industrial activities in a manner that results in no discharge of pollutants into the environment.

As we attempt to treat effluents for discharge into the environment, one must consider the water quality standards and criteria that must be met. The very low recommended limits for various parameters would mean extensive effluent treatment coupled with stringent analytical and monitoring programmes. As the efficiency of pollutant removal approaches 100%, the incremental cost of effluent treatment also rises sharply for each small percentage change in additional removal efficiency. It is for this reason that industries may find treatment of effluents for harmless discharge may well be less desirable compared to a no discharge system where a less stringent water quality criteria may be required.

In terms of cost and pollution control, the closed cycle water management system may well be the best long term viable approach for containment of toxic pollutants within industrial plants. In the closed cycle system, the approach taken to environmental protection is based on the premise of removing only what is essential to permit reuse of effluents in an industrial operation.

2.2 WASTE WATER RECLAMATION TECHNIQUES

Most of the current waste water reclamation technologies are essentially the same as those used for water and waste water treatment. In certain cases, however, additional treatment processes may be required for the removal of selected physical and chemical contaminants and for inactivation or removal of microbiological pathogens. Some of the most commonly used treatment processes include chemical precipitation, carbon adsorption, selective ion exchange, and membrane treatment which are elaborated hereafter.

2.2.1 Adsorption

Adsorption is the process of collecting soluble substances that are in solution on a suitable interface. Adsorption at a surface or interface is largely the result of binding forces between the individual atoms, ions or molecules of an adsorbate and the surface, all of these forces having their origin in electromagnetic interactions (Webber and Van Vhel, 1980). The process can occur between any two phases, such as a liquid-liquid or liquid-solid interface. The adsorbing phase is termed as the adsorbent while the material being concentrated or adsorbed is the adsorbate. Adsorption is a surface phenomenon, as such all adsorbents are characterised by their surface area. The quantity of adsorbate that can can taken up by an adsorbent is a function of both the characteristics and concentration of the adsorbate and temperature. Generally, the amount of material adsorbed is determined as a function of the adsorbate concentration at a constant temperature, and the resulting function is called an adsorption isotherm.

Activated carbon is the most widely used adsorbent because of its capability to adsorp a broad range of different types of adsorbates. It is most widely used for the removal of organic contaminants. In waste water treatment, activated carbon treatment is thought of as a polishing treatment for waste water that has already received primary and secondary treatment. Dissolved organics and particulate matter can be effectively removed by adsorption process. Huang and Blakenship (1984) suggested that activated carbon adsorption can be particularly competitive and effective for the removal of heavy metals at trace quantities.

2.2.2 Ion Exchange

Ion exchange is considered to be a stoichiometric process; that is, every ion removed from the solution by electrostatic attraction to the charged surface is replaced by an equivalent amount of a similarly charged ionic species displaced from the interfacial region. The whole process is conceptualised as the reversible exchange of electrolyte counter ions in the diffuse layer near a charged surface or in a separate phase, as in Donan equilibrium (Webber et al.; 1972).

Ion exchange resins are made in the form of very small spheres or beads so that when packed in a column, they present an enormous surface area to the effluent and each bead has on its surface thousands of functional groups (Robert, 1991).

In an aqueous system, sorption of an ion on a charged solid is governed by two main processes :

1) Non-specific electrostatic attraction to the charged surface
2) Chemical bonding at discrete sites on the surface

Ion exchange resins can be regenerated and used over and over again. Cationic resins are regenerated by mineral acids but a high concentration of salt residue is produced in the regeneration process (Higgins, 1989)

2.2.3 Chemical Precipitation

Chemical precipitation involves the addition of chemicals to alter the physical state of dissolved and suspended solids and to facilitate their removal by sedimentation. Over the years a number of different substances have been used as precipitants, namely alum, ferric chloride, ferric sulphate, ferrous sulphate and lime.

An important factor in the stability of colloids is the presence of surface charges. Surface charges develop through preferential adsorption, ionisation or isomorphos replacement. A double layer is formed when counter ions become attached to the charged surface of the particle. The existence of this double layer surrounding the colloidal particles inhibits the close approach of colloids to each other (Webber et al.; 1972). In order to remove suspended solids from liquids, charge destabilisation and charge neutralisation of the particles must be achieved, to allow aggregation of the particles to form larger particles with enough mass to settle easily (Feledy and Antonucci, 1981).

The effect of the charge can be overcome by the addition of coagulants such as potential determining ions, polyelectrolytes or chemicals that form hydrolysed metal ions such as ferric chloride, alum etc. Factors influencing the destabilisation mechanisms include the type and dosage of coagulants, pH, chemical composition of the waste water and mixing conditions (Clark and Srivasta, 1993). Generally chemical precipitation yields high sludge volumes which is dewatered and stabilised prior to disposal.

Studies by Feledy and Antonucci (1981), highlighted that in the treatment of paint waste water, successful chemical treatment could only be achieved by the use of polyelectrolytes. Coagulants containing charges opposite to that of the suspended solids were used to neutralise the colloidal surface charge. In treatment of paint waste water, anionic charges of the suspended solids were neutralised by the addition of cationic coagulants. Neutralisation of surface charges allows the particles to readily collide with each other and in the process form hydrogen bonds to form larger solids called microflocs or pinflocs. High molecular weight polymers are then added to promote floc growth by mechanically and chemically binding microflocs together. As the flocs settle they capture smaller unattached microflocs further improving solids removal. Physical entrapment is only effective for suspended solids removal. Removal of dissolved contaminants can only occur by chemical conversion via pH changes, resulting in insoluble particles, while removal of colour can be effected by the addition of acidic salts such as ferric chloride or alum which reduce pH while acting as a coagulant.

2.2.4 Membrane Separation Processes

Membrane separation covers a wide range of fundamentally different processes, from microfiltration to electrodialysis. The common factor linking this diverse range of separation operations is the physical arrangements of the process. In all, the separation occurs between two fluids that are separated by a thin physical barrier or interphase. This interphase constitutes the membrane and permits the selective transport of components of the two phases thus allowing some material to pass through the membrane while others are retained.

The potential advantages of membrane separation processes are significant. Membrane separation processes usually require low energy and mild operating conditions. Most do not involve a change in phase that is required in other desalination processes such as distillation, crystallisation or evaporation.

The various membrane separation processes include microflitration, ultrafiltration, reverse osmosis, gas separation dialysis and pervaporation. Some of the common membrane treatment processes are discussed below. The salient features of each process is shown in **Table 2.1.**

Table 2.1 Salient Feature of Various Membrane Separation Processes

Process	Pore Size	Driving force	Mechanism
Microfiltration	0.02 - 10 μm	Pressure 0-1 bar	Sieving
Ultrafiltration	0.001 - 0.02 μm mol. Wt. 10^3 - 10^6	Pressure 0-10 bar	Sieving
Nanofiltration	0.0007 – 0.01 μm	Pressure 0-20 bar	Sieving and diffusion
Reverse Osmosis	0.0001 – 0.001 μm Mol. Wt. < 1000	Pressure 0-100 bar	Solution-diffusion
Gas Separation	Non-porous	Pressure 0-100 bar	Solution-diffusion
Dialysis	10 - 30 Å	Concentration difference	Sieving and diffusivity differences
Electrodialysis	< 5 nm Mol. Wt. < 200	Electrical potential	Ion migration
Pervaporation	Non-porous	Partial pressure difference	Solution-duffision

Source : Engineering Processes for Bioseparations.

Microfiltration

Microfiltration is the membrane process that most closely resembles conventional filtration. The pore size of microfiltration membranes are in the range of 0.1 - 10 μm. Membrane filtration separates macro solutes by transporting only solvent across a membrane by application of pressure. Cross-flow microfiltration is a special case which applies the same principles, however in this process fluid passes tangentially over the surface of the membrane to prevent the accumulation of rejected species at the surface of the membrane.

In waste water treatment, microfiltration processes are employed for the removal of suspended solids and the recovery of materials.

Ultrafiltration

Ultrafiltration is a pressure driven process similar to microfiltration. The pore size for ultrafiltration units range from 0.001 - 0.02 μm. Ultrafiltration techniques have been widwly employed in the treatment of effluents. Kemira Coatings U.K.(1993) reported the use of an ultrafiltration unit to treat booth water and paint overspray. The unit, which utilises a semi-permeable membrane, retains and concentrates the overspray while returning clean water to the spray booth. In this process the paint formulation is specifically designed to coordinate with the ultrafiltration membrane to ensure easy separation and continous cleaning of the membrane to prevent blocking.

Reverse Osmosis

Reverse osmosis is a pressure driven process that separates low molecular weight solutes such as dissolved salts and amino acids from a solvent. The transport mechanism is primarily solution-diffusion rather than sieving action as in microfiltration and ultrafiltration processes (Bell and Cousins, 1994). Reverse Osmosis was initially used for the desalination of sea water. Reverse osmosis has successfully been employed in the treatment of waste water from pulp and paper industries which contain high levels of BOD, strong colour and high loadings of solids. In the metal plating industry, reverse osmosis has proved to be extremely useful in recovering metal ions from the effluent stream.

2.3 GLOBAL TRENDS IN WATER RECYCLING

Due to increased water resource restrictions as a result of changing climatic conditions and with more stringent environmental regulations, waste minimisation by water reuse and recycle is becoming essential in many industrial activities. There is especially a great deal of interest in the utilisation of waste water in arid regions in the world such as in Australia, Israel, Saudi Arabia, South Africa and the United Arab Emirates. In countries such as India where conservation of their natural resources (water and nutrients) is needed, waste water utilisation is important in order to promote agricultural production. A brief account in waste water reclamation and reuse trends in the U.S and in the countries mentioned above is presented here. However, many other countries in the arid, semiarid and humid regions are also involved in waste water reclamation and reuse. They include Canada, Cyprus. Egypt, France, Germany, Indonesia, Japan, Jordan, Kuwait, Mexico, Poland, Portugal, Syria and the United Kingdom.

2.3.1 Waste Water Reclamation and Reuse in the U.S.

Fresh water withdrawals has decreased from a high of 378 billion gallons per day (bgd) in 1980 to 338 bgd in 1985. The U.S. Water Resource Council (1978), estimates that by the year 2000, fresh water withdrawals would further decrease to 306 bgd. Water quality regulations, water reuse, recycling and conservation are the main factors contributing to reduction in fresh water withdrawals. Between the years 1975 to 2000, it was anticipated that fresh water withdrawals by the manufacturing sector would be reduced by 62%. The user pay principle as well as the pricing of water related services were also expected to contribute to the reduction in fresh water withdrawals. (Council on Environmental Quality, 1988). It is anticipated that in the near future, waste water recycling and reuse will undoubtedly increase.

Most waste water reclamation projects in the U.S. are in Arizona, California, Colorado, Florida, Georgia, Kansas, South Carolina and Texas. Recently, South Carolina reported at least 66 waste water reclamation and reuse projects involving over 57,000 m^3/d (15 mgd) (Caughman, G. M., 1992)). Between 1970 to 1987, California had reported an increase of 35% in the volume of waste water reclaimed and reused. In 1975, California had a total of 379 waste water reclamation and reuse projects involving 727,000 m^3/d (192 mgd), in 1987 however, the number of projects increased to 854 involving 900,000 m^3/d (238 mgd), indicating an increase of 20% in volume of reuse from 1975 to 1987. **Table 2.2** shows the municipal waste water reuse in California between 1975 to 1987. A summary of waste water reuse projects in the U.S. is shown in **Table 2.3.**

Table 2.2: Municipal Waste Water Reuse in California, 1975 and 1987

Category	Number of Projects		Reclaimed Water (mgd)	
	1975	1987	1975	1987
Agricultural Irrigation	232	240	132 (68%)	148 (62%)
Landscape Irrigation	104	571	26 (14%)	30 (13%)
Groundwater Recharge	5	7	27 (12%)	34 (14%)
Industry	22	12	9 (5%)	35 (2%)
Recreational Impoundments	13	4	1 (0.5%)	36 (2%)
Other	3	20	2 (0.5%)	37 (7%)
Total	379	854	192 (100%)	238 (100%)

Source : Culp/Wesner/Culp, 1979 and Asano and Madancy, 1982.

Table 2.3: Municipal Waste Water Reuse Projects in the U.S in 1975

Category	Number of projects	Reclaimed Water (mgd)	
Irrigation – total	470	420	(62%)
Agriculture	150	199	
Landscape	60	33	
Not Defined	260	188	
Industrial – Total	29	215	(32%)
Process		66	
Cooling		142	
Boiler Feed		7	
Groundwater Recharge	11	34	(5%)
Others (recreation etc.)	26	10	(1%)
Total	536	679	

Source : Asano and Madancy, 1982.

2.3.2 Waste Water Reclamation and Reuse in Europe

There are examples all over Europe where fresh water has either been over abstracted from ground waters (resulting in seawater ingress) or contaminated by surface spillage or waste water disposal. The respective Environmental Agencies are strongly encouraging protection of water resources and the reuse of low quality water for non-potable applications. European law and individual governments are encouraging industrial users to reduce their use of high quality groundwater or potable water (Durham, 1997) by :

- increasing effluent costs by up to 50% a year
- increasing water costs incrementally until demand reduces
- encouraging and part financing best practice examples on water reuse; and
- empowering water supply companies to encourage their industrial customers to reuse waste water.

Without sound economic paybacks, legislative requirements or similarity in quality of effluent with influent stream, industries would not be prompted to reuse their waste waters. The rapid expansion of domestic and industrial water usage and waste production at present necessitates the consideration of waste water reuse, rather than continuing to unnecessarily install new potable and sewerage infrastructure.

Enabling technologies such as the kidney for cities approach developed by Memcor, allow reuse of waste water especially from sewage for industrial purposes. This approach employs continuous cross-flow microfiltration and RO for the reclamation of water. This innovative approach has also been successfully applied to large systems that are treating algae laden surface water for the boiler feed to power stations in Hungary and Poland. There are now over 600 CMF installations, with the largest treating 3300 m^3/h. (Durham, 1997)

2.3.3 Waste Water Reclamation and Reuse in Australia

Certain arid areas in Australia receive an average annual rainfall of about 488 mm (19 in/yr) and experience an evapotranspiration rate of about 1,460 mm/yr (57 in/yr). One such place is the Werribee Farm located 35 km southwest of Melbourne. Here treated and untreated waste water effluent from over 50 municipal facilities are utilised for land irrigation purposes. Three treatment methods, land filtration, overland flow (grass filtration) and lagooning are practised. Land irrigation utilises mainly raw sewage and provides water for the irrigation of pastures. About 50% - 60% of the applied water percolates through the soil and is collected in drainage ditches. Land filtration is capable of removing most heavy metal and nutrients. Removal rates of

99% for BOD, 98% for Suspended Solids, 94% for organic carbon, 95% for Nitrogen and Phosphorus, 95% for Zinc, Copper and Lead, 90% for Chromium, 85% for Cadmium and Mercury and 75% for Nickel have been noted (Feigin, Ravina and Shalhevet, 1991). Overland flow is employed during periods of low evaporation when irrigation is not practised. Lagooning is practised throughout the year and is considered to be the safest reclamation technology thus far amongst the three methods practised.

Irrigation with reclaimed water is also practised in other areas in Melbourne. These areas have reported 30%, 33% and 40% reduction in N, P and K fertilisers which accounts for about 35% in fertiliser cost.

Another sewage reuse project is the Eraring Power Station Project, located on the shore of Lake Macquarie. Eraring power station, one of the largest power station in Australia is a 4 x 660MW coal fired station providing 25 % of the power to the state of New South Wales (Smith, 1997). Until recently, the power station consumed up to 4 mega litres per day (MLPD), 168 m^3/hr of potable water. The diversion of sewage effluent from the Dora Creek sewage treatment plant to a new membrane treatment facility incorporating microfiltration and reverse osmosis provides water for the boiler feed, cooling water, dust dispersion and fly ash handling which would otherwise use potable water.

2.3.4 Waste Water Reclamation and Reuse in Israel

Israel is a semiarid country with a mean annual rainfall of about 450 mm (18in./yr). Rowe and Magid (1995) reported that the per capita water consumption in Israel is only 450 m^3/yr (326 gpd) compared with the per capita consumption of 2310 m^3/yr (1672 gpd) in the U.S. In 1984 about 60 x 10^6 m^3/yr (44 mgd) of treated waste water effluent was used for agricultural irrigation. The reuse of reclaimed waste water by 1986 was expected to be 140 x 10^6 m^3/yr (101 mgd) . It was anticipated that the use of reclaimed waste water will replace about 30% of the total amount of water used today for agricultural irrigation. Only about 1% of the total 250 x 10^6 m^3/yr (66,050 mg/yr) of municipal waste water in 1984 was used for industrial purposes, and about 7.5% of this quantity for aquifer recharge (Zoller, 1984)

2.3.5 Waste Water Reclamation and Reuse in Saudi Arabia

In Saudi Arabia waste water reclamation and reuse projects are currently in operation at Riyadah, Madinah, Qassim, Jubail, Jeddah, Makkah, Hail and Dammam. The emphasis on the utilisation of reclaimed waste water is due to the lack of rainfall in this arid region. Agriculture, domestic and industrial activities are the major waster consumers in Saudi Arabia. By the year 2000, 9% of the water demand is expected to be met by waster water reclamation. A summary of water demands and estimated reclaimed water available for 1990 and 2000 is shown in **Table 2.4**.

Table 2.4 : Summary of water demands and estimated reclaimed water available. (Source : Kalthem and Jamaan, 1988)

Category	1990		2000	
	Mm³/yr	%	Mm³/yr	%
Agriculture	3.684	76	5.119	71
Domestic	1.117	23	1.940	27
Independent Industry	74	1	182	2
Total	4.875	100	7.241	100
Waste water available for reuse	368	8	674	9

Riyadh, which has a mean annual rainfall of 100 mm/yr, has at least 30 waste water reclamation and reuse projects. The largest waste water reclamation and reuse projects are located in Dirab, Diraiyah and Ammariyah. These plants receive treated sewage effluent from the Riyadh Sewage Treatment Plant located at Manfouha. The reclaimed water is used for the purpose of agricultural irrigation.

The treatment effluent from the Riyadh Sewage Treatment Plant consists of three stages. The first stage is the equalisation in a surge pond prior to lime treatment. The second stage involves the use of cooling towers and dual media filtration while the third stage consists of carbon adsorption, reverse osmosis and ion exchange processes.

2.3.6 Waste Water Reclamation and Reuse in South Africa

South Africa has an annual rainfall of 487 mm (19 in/yr), of which 91% is lost to the atmosphere by evaporation and transpiration and only 9% reaches the rivers. In the early 1970s the waste water flows from over 20 major cities indicated that 1, 230, 000 m^3/d of treated waste water was available for reclamation and reuse. Of this flow, 31.9% was reclaimed and reused, 61% for irrigation of crops, parks, trees and sports fields, 8.7% for power station cooling water and 7.1 % for industrial purposes. Windhoek, Namibia has a full scale plant where potable water is reclaimed from municipal waste water. About 20% to 50% of the municipal waste water is reclaimed and reused. (Hart and Van Vuuren, 1997)

2.3.7 Waste Water Reclamation and Reuse in India

In India, land disposal of waste water has been practised for up to 60 years at some sites. Sewage farming as a method of waste water disposal is reported to take place at more than 200 sites. About 10 x 10^6 m^3 (2642 mgd) of waste water flow is available for this purpose. The percentage of waste water given primary treatment is 37%, with 8% of waste water flow given secondary treatment (Rowe and Magid, 1995). A recent survey conducted by the National Environmental Engineering Research Institute (NEERI) in Nagpur, India showed that many of the environmental and public health problems at these waste water utilisation sites could be attributed to over application of the untreated sewage. Hookworm, roundworm, whipworm, pinworm, dwarf tape worm, *Entamoeba histolytica*, and *Giardia intestinalis* occurred from 15% to 60% more often in farm workers than in control groups (Rowe and Magid, 1995).

Experimental results showed that primary treated and secondary treated waste waters were superior to untreated sewage in terms of crop yields and soil nutrient utilisation efficiency and would reduce the health problems associated with utilising raw sewage.

2.4 WATER RECYCLING PRACTICES IN VARIOUS INDUSTRIES

2.4.1 Waste Water recycling Practices in the Pulp and Paper Industry

The pulp and paper industry uses large volumes of water and with the application of more stringent effluent discharge standards and increasing costs of process water, waste water recycle and reuse are becoming increasingly attractive as water resource management tools. There has been many efforts to close the process water loop to reduce bleed and water usage. Zero-effluent discharge has been successfully implemented in many board mills and kraft mills and the water consumption rate for newsprint production has also been reduced significantly in the last few decades.

At the initial stage, reduction in fresh water consumption was achieved through whitewater treatment and recirculation. Closed loop systems however, soon develop problems due to build-up of dissolved and colloidal substances and thermal energy in the system. A list of potential problems encountered in water reuse in paper manufacture is listed in **Table 2.5**.

The first documented problems arising from the use of recycled water were those associated with suspended solids build-up which lead to plugging of shower nozzles, small lines and felts. The suspended matter also lead to deposit formations which could be biological or non-biological in nature. After extended periods of running under low water use conditions, problems of scale and corrosion begun to appear, difficulties due to intensification of biological sludge were also experienced. High degrees of water recirculation caused an increase in the concentration of dissolved material to a point where the wet-end chemistry of the paper making system was affected and difficulties with foam, sizing and product appearance begin to manifest themselves.

Table 2.5 : Potential Problems Encountered in Water Reuse in Paper Manufacture (Springer & Marshal, 1975)

Dissolved Solids Build-up	Suspended Solids Build-up	Thermal Energy Build-up
Slime	Dirt	Temperature
Foam	Corrosion	Sizing Problems
Pitch	Fines	Machine Room Problems
Corrosion	Felt Plugging	
Sizing	Wire Plugging	Reduced vacuum Capacity
Product Mottle	Wire Life	
Colour	Felt Life	
pH Control	Reduced Drainage Rate	
Precipitation	Shower Plugging	
Scale		
Odour		

Whitewater treatment and increased recirculation reduced the intake of freshwater. This however had the potential to affect process stability and availibility, increase operation complexity and cause problems with the heat balance. As an alternative, Chen & Horan (1997) studied the possibility of using secondary effluent from a biological treatment plant as a potential water resource.

Tertiary treatment of secondary effluent from a biological treatment plant followed by a desalination process can be employed to produce recycled water of adequate quality. Chemical coagulation and solids separation as a tertiary treatment for residual organic removal, and applied electrodialysis reversal (EDR) as the deep treatment stage for desalination produced recycled water quality that was close to or better than fresh water supply. In a pilot-plant study at Shotton Paper Co., Chen & Horan (1998) successfully employed a Dissolved Air Flotation unit that combined chemical coagulation and flotation and a multimedia filter followed by desalination with an EDR unit to reclaim 25% of its wastewater.

The use of inorganic coagulants with the aid of polymers produce floc sizes in the region of 1.5mm - 2.5mm which is essential for swift and stable flotation. Addition of chemical coagulants at optimum pH would minimise use of chemicals and at the same time reduce production of sludge. Desalination processes applying pressure driven membrane filtration applications such as nanofiltration and reverse osmosis (RO) are not cost effective in the treatment of high flows of pulp and paper waste waters which contain moderate levels of total dissolved solids (TDS). RO units require extra energy for the removal of neutral particles and are prone to fouling problems. EDR on the other hand allows neutral particles through the system and requires less rigorous pre-treatment than RO due to the nature of the salt separation and the larger flow passages (Elyanow, D. et. al., 1994). EDR operates on the same basic principles as electrodialysis (ED) but incorporates a polarity reversal process. (Katz, 1997) In an ED process, electrical energy is supplied as the driving force to transfer electrolytes (solutes) through an ion exchange membrane to produce a diluted solution and a concentrated stream. The polarity reversal process provides self-cleansing of the membrane surfaces, EDR processes therefore show good fouling resistance.

The purification of industrial waste water and recycle of this waste water back to the production process represents an alternative approach to whitewater treatment and recirculation for reducing mill effluent water consumption in a straight forward and economically viable manner.

2.4.2 Waste Water Recycling Practices in the Textile Dyeing Industry

The textile industry affords excellent opportunities for the recycle of renovated industrial waste water. The renovation and reuse of waste waters are of current interest not only as a measure to reduce fresh water intake but also as a means of pollution abatement and the recovery of valuable chemicals.

Dyehouse waste waters are coloured, high in temperature, Chemical Oxygen Demand (COD), Total Dissolved Solids (TDS) and at times highly alkaline. The removal of colour from dyehouse waste waters is one of the major environmental problems facing the textile industry. Discharges of coloured effluent into the environment may interfere with the transmission of sunlight into the water and thus decrease the rate of photosynthesis. Most dyes are of the non-biologically degradable type and thus are not effectively removed via municipal waste water treatment processes. The discharge of dyehouse effluents into public sewers could also cause foaming, colour persistence, excess in pH, temperature and heavy metals and variations in hydraulic flow rate problems in the operation of sewage treatment plants.

The variety of dyes and finishes employed produces a complex and variable waste stream. Hyperfiltration or reverse osmosis separation processes involving filtration of aqueous solutions by membranes capable of removing not only suspended solids but also substantial fractions of dissolved impurities including organic and inorganic material has been successfully employed in many industrial applications where the recovered products have significant value. The successful use of hyperfiltration for recovery of water and chemicals from a textile waste stream was demonstrated by the use of a pilot plant by Brandon, Nasher & Porter (1975). Treatment of composite dye waste streams via spiral, tubular and hollow fine fibre configurations employing cellulose acetate and polyamide membranes respectively, and dynamic hyperfiltration modules employing hydrous Zr(IV) oxide- polyacrylate membranes are able to satisfactorily produce purified water and concentrated residues for reuse in dyeing productions. Water recovery of up to 90% can be achieved by employing hyperfiltration as an advanced treatment for dye house waste water with minimal pre-treatment (filtration and pH adjustments).

Cohen (1975) reported that the development of a solid layer on the membrane wall could play a critical role in the performance of cellulose acetate membranes. As the thickness of the secondary membrane increases, a decline in flux and an increase in contaminant rejection was observed.

Membrane processes such as microfiltration, reverse osmosis, dynamic membrane and nanofiltration have successfully been employed for the treatment of dyehouse waste water with the primary objective of producing water for reuse. The success of each process however depends on the class of dyestuff used and the degree of effluent segregation chosen (Buckley, 1992)

Microfiltration processes are suitable for use in the treatment of effluent produced from the disperse dyeing of polyester and the sulphur, vat and azoic dyeing of cotton and viscose. Colloidal dyes from the exhausted dye bath and subsequent rinses are effectively removed. Auxiliary chemicals are however retained in the permeate. Chemical pre-treatment of the effluent is required prior to being passed through a microfiltration unit. The permeate can be used in the subsequent dyeing or rinsing of 100% polyester fabric. In the case of cotton and viscose dyeing the permeate is discharged due to precipitating agents that interfere in the dyeing process (Buckley, 1992).

In applying reverse osmosis for the treatment of a mixed dyehouse effluent, pre-treatment of the effluent via chemical coagulation followed by cross-flow microfiltration was required for successful recycling of the waste water. Untreated effluent causes membrane fouling due to the presence of scouring chemicals and cotton waxes. A two stage RO unit employing brack water RO membranes in the first stage and seawater RO membranes in the second stage produced permeate that compared favourably with tap water. In the first stage, 96% rejects for conductivity, total solids and sodium ion, 90% rejects for colour and 87% rejects for total carbon was achieved. In the second stage, concentrates from stage 1 produced permeates with 98% rejects for conductivity, total solids and sodium ions and 94% rejects for colour (Groves et al., 1988).

Nanofiltration or charged ultrafiltration is a membrane process with separation characteristics in between reverse osmosis and ultrafiltration. Reactive dyeing of cellulosic fibres produce effluent containing reactive dyes and their hydrolysed residues, electrolytes (sodium chloride or sodium sulphate) and ethylene diamine tetra-acetic acid (EDTA). Nanofiltration can be utilised to decolourise the effluent and to recover the electrolyte liquor for reuse.

The selection of membranes suitable for the treatment of dyehouse effluents is limited by the variable nature of the effluents produced. Incompatibility of the membrane with the chemical nature of the effluent, temperature and solids content also restrict the choice of available membranes. Extensive pre-treatment of the effluent is usually necessary, adding to treatment cost. The use of dynamic membrane may overcome many of these problem areas. The advantages of a dynamic membrane include :

i) long service life of the support tube

ii) ability to be operated at high temperatures and pressures

iii) ease of membrane removal in cases of severe fouling and refouling of the membrane in situ

iv) and removal of solids, while desirable, is not critical in terms of mechanical damage to the membrane.

Dynamic membranes are formed in situ when a dilute colloidal suspension of one or more specific additives is passed over the surface of a porous support, which may be either made from porous stainless steel, carbon or ceramic material. An ultrafiltration plant using dynamic membranes was able to achieve 85% water recovery of a dyehouse effluent containing both soluble and colloidal dyestuffs, acetates, alkali, salt and organic auxiliary chemicals. Colour removal from the effluent was 95% or more while ionic rejection (conductivity) was approximately 80% (Neytzell-de Wilde et al., 1989).

2.4.3 Waste Water Recycling Practices in the Paint Industry

Waste generation during the production of paints and allied products pose a serious problem to the environment if disposed in an unsafe manner. Variable waste quality and characteristics due to changing product mix at a given factory complicate the problems of waste management.

In the manufacture of paint and allied products, all the constituents entering mixers or reactors come out as products and, as such, there is no major stream of waste water associated with the production. Waste water is generated primarily due to washing operations of mixers, reactors, blenders, packing machines and floors. During washing, the waste water is expected to carry all the ingredients that go into the manufacturing process like pigments, extenders, emulsion, solvents, biocides, surface wetting and dispersing agents, thickeners, rheology modifiers etc. Paint waste water are characterised by high BOD, COD and suspended solids load; are alkaline in pH and contain heavy metals and coloured materials.

Anderson, Springer and Strosberg, (1981) reported the use of reverse osmosis for the treatment of paint waste water for recycling purposes. Field and bench scale reverse osmosis experiments demonstrated the technical feasibility of applying reverse osmosis on ultrafiltration waste water derived from an automotive electrocoat paint operating utility.

In this process reverse osmosis feed water is derived from the electrocoat painting bath. The principal ingredients of the bath include alkaline cathodic polymers solubilised in deionised water with 0.05% acetic acid. The feed stream passes through an ultrafiltration unit that removes high molecular weight paint residues before reaching the reverse osmosis unit. The reverse osmosis feed stream contained ethyl, butyl and hexyl glycol ethers in a total concentration of 3%. Lead, strontium and other organic matter were also present in the feed stream. Contrary to usual custom, rejection of all solutes dissolved in the RO feedwater was not the main objective. The primary objective was the isolation of inorganic contaminants. Glycol ethers were allowed to permeate through the membrane along with water. This permitted solute recycling and reuse. Rejection of glycol ethers in the feed stream would have caused a concentration build up which would greatly increase the osmotic pressure drop across the membrane and reduce the permeate flux.

A 60-65% recovery rate was recorded for the permeate. Rejection rates above 80% were recorded for lead and strontium.

2.5 MICROBIOLOGICAL FOULING OF WATERBASED PAINTS

Microbiological spoilage of aqueous based surface coatings can result in severe economic loss to the manufacturer if it happens during production, with even greater problems occurring if such growth is not noticed until the paint reaches the end user.

The effect of bacterial and fungal activity are viscosity loss, gassing, malodour and visible surface growth. In addition discoloration and alteration in the rheology of the formulation can result in the product being unacceptable to the customer. In addition to these obvious problems, the presence of microbially produced enzymes can lead to changes in the product long after manufacture. Breakdown of cellulosic thickening agents may result in viscosity loss even after the microorganisms causing it have been destroyed. (Gillatt, 1991) Therefore, it is important to understand the problems that can arise during manufacture and storage and to be aware of the precautions which must be taken if such loss is to be avoided.

During the production of paint, several factors will affect the growth of microorganisms in emulsion paints. These include raw materials, manufacturing procedures and the effectiveness of biocides used.

2.5.1 Contamination From Raw Materials

Many raw materials used during manufacture mar either introduce microbial contamination into the mix or may provide nutrition for the organisms that may already be present. Powdered raw materials especially originating form natural sources, such as extenders and pigments, can be contaminated with dormant spores of bacteria and fungi which can germinate once in an aqueous environment (Gillatt, 1991). Liquid raw materials such as defoamers, pigment dispersions and polymer emulsions may themselves be susceptible to microbial attacks and unless carefully manufactured and protected with biocide, can also introduce contamination into the formulation.

Water used in the production of paints may also contain bacteria, depending its source of origin, either from wells boreholes, rivers or recycled wash up water. Even good quality tap water contains bacteria, for example *Pseudomonas* species, at up to 1,000 cells per cm^3. Stored wash water is a perfect growth media for microorganisms. They thrive in the diluted product, reaching high numbers. They quickly consume the available oxygen allowing anaerobic growth to commence. When the microorganisms grow under anaerobic conditions the tendency is to produce foul odours and discoloration.

2.5.2 Manufacturing Procedures

Increased attention to quality control and detailed examination of raw materials will help isolate contaminated materials. However, the method of manufacture itself may result in contamination of end product.

Incorporation of biocides at an early stage in the process is desirable. The use of more environmentally acceptable but less persistent organic types, require more attention to plant hygiene (Briggs, 1980). The splash zone or head space in a mixing vessel above the bulk phase of product may be irrigated with condensation water, washing less persistent biocides away and allowing microbial growth. Wooden hatch covers may support and encourage growth, particularly fungi. Powders caked onto the stirrer shaft and lid, moistened with condensation can also become contaminated with microorganisms. Transfer pipelines which are lengthy with sharp end and dead spots allow accumulation of product which can become infected. Empty mixing and holding tanks which are cleaned down, may contain residual rinse water which is also a source of contamination.

2.5.3 Effect of Microbial Spoilage

Both bacteria and fungi are capable of producing cellulase, an enzyme remarkably effective at concentrations as low as 10^{-5} units per cm^3, at breaking down long chain cellulosic thickening agents, producing small oligomeric residual units which do not fulfil the function of the original material. Fermentative bacteria will produce gas from breakdown of the cellulosic thickener (Skinner, 1970) degrading the cellulose first to glucose which is then fermented to yield acid plus carbon dioxide (Stainer et al, 1971). In the presence of fillers such as calcium carbonate, further gas can be produced by action of the biogenic acids (Briggs, 1977). Other bacteria known as sulphate reducers, for example *Desulphovibrio desulphuricans* are able, under anaerobic conditions, to utilise oxygen from sulphates leading ultimately to the formation of hydrogen sulphide. Opperman and Goll (1984), in their study of contaminated emulsions paints concluded that more than a quarter were infected with these and other anaerobic organisms. Such sulphate reducing bacteria are responsible for the most commonly noticed malodour associated with emulsion paint spoilage. Formation of insoluble sulphides such as iron sulphide can cause discoloration. Other organisms such as

Rhodotorula rubra and *Sporobolomyces roseus* and pigmented mould fungi can produce other discoloration. Acid production by microorganisms can cause pH shifts. However, paints are normally well buffered. Production of microbial metabolites can cause other effects such as increase in paint viscosity by an as yet unknown mechanism. A summary of effects of microbial degradation on paint ingredients in a formulation is shown in **Table 2.6**.

Table 2.6 Effects of Microbial Degradation on Paint Ingredients

Cause	**Effect**
Attack on cellulosic thickeners	Viscosity loss, gas production, pH shifts
Attack on dispersants	Poor hiding, colour shifts, precipitation of pigments, gelling
Attack on glycols, coalescing agents	Gloss reduction, poor freeze thaw stability, chalking, porous film, poor adhesion, poor levelling
Attack on antifoam	Foam, porous film
Attack on dispersed colour	Off-colour, uneven colour, agglomeration of colorant