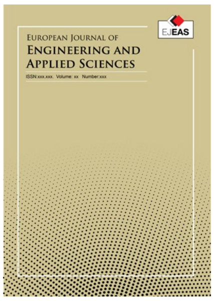
European Journal of
Engineering and Applied Sciences

ISSN: 2651-3412 (Print) & 2667-8454 (Online)
Journal homepage: http://dergipark.gov.tr/EJEAS
Published by Çorlu Faculty of Engineering, Tekirdağ Namık Kemal University

European J. Eng. App. Sci. 2(1), 19-43, 2019



Review

Assessment of Recovery & Reuse Activities for Industrial Waste Waters in Miscellaneous Sectors

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Received: 21.05.2019 *Accepted: 28.06.2019*

Abstract: At the beginning of the industrial revolution and rapid urbanization, it was thought that the nature has the power of hide the increasing pollution forever or have the capacity of an endless treatment. However, over time the whole ecosystem is negatively affected by environmental pollution, activities for understanding, identifying, emerging issues, and finding solutions to take measures have gained tremendous importance. Therefore, if we can provide the right usage of water and soil resources and consider the balance of ecosystems within the limits of their usages and protect them, 'sustainability' can also be secured. Protecting water resources in a sustainable way is the only way to reclaim and reuse waste water. Re-using of waste water reduces fresh water resources consumption and both the environmental impact of treated waste water that is discharged can be minimized.

In this study, the literature research was performed for different sectors such as metal, pulp and paper, pharmaceutical, chemicals industries, in terms of water consumption, processwater quality, waste water sources, treatment, reuse of waste water and focused on re-use alternatives. As a result, when designing plants, their production dynamics must be taken into account and evaluated. In addition, similar studies should be conducted to select the most economical treatment and reuse option for different industrial wastewater.

Keywords: *Industrial waste water, Process water, Re-use/Recycling/Recovery, Water consumption.*

Çeşitli Sektörlerde Endüstriyel Atıksuyun Geri Kazanılması ve Yeniden Kullanılmasının Değerlendirilmesi

Özet: Endüstri devriminin ve hızlı kentleşmenin başlangıcında, doğanın sonsuza kadar artan kirliliği gizleme gücünün olduğu veya sonsuz bir muamele kapasitesine sahip olduğu düşünülüyordu. Bununla birlikte, zamanla bütün ekosistem çevre kirliliğinden olumsuz olarak etkilenmiş, gelişmekte olan problemlerin anlaşılması, tespit edilmesi ve ölçümlenerek önlem alma çözümlerinin ortaya konulma faaliyetleri büyük önem kazanmıştır. Bundan dolayı, su ve toprak kaynaklarının doğru kullanımını sağlayabilir ve ekosistemlerin kullanım ve koruma sınırları dahilinde dengesini göz önünde bulundurursak, 'sürdürülebilirlik' de sağlanabilir. Su kaynaklarını sürdürülebilir bir şekilde korumak, atık suları geri kazanmanın ve yeniden kullanmanın tek yoludur. Atık suyun tekrar kullanılması tatlı su kaynakları tüketimini azaltır ve arıtılan atık suyun çevresel etkisi en aza indirilebilir.

Bu çalışmada metal, kağıt hamuru ve kâğıt, ilaç ve kimya endüstrisi gibi farklı sektörler için su tüketimi, proses suyu kalitesi, atık su kaynakları, atık suların arıtılması ve tekrar kullanılmaları açısından literatür araştırması yapılmış ve yeniden kullanım alternatiflerine odaklanılmıştır. Sonuç olarak, her endüstriyel tesis kendi üretim dinamikleri dikkate alınarak tasarlanmalı ve değerlendirilmelidir. Ek olarak, en ekonomik arıtma ve yeniden kullanım seçeneğini seçmek için farklı endüstriyel atık sular için benzer çalışmalar yapılmalıdır.

Anahtar kelimeler: *Endüstriyel atıksu, Proses suyu, Yeniden kullanım/Geri kazanım, Su tüketimi.*

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Contents

1. Introduction

1.1. The Importance of Water Use, Recycling and Re-use of Wastewater in Industries

Clean water (drinking and potable water) resources and their protection is one of today's most important issues. The reason of it may be summarized as below;

- Gradual increase of the world population
- Increasing global warming as the results of operations adversely affecting the atmosphere and the nature
- Climate change; flash floods or prolonged droughts
- Reduction of fresh water reserves in our World
- Distribution of water on Earth
- Increased industrialization
- Unconsciously pollution and use of water resources
- Waste of waters

Consequently, it is a fact that in today's world of rapidly increasing freshwater crisis in many regions. Although Turkey has more advantageous in comparison with some countries in the Middle East in terms of the amount of freshwater resources, since not a homogeneous dispersion of our freshwater resources as the location, it is inevitable that freshwater crisis will be a big trouble for our country in the near future [1]. For this reason, " sustainable management of water resources" must be implemented urgently. Sustainable management of water resources can be provide either to protect and to increase of drinking water resources or to prevent of pollution of surface waters and groundwater or to recycle and reuse of used water and to raise awareness for the protection of community water [1]. The only way as a rational solution is to protect water resources in a sustainable manner recycling and reuse of waste water. By the reuse of waste water, both consumption of freshwater resources is reduced and environmental impact of discharged treated waste water can be minimized.

Water, used for recovery, is classified as; domestic waste water, rainwater surface flow and industrial waste water [2] and should be prepared prior to use in industry. The amount of water used by each branch of industry and expected water features are different. When tap water used in the beer industry, it can be found salts in that water, affecting adversely the flavor of the beer. All carbonates reduce the acidity of mash, other salts increases particularly calcium sulphate. Calcium sulphate acts well in light color beer production. However, dark beer can not be achieved with such kind of water. Iron and manganese salts are discolor beer [3]. Aseptic water should be used in the production of starch and it should not be included organic substances, ferrous and manganese. Sugar factories require aseptic, organic matter-free water containing less salt as possible. In particular, nitrate, sulfate and alkaline carbonates cause to hamper difficult to crystallization of the sugar. Water used in the artificial ice production should be of drinking water quality. More attention should be given to water used in milk, butter and cheese factories than drinking water. First of all, water, will be used for production, is required to be free of harmful and harmless microbes. In addition, it must not been included ferrous and manganese and saline and dissolved gases must be less than that. Rubber industry chlorides, magnesium chloride, especially due to making vulcanization difficult, require a little amount of water. Water requirements of the paper industry is very high. The water, will be used, must be soft, ferrous-free and mangenese-free. Presence of magnesium chloride in the water is not required because of leading to yellowing of the paper and deterioration of durability. In textile industry, the water, which has less hardness and salt, clear, ferrous-free and mangenese-free, is used. Otherwise these substances produce undesirable precipitates with the dyes on textile fibers. Inorganic industry uses water as a solvent. Therefore, water must be very clean and distilled in some cases. Drinking water and water, will be used at homes, should not contain microorgamisms and toxic metals disease-causing and harmful to human health [4]. As seen in various branches of industry, water is used at different rates for different purposes. Re-use of water in recent years is widespread. Since inudstrial reuse of water decreases chemical, thermal and biological contamination.

1.2. Environmental Impacts of Industrial Wastewater

The industrial waste water discharged into receiving water bodies, as an environmental point of view, constitutes a much greater danger than the domestic waste. This kind of waste water, containing both biodegradable and non- biodegradable substances and toxic substance additionally, have high pollution concentration. Toxic substances can be found in industrial waste water, leads to depletion of water living life in a short time. Toxic substances, which can reach up to people entering the food chain. This kind of accumulating substances have been demonstrated carcinogenic effects in long-term by numerous studies. The most important group in industrial waste constitutes hazardous substances such as Metals and heavy metals (aluminum, antimony, arsenic, beryllium, cadmium, Cr (III) , Cr (VI), copper, lead, magnesium, mercury, nickel, thallium, zinc), asbestos, paint waste, phenol-containing waste, pharmaceutical industry wastes, halide solvents, chlorine, sulphide-containing wastes, organic peroxides, PCBs, pesticides, refinery waste, cyanides. Since these substances have the properties of toxic, explosive or irritating, are required to be producing, storage, transportation, treatment and disposal conditions after special precautions.

Advers effects of industrial waste water on the environment are aligned such as reduction of dissolved oxygen, formation of suspended solids, precipitation of suspended solids (affect aquatic organisms adversely. Furthermore, organic solid containing sludge blanket causes use of oxygen and malodorous gaz outlet during decompositon process.), formation of heavy metal and cyanide and toxic organics, colour and turbidity, nitrogen and phosphorus formation (it causes eutrofication when discahrged into waste water lakes, ponds and other recreational areas.), formation of biodegradation resistant refractory material (some refractory material is toxic to aquatic organisms.), formation of oil and supernatants, formation of volatiles [5].

On the other hand, according to the Regulation on the Control of Pollution Caused by Dangerous Substances In Aquatic Environment (76/464 / EC), Industrial waste water was defined as any operation and wash residue waters, boiler and cooling waters mixed with process water which is removed separately from the process obvious resulting from manufacturing sites, ateliers, maintain and repair department, the small industrial estates and organized industrial zones. Besides, waste water resources in an industrial systems can be listed as process waste water, cooling water, cleaning and washing waters, waste water from auxiliary enterprises, domestic waste water consisting of shower, toilet, cafes etc., activities, rain waste water and drainage waste water [6].

Toxic elements occur naturally at trace or ultra trace levels in the aquatic environment. However, waste waters from mining activities, electroplating factories or chemical laboratories contain very high concentrations of a wide variety of toxic heavy metals, including cadmium. Release and dispersal of this toxic element to aquatic system can have disastrous consequences for living organisms.

Cadmium attacks the kidney and may produce lung cancer [7]. Manufacturing process of the polyfilm, used in food packaging material and detergent production, involves mono-ethylene glycol (MEG) and ethyl acetate (EA) as the main constituents. The presence of such organic compounds is responsible for the higher toxicity and BOD_5 (Biological Oxygen Demand) and COD (Chemical Oxygen Demand) values of the polyfilm effluent [8]. Industries including toxic elements result in various pollution problems. Waste water, having too much and various chemical composition such as textile waste water, is the basis of pass through human and animal food chain. Textile dyeing waste water is required to removal of COD, TSS (Total Suspended Solid), Color, Dissolved Salts (DS), and Metals before discharging. Numerous industries including textile dyeing industry use various synthetic dyes which consist of chemically different basic structures such as diazonium, acridine, anthraquinone, triarylmethane, azo, quinone-immine, phthalocyanine, and xanthene [9]. In waste water treatment, the decolorization of dyeing effluents is one of the most crucial steps, because the dyes in the waste water are a potential environmental pollutant. It is estimated that 10–500 mg/L dyestuff is included in textile effluents [10], although dyes are highly visible at low concentrations (>1 mg/L). Additionally, numerous synthetic dyes have a toxic potential; some of them are known to be carcinogenic. Today, physicochemical methods have been applied to get high removal efficiency of dye waste water. However, in large-scale applications, due to high operating costs and the use of chemicals, is necessary to develop alternative methods for overcoming some of the secondary issues such as environmental pollution. In the aquatic environment, copper, lead, cadmium, chromium, zinc, mercury, heavy metals, etc. may accumulate in living organisms and can not be biodegradable and can cause a wide variety of diseases and disorders [11].. Especially, when they can not be decomposed and when permanent ones are exceeded permitted limits, they give severe damage due to increasing concentrations of these metals in the aquatic systems. Environmental Protection Agency and World Health Organizastion proposed limit values for safe drinking water containing respectively 0.015 and 0.01 mg/L. There are many sources of industrial waste water containing metal salts and metal ions and making harmful effects on aquatic organisms; such as metallurgical activities [11], tanneries [12; 13], local mining [14], welding, canned meat-vegetables, seafood processes and industrial cheese business [15;16] . Especially in developing countries, with the rapid development of sectors such as metal coating plants, mining operations, fertilizer industries, tanneries, batteries, paper industries and pesticides, heavy metal waste water is discharged directly or indirectly to the environment. Toxic heavy metals, unlike organic pollutants, are biodegradable and tend to accumulate in living organisms, and many heavy metal ions are known to be toxic or carcinogenic. Industrial wastewater treatment environment includes toxic heavy metals zinc, copper, nickel, mercury, cadmium, lead and chromium [17]. These harmful effects has led to be studying and investigation of them at laboratory scale and at site [15;18;19]. Zinc, which is essential for human health, is important for the physiological functions of living tissue and regulates many biochemical processes. On the other hand, excess zinc can cause serious health problems such as stomach cramps, skin irritations, vomiting, nausea and anemia [20]. Copper does essential work in animal metabolism. Although it performs the necessary functions in animal metabolism, excessive copper uptake causes serious toxicological effects such as vomiting, cramps, contractions and even death [21]. Above the critical level, nickel uptake results in gastrointestinal distress, pulmonary fibrosis and skin dermatitis as well as serious lung and kidney disease [22]. Nickel and Mercury, known to be carcinogenic, are chemicals in a neurotoxin structure that can damage the central nervous system. Taking mercury at high concentrations results in deterioration of lung and kidney function, chest pain and dyspnea [23]. Mimata Bay is a classic example of mercury poisoning. The US Environmental Protection Agency has classified Cadmium as having a carcinogenic effect for humans. Chronic exposure to cadmium, which leads to serious risks to human health, has an effect on renal dysfunction and high exposure causes in death. Lead, which causes damage to the central nervous system, can cause damage to the kidney, liver and reproductive system, basic cellular processes, and brain functions. Anemia, insomnia, headache, dizziness, irritability, muscle weakness, hallucinations and kidney damage are the main toxic symptoms [24]. Chromium, which is mainly found in two forms in aqueous medium; Cr (III) and Cr (VI). In general, Cr (VI) is more toxic than Cr (III), and Cr (VI) accumulates in the food chain, affecting human physiology, causing serious health problems from simple skin irritation to lung cancer [25].

With the development of the chemical industry, waste water from industrial sectors, such as especially dye, detergent, adhesive, have been caused and still causes extinction of species and reduction of biodiversity and destruction of ecosystem. Storage, packaging, shipping and handling of chemicals makes acute effects on the environment; such as air, water and soil pollution.

1.3. Sources for the Industrial Waste water

According to the Regulation on the Control of Pollution Caused by Dangerous Substances in Aquatic Environment (76/464 / EC), Indistrial waste water defines;

- Any operation and wash residue waters
- Boiler and cooling waters mixed with process water which is removed separately from the process obvious

and resulting from

- Manufacturing sites
- Ateliers
- Repair garages
- Small industrial estates and organized industrial zones

Waste water resources in industrial systems can be listed as follows [6];

- Process waste water
- Cooling water
- Tools, equipment, buildings and so on. cleaning and washing waters
- Waste water from auxiliary enterprises
- Domestic waste water consisting of shower, toilet, cafes etc., activities
- Rain water
- Drainage water

1.4. Expected Features from Water used in Industry

Water should be prepared prior to use in industry. The amount of water used by each branch of industry and expected water features are different. When tap water used in the beer industry, it can be found salts in that water, affecting adversely the flavor of the beer. All carbonates reduce the acidity of mash, other salts increases particularly calcium sulphate. Calcium sulphate acts well in light color beer production.

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As seen in various branches of industry, water is used at different rates for different purposes. Re-use of water in recent years widespread. Inudstrial reuse of water decreases chemical, thermal and biological contamination.

2. Recovery and Re-use Applications of Industrial Wastewater on a Sectoral Basis

2.1. Metal Coating Industry

2.1.1. An Overview of the Metal Coating Industry

Metal coating industry has an important place among the rapidly growing industry. Metal plating industry, despite growing technology and facilities, leads to a large amount of environmental pollution. By manipulating the metal surface, processes at metal coating industry, aimed bringing the favorable situation in general use, are divided into three main groups:

- Cleaning and intermediate coating
- Painting
- Metal coating

General flow diagram of the coating process is given in Figure 1.

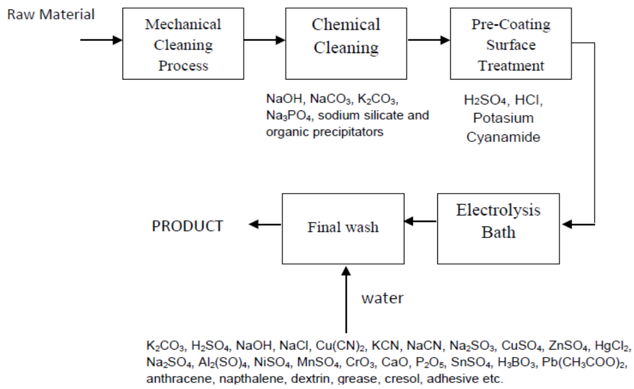

Figure 1. General flow diagram of the coating process [26].

2.1.2. Water Consumption and Water Quality Used in Metal Coating Industry

Processes, such as surface treatment, conditioning, electrolysis bath, wash, rinse before metal coating industry, consume the highest amount of water. Industries use tap water as water sources. The conductivity of the water used in the process of metal coating and processing industry should be kept below 10 µs/cm. Preferred COD concentration is below 50 mg/L. The water, will be used for coating processes, should not be contained ionic impurities and should be deionized. As supplement water used with evaporation or transportation, deionized water must be preferred for the step of bathroom preparation. By the addition of organic additives, the most successful leveling and brightness is realized at 3.8 – 4.5 pH range. pH value of solution should be controlled daily by using pH meter in order to maintain the bath balance. Where necessary, it should be reset to desired range with diluted sulfiric acid solution [26].

2.1.3. Waste Resources and Wastewater Characterization of Metal Coating Industry

In the metal plating industry, town water is generally used in the cleansing rinse of solvent, alkaline and acid, while de-ionized water is employed in the plating rinse and final rinse. The water in the rinsing baths becomes contaminated during the cleaning or plating process . The contaminants may include solvent, O&G (Oil and grease), organic compounds, heavy metals such as chromium, copper, zinc, lead, nickel and iron, as well as other cations and anions, depending on the cleaning or plating process [27]. In metal coating industry, processes, such as electroplating, electroless plating, chemical conversion coating, cleaning, are utilized the highest amount of water and forming waste water. Waste of metal processing industry, mostly does not change the BOD_5 values (inside less amount of oxidizable biological) and indicates toxic effects almost on all living organisms (on microorganisms on domestic waste treatment systems) Pollution Sources, in Metal Plating Industry Manufacturing Process, are illustrated in Table 1 [26].

Table 1. Pollution Sources in Metal Plating Industry Manufacturing Process [26].

Manufacturing Processes	Pollutants
Acid baths	Nitric acid, Hydrochloric acid, Sulfuric acid, Hydrofluoric acid, Phosphoric acid, Acetic acid and Alkali
Lubrication baths	NaOH, Na_2CO_3, $NaSiO_3$, Cynanide, Organic solvents
Electroplating baths	Cu, Ni, Zn, Cd, Mn, Al, Fe, Co, Cr_2O_4
Cynanide baths	Cu, Zn, Cd, Cynanide
Polishing baths	Acid, Chromats
Hardening processes	Cynanide, Nitrate
Phosphate baths	Phosphoric Acid, Metal ions
Anodizing baths	Metal ions, Chromic acids
Other bathroom operations	Nitrite and Metal ions

Cleaning baths are often used to achieve a surface cleaned chemically. Although H_2SO_4 forms the basis of acid baths, hydrochloric, nitric, and hydrofluoric acids or mixtures are also used occasionally. In some cases, waste from these processes can hold substances (e.g., ketones, hydrocarbons or surfactants) which will affect BOD_5 values. Cyanide dyes are also used for surface preparation prior to coating. There are contaminants, in painting waste, which have escaped from washing and paint spraying units such as grease, solvent and pigments. Various and numerous chemicals are used in the metal finishing wash baths. Waste, from the metal finishing wash baths, can be divided into seven groups in terms of their characteristics. They are [26];

- Waste water containing cyanide
- Waste water containing hexavalent chromium,
- Oily waste water,
- Solvents
- Complex waste water containing metals,
- The waste water containing precious metals,
- Common metals containing waste water

2.1.4. Applications About Wastewater Treatment and Reuse of Metal Coating Industry

Treatment applications, to be applied to metal coating plant waste waters, can be summarized as follows [17];

- Reduction $^{+}6$ valent Chromium to $^{+}3$ and precipitation
- The neutralization of acidic waste
- Chemical precipitation of metal waste
- Precipitation
- Ion Exchange
- Adsorbtion
- Reverse osmosis
- Membrane filtration,
- Electrochemical treatment technologies,
- Neutralization

Chemical precipitation is a process used in industry for the heavy metal waste water treatment techniques being more easy and inexpensive to operate regarding other techniques at the begining of 2000s [28]. This tecnique more easy and inexpensive to operate regarding other techniques. In precipitation processes, chemicals react with heavy metal ions to form insoluble precipitates. Hydroxide precipitation and sulfide precipitation processes are used for chemical precipitation processes. Due to its relative simplicity, low cost and ease of pH control, hydroxide precipitation is the most widely used chemical precipitation technique. It is preferable to use more lime for industrial scale precipitation. In 2005 by Mirbagheri and Hosseini, $Ca(OH)_2$ and NaOH using hydroxide precipitation process to remove Cu (II) and Cr (VI) ions from waste water. It was converted Cr (VI) to Cr (III) by using iron sulfate. Maximum precipitation of Cr(III) occurred at pH 8.7 with the addition of $Ca(OH)_2$ and the concentration of chromate was reduced from 30 mg/L to 0.01 mg/L.

Sulfide precipitation is another effective process for the treatment of toxic heavy metals ions from industrial waste water. In order to remove Cu^{2+}, Cd^{2+}, and Pb^{2+}, pyrite and synthetic iron sulfide are used. [29]. Sulphide precipitatants can cause formation of toxic H_2S fumes in acidic conditions. Chemical precipitation has been shown to be successful in combination with other methods. In 2006, González-Muñoz *et al.* are investigated sulfide precipitation in order to reuse and recover heavy metal ions for reducing the metal content from waste water and to reuse directly nanofiltration as the second step [30]. With Electro- Fenton process rayon industry waste water's COD value (2400 mg/L) has reduced by Ghosh *et al.* at the rate of 88% COD was reduced and % 99-99.3 zinc was reduced using lime precipitation at pH 9-10 [31].

Ion-exchange processes have been widely used to remove heavy metals from waste water due to their many advantages, such as high treatment capacity, high removal efficiency and fast kinetics [32]. Papadopoulos *et al.* (2004) reported that nickel has been removed, from a rinse bath of aluminum up to 74.8%, by using ion exchange and precipitation processes combined [33]. Synthetic resins are more effective to remove the heavy metals from waste water than other materials used in ion-exchange processes, therefore they are more commonly used [34] where pH, temperature, initial metal concentration and contact time is very important for these processes [35]. Due to their low cost natural zeolites, (especially Clinoptilolite) have been preferred by many researchers at laboratory scale and industrial scale studies to remove Cu, Mn and Zn [36;37;38;39;40].

Adsorbtion is another accepted process for heavy metal removal from industrial waste water as an economic and effective method due to their flexibility and ease in design and operation and high-quality treated effluent. Additionally adsorbtion is reversible and its adsorbents can be regenerated. Activated carbon (AC) adsorbents are widely used in the removal of heavy metal contaminants [41;42]. Carbon nanotubes (CNTs) have been proven to possess great potential for removing heavy metal ions such as lead [43;44] , cadmium [45], chromium [46], copper [47], and nickel [48] from waste water [17]. 75.3% of all the Pb(II) adsorption capacity of CNTs has been investigated by Pillay *et al.* (2009) [46]. The copper adsorption capacity by CNTs/CA canattain 67.9 mg/g at copper equilibrium concentration of 5 mg/L [17]. Based on literature search after the year 2007 biosorption of heavy metals from waste water become very promising by using bioadsorbents which are inexpensive and have high effectiveness in reducing the heavy metal ions. Typical biosorbents can be;

- Non-living biomass such as bark, lignin, shrimp, krill, squid, crab shell,
- Algal biomass,
- Microbial biomass, e.g. bacteria, fungi and yeast.

Biosorbents have low-cost and rapid adsorption characteristics, moreover the separation of biosorbents would be difficult after adsorption [17].

Coagulation and flocculation is also used to remove heavy metal from waste water. sedimentation and filtration is applied after coagulation and flocculation. Many coagulants are widely used in the conventional waste water treatment processes such as aluminium, ferrous sulfate and ferric chloride. Ferric chloride solution and PACl (Polyaluminium chloride), which are commercial coagulants, has ben studied to remove heavy metals [49]. Coagulation / flocculation must be followed by other treatment techniques to get high removal performance [50]. Flotation especially DAF (Dissolved Air Flotation) , ion flotation and precipitation flotation are used for the removal of metal ions from waste water. Cadmium, lead and copper have been removed from diluted solution by a plant-derived biosurfactant tea saponin; removal efficiency were 90%, 81% and 71.2% for Pb^{2+}, Cu^{2+} and Cd^{2+}respectively [51].

Membrane processes (ultrafiltration, reverse osmosis, nanofiltration and electrodialysis) used to remove metals from the waste water with high efficiency and easy operation. To obtain high removal efficiency of metal ions, the MEUF (Micellar Enhanced Ultrafiltration) and PEUF (Polymer Enhanced Ultrafiltration) is proposed by Scamehorn *et al.* in 1980s to remove dissolved organic compounds and multivalent metal ions from waste water [52]. Metal removal efficiency of MEUF is related to characteristics and concentrations of the metals and surfactants, solution pH, ionic strength and membrane operation. Rejection yield can reached up to %99 [53]. Main disadvantageous of membrane processes are stuck problem, necessity of regeneration of membran surface and high-cost operation conditions. NF (Nanofiltration) processes is an advantageous technology for the removal of heavy metal ions such as nickel [54], chromium [55], copper [56;57] and arsenic [58] from industrial waste water. Rejection yield of nickel has been found to be 98% and 92% by using NF membrane process by Murthy *et al.* [59].

ED (Electrodialysis) is another membrane process to remove metal ions across charged membranes from one solution to another using an electric field as the driving force. Two type mebrane is used; cation-exchange and anion-exchange membranes. Cu and Fe are seperated from waste water effectively by electrodialysis process [60;61]. In order to increase Pb^{+2} rejection success of membrane from waste water using ED, voltage and temperature should be increased, flow rate should be decreased during operation [62].

In the early 2000s, RO (Reverse Osmosis) treatment for waste water treatment and recycling has become increasingly attractive in the metal coating industry due to its high efficiency, ease of use and low cost. Furthermore, the Fenton process (H_2O_2/Fe^{2+} system), which is an advanced oxidation process, is seen as the most promising method for the decomposition of organic compounds that cannot be biodegradable due to the lack of toxicity of reagents, cost effectiveness and ease of use [63;64; 65]. In 2011 in China. Fenton–biological treatment of reverse osmosis is studied by R.M. Huang, J.Y. He, J. Zhao and others, which is membrane concentrated from a metal plating waste water recycle system. This study revealed that RO treatment is difficult to remove the organic compounds and heavy metals in the RO concentrate by conventional processes, although metal coating is widely used in the recycling of wastewater. In order to treat RO concentrate containing complex Cu and Ni from metal plating, it was used a combination process, including Fenton oxidation and a biological aerated filter. Cu and Ni ions were released by degradation of organic compounds and afterward these ions were removed by pH adjustment and coagulation during the Fenton treatment. Biological aerated filter process was applied for further treatment of the concentrate. The concentrations of effluent COD, Cu and Ni ions were less than 40 mg/L, 0.5 mg/L and 0.3 mg/L, respectively; this shows that the treated effluent meets the emission standards for pollutants from electroplating set by China's Environmental Protection Agency [65].

Literature survey has been revealed that the most preferrable methods, for the treatment of waste water containing metal processing wastes, are ion-exchange, adsorption and membrane filtration. In particular, membrane filtration process is fore in recent years.

2.2. Pulp and Paper Production Industry

2.2.1. An Owerview of the Pulp and Paper Production Industry

A variety of production methods and many different types of raw materials have been using in pulp and paper production industry. As the cellulose fiber containing raw material; usually wood, recycled paper and agricultural residues are considered. In developing countries about 60% of the cellulose fibers are wood made of -originating materials such as; sugar cane fibers, straw, bamboo, reeds, straw, jute, flax, sisal (sisal).

Paper production process comprises the steps shown in Figure 2; Paper production is a two step process. Before the raw material is converted into pulp fibers into first. Then the paper produced from the pulp.

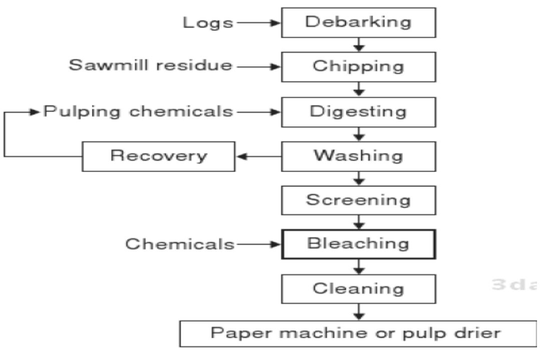

Figure 2. Pulp and Paper production process flow chart [66].

Firstly gathered wood has been processed of separation from wood components to get lignin. Pulp can be prepared mechanically or chemically. Afterwards the pulp is belached and subjected to the process according to type, thickness and weight. It is dred in paper mill and pressed to form paper sheets.

2.2.2. Water Consumption and Water Quality Used in Pulp and Paper Industry

One of the most water and energy consuming sectors is the pulp and paper industry which requires 250 tonnes of water for the production of one tone of .[67]. Nearly in every cycle of pulping and paper making process needs water. While 500 m^3 of water was used to produce one ton of paper in the past, the latest technological developments have reduced the amount of water required to 15 m^3. The research results show that approximately 50 m^3 of water is needed per ton of paper [68; 69].

During pulp and paper manufacturing clean water is utilized as cooling water, boiler feed water process water intensively. It is reported that significant amount of water, in the range of 15-100 m^3/tonne, is consumed in European pulp production mills, about more than 50 m^3/tonne is spent as cooling water. Cooling of grinding wheels is one of the most water dependent processes to berak up fibers and to transport to other processes. In mechanical pulp mills water systems are used in a closed for the continuation of the high temperatures. Fresh water is spent only as insulation water and cooling water [70; 71]

2.2.3. Waste Resources and Wastewater Characterization of Pulp and Paper Industry

The pulp and paper manufacturing industry, which is a very large industry, is seen as the biggest pollution threat to the environment. The waste water load discharged from the mill determines the volume of water used [70]. In the pulp processing and paper making process, a large amount of water is consumed at each step and converts the process water into waste water with a high pollution load. Wood preparation, pulping, pulp washing, sieving, washing, bleaching and paper machine and coating are processes with high pollution load. One of these processes, pulping, especially chemical pulping, leads to the production of high-strength waste water. This type of waste water, which contains wood residues and soluble wood materials, makes up most of the toxic substances since paper pulp bleaching uses chlorine to light pulp. The vast majority of plants in nature, such as woods, reeds and grasses, bamboos or canes and reeds, can be used in the preparation of pulp fibers. Wood is often used as a source of papermaking fibers. The wood and derivatives of various compounds (lignin, carbohydrates and extracts), which are difficult to biodegrade, are washed from fibers during washing, dewatering and sieving. Depending on the type of pulp process, a variety of toxic chemicals are produced in the pulp and papermaking process, such as resin acids, unsaturated fatty acids, diterpene alcohols, canyons, chlorinated resin acids and others, which vary depending on the type of pulp process [72].

In the pulp and paper manufacturing industry, the type of process, the type of wood materials, process technology, management practices, internal recirculation of waste water for recovery and the amount of water to be used determine the characteristics of waste water. For instance, the organic material content of mechanical pulp process effluent changes between 1000 and 5600 mg/L COD, it increases up to 2500–13,000 mg/L COD in chemical pulp process [73]. Pulp and paper industry effluents may contain non-biodegradable organic materials, AOX (Adsorbable Organic Halogens), Color, Phenolic compounds, etc. However, in general, high organic material and suspended solid contents are considered major pollutants of pulp and paper industry effluents [74].Typical waste water characterization of pulp and paper industry is illustrated in Table 2.

Table 2. Typical wastewater generation and pollution load from pulp and paper industry [75].

Processes	Watewater (m^3/adt pulp or paper)	SS (kg/adt pulp)	COD (kg/adt pulp)
Wet dabarking	5-25	nr	5-20
Groundwood pulping	10-15	nr	15-32
TMP-unbleached	10-30	10-40	40-60
TMP-unbleached	10-30	10-40	50-120
CTMP-unbleached	10-15	20-50	70-120
CTMP-unbleached	10-15	20-50	100-180
NSSC	20-80	3-10	30-120
Ca-sulfite (unbleached)	80-100	20-50	nr
Ca-sulfite (bleached)	150-180	20-60	120-180
Mg-sulfite (unbleached)	40-60	10-40	60-120
Kraft unbleached	40-60	10-20	40-60
Kraft bleached	60-90	10-40	100-140
Paper making	10-50	nr	nr
Agrobased small paper mill	200-250	50-100	1000-1100

nr=not reported; adt=air dry ton; NSSC=neutral sulfite semi-chemicals

A large number of studies have been carried out to investigate bleaching processes causing to generate chlorine dioxide and other chlorine organic chemicals (AOX), which are very toxic, non-biodegradable and contaminating food chain by means of bioaccumulation, during pulp and paper manufacturing processes. In addition to being toxic, chlorine dioxides are also carcinogen and almost insoluble in water.Adverse effects of dioxins have been observed in almost all the species tested. Bleached kraft mil waste water affects the biological properties of receiving water, causes fish deaths and mutagenic effects in the aqautic fauna [66]. Unbleached and Bleached pulp waste water contamination loads are shown in Table 3.

Table 3. Unbleached and Bleached pulp waste water contamination loads [70].

	Bleached pulp	Unbleached pulp
Flow (m^3/adt)	30 - 50	15 - 25
COD (kg/adt)	8-23	5-10
BOD_5 (kg/adt)	0.3-1.5	0.2-0.7
TSS (kg/adt)	0.6-1.5	0.3-1.0
AOX (kg/adt)	< 0.25	-
Tot-N (kg/adt)	0.1-0.25	0.1-0.2
Tot-P (kg/adt)	0.01-0.03	0.01-0.02

(adt—air dry ton)

Furthermore, the evaluation of the pollution load on the waste water occurs in some process is given below [70];

- Debarking waste water is toxic and have high COD value (20-60 kg/m^3).
- At sulphite pulp mills, COD load is 10-20 kg in approximately 1 m^3 of condensate
- The COD load in condensates is normally much higher at sulphite pulp mills compared to kraft mills. The total load in condensates is up to 60 - 70 kg of COD/tonne. Generally, COD load vary between 80 and 200 kg/tonne.
- At sulphite pulp mills, COD load of condensate from evaporation is 30-35 kg COD/tonne, is 35-40 kg COD/tonne from bleaching unit and is 5-10 kg COD/tonne from washing losses, rinsing, spilled waters.
- Generally, starch and starch degradation products, that are biodegradable, contribute a significant amount of organic material in pulp and apaper manufacturing.

2.2.4. Applications about Wastewater Treatment and Reuse of Pulp and Paper Industry

Pollution from the pulp and paper industry can be minimized by various internal process changes and management measures such as the Best Available Technology (BAT) such as [70];

- Recycling of cooling and sealing waters can be increased by use of heat exchangers or a cooling tower. However, microbial and water quality monitoring and control methods are required to ensure disturbance-free performance of the system
- Separate pre-treatment of coating waste water
- Effluent treatment of waste water by installation of an equalisation basin and primary treatment
- Secondary or biological treatment of waste water, and/or in some cases, secondary chemical precipitation or flocculation of waste water. When only chemical treatment is applied the discharges of COD will be somewhat higher but mainly made up of easily degradable matter

Treatment methods for pulp and paper industry vary. In order to remove suspended solids, colloidal particles, floating matters, colors, and toxic compounds physicochemical treatment processes have been applied, composed with either coagulation, oxidation, ozonation, electrolysis, reverse osmosis, ultra-filtration, and nano-filtration technologies. In additon to chemical treatment methods, biological methods (aerobic treatment; Activated sludge, Aerated lagoons, Aerobic biological reactors; anaerobic treatment, fungal treatment and integrated treatment processes) also have been applied to treat pulp and paper industry waste water [72; 76;77; 78;79;80].

The status of water treatment technologies in paper industry can be summarised as the following [70]:

- Save-alls filters (common technique). The output of super clear filtrate for re-use can be increased
- Flotation (industrially proven)
- Washing presses (industrially proven)
- Reject and sludge de-watering technique (industrially proven)
- Conventional biological treatment in different variants as e.g. activated sludge (single-stage or two-stage, with and without carrier material), trickling filter (combined with activated sludge), stand-alone submerged biofilters (one- or two-stage) or combined with activated sludge. All these techniques can be considered as industrially proven.
- Biological in-line treatment (first industrial applications realised)
- Pre-filtration + membrane filtration (UF-Ultrafiltration, NF) (first industrial applications realised)
- Pre-filtration + evaporation (first industrial applications realised). If fresh water is replaced with evaporated water there are probably no effects on chemistry and on papermaking.
- Ozonation (first industrial application are to be expected soon). If fresh water is replaced with partially purified water there is a potential of built-ups of disturbing substances. For example, the inorganic salts are not affected and they can interact with process chemicals and equipment. Ozonation is still considered as relatively expensive and less expensive techniques must be developed. These potential effects have to be controlled and the knowledge on the water quality needed have to be increased.
- Enzymatic treatment of process water (under research phase)

The literature review found that aerobic and anaerobic treatment systems are suitable for the treatment of wastewater from all pulp and paper mills, except that bleach kraft wastes are less suitable to anaerobic bacteria, since they are less toxic to anaerobic bacteria [72].

Chemical coagulation and flocculation are widely used processes for the removal of suspended solids followed by sedimentation. As a tertiary treatment, these processes have been applied to pulp and paper effluents [72]. In 2008, coagulation with alum and polyaluminum chloride is studied on the treatment of pulp and paper mill waste water. 99.8%, 99.4%, and 91% turbidity, TSS, and COD removal efficiencies were achieved at the optimum alum dosage of 1000 mg/L and pH of 6.0 ; reduction of turbidity was 99.9% , TSS removal was 99.5% and COD reduction was 91.3% of at the optimum dosage and pH for PACl at 500 mg/L and 6.0, respectively [81].

Adsorption, advanced oxidation and membrane filtration processes can be applied for the treatment of pulp and paper waste waters containing resistant compounds. In 2005, Temmink and Grolle obtained an excellent polishing in color in activated carbon treatment in biologically treated waste water from the paper and cardboard industry [76]. 79.6% TOC (Total Organic Carbon) and 94% toxicity removal are obtained by Titania (TiO_2) supported photocatalysis (UV/TiO_2) with a concentration of 0.75 g/L TiO_2 at pH 11 within 60 minutes. [76]. 79.6% TOC and 94% toxicity removal is obtained by the TiO_2-assisted photo-catalysis (UV/TiO2) with a titanium dioxide concentration of 0.75 g/L at pH 11 within 60 min [79].

Today techniques, allowing reuse possibilites of effluent from pulp and paaper, are preferred due to limited water sources and cost effect. Particularly, membrane separation techniques like microfiltration (MF), NF, UF)and RO have been most widely used for treating pulp and paper waste water as polishing step to return it back into the process for reuse.

All paper mills use untreated, fibre enriched white water from the paper machine. White water is clarified applying filtration (polydisk filters, drum filters), flotation (DAF) or sedimentation (sedimentation funnels, laminated separators). The clarified water is then re-used for the replacement of fresh water, for example, at the showers used for cleaning machine clothing (wires, felts) [70].

Pizzichini et al. studied different ceramic MF, polymeric MF, UF and RO modules for the treatment of pulp and paper waste water for water reuse in a closed loop, to reduce energy requirement, to get good permeate flow [82]. It was concluded that cellulose membranes could offer the most optimal membrane performance for such applications [83;84] Membrane processes effectively reduce BOD_5, COD, Total Dissolved Solids (TDS), TSS, AOX and Color from pulp and paper effluents [82;72;85].

Treatment of paper industry wastewater was carried out using membrane based microfiltration / electrodialysis hybrid process by S.K. Nataraj, S. Sridhar *et al.* in 2007. The pilot plant of a hybrid MF and ED system was designed, constructed and employed successfully for this study in order to remove the color and contaminants of paper industry waste water. As a pretreatment step, microfiltration membrane was used. In order to filter the waste water at 60 °C and ambient temperature, tubular ceramic module was equipped. Paper industry effluent was treated by electrodialysis process for the first time with MF as a pretreatment step. The combined hybrid process at the applied potential of 50V showed a low content of TDS of 546 mg/L, conductivity of 0.61 mS/cm and COD of less than 20 mg/L. Usage of the hybrid MF/ED module in this study provided a recovery and reuse of more than 90% of original waste water. Result of the study showed that the hybrid process is more efficient than the single unit process [86].

However, increasing of the usage of UF for recycling (e.g. for press section showers) of the papermill waste water is not yet considered feasible because of only dissolved materials removal. Runnability, paper quality and performance of papermaking chemicals can be impaired by the accumulation of dissolved materials. More efficient separation techniques like nano-filtration or reverse osmosis or other complementing techniques are must for the closed water circulation of paper machine waters. Negative cross-media effects (mainly energy) and membrane surface fouling problems are caused that these techniques are not suitable due to high costs [70].

In pulp and paper industry, advanced waste water treatment is mainly focused on additional biological-membrane-reactors, membrane filtration techniques such as micro-, ultra or nano-filtration, ozone treatment and evaporation in pulp and paper industry. Figure 3. 9 illustrates an example of how to apply a combination of membrane filtration, ozonation and evaparation for process water treatment in a paper mill.

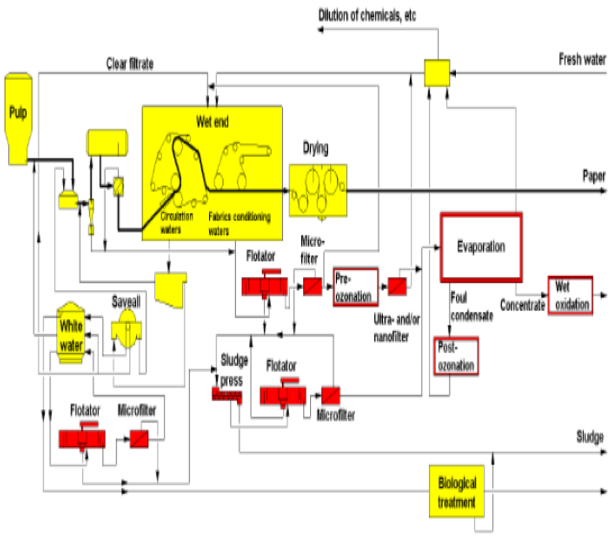

Figure 3. Toolbox for possible internal treatment and reuse of paper machine waters [87].

Advanced waste/process water treatment technologies are applied to further remove pollutants that are not removed by common biological treatment like activated sludge plants. Those pollutants are residual COD, Color, Nutrients or TSS. Advanced water treatment processes produce a high water quality. As a consequence there is a better chance to re-use the "effluent" in the process as fresh water [70].

Advanced effluent treatment was applied with a combined process of ozonation and fixed bed biofilm reactors in Fa. Lang, Germany. A treatment process was developed to improve the treated effluent quality and to reuse in the process. This tertiary effluent treatment consists of a combination of ozone with fixed bed biofilm reactors and results in a significant elimination of COD, Color and AOX with a minimum of ozone dosage. A typical scheme of this process is shown in Figure 4 [70].

The treated effluent has a low content of disturbing matters so that the reuse of tertiary treated effluent in the process seems to be an interesting option. That means, the ozone treated water can be either discharged or re-used in production [70].

In order to recover and recycle of coating-color-containing effluent from paper mills generating a hydraulically low flow waste water (about 2 - 5% of the total flow) which, however, is rich in pigments and adhesives. The heavy solid load and by nature sticky compounds in these waste water causes operating problems. After feeding effluent into UF process to remove coating colors and separate coating effluents, amount of waste is reduced markedly. There is also a little reduction of water consumption because the permeate can be re-used. Reduction of coating waste water discharge with separate treatment of these waste water improves the performance of an external effluent treatment. Depending on the ratio coating/paper produced the amount of solid waste can be lowered by 70% [70].

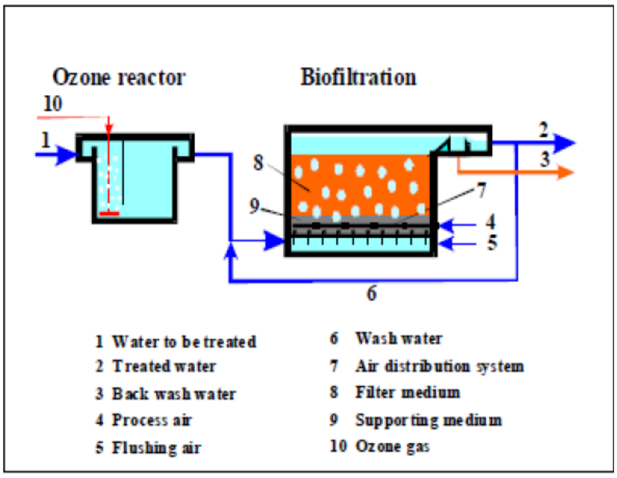

Figure 4. Combined process of ozonation and fixed bed biofilm reactors [70].

Zhanga *et al*. were studied on Chinese Paper Mill Waste water in 2009 in Tianjin Polytechnic University. They treated it with the conventional A–O–O method, which consists of a balance tank, a first sedimentation tank, an anoxic tank, an aerobic tank and a secondary sedimentation tank. The integrated membrane process in pilot scale which consists of the membrane bioreactor (MBR), the continuous membrane filtration (CMF) and RO, is used to treat the waste water of this paper mill. The discharged water from the first sedimentation tank was treated with the anoxic/aerobic/MBR membrane system to eliminate NH_3–N and organic compound dissolved or undissolved. The recovery of water for RO system was over 65%. RO permeate with the high quality met the whole standards of process water of paper mill. The conductivity of RO permeate was less than 200 µS/cm, COD less than 15 mg/L, the turbidity less than 0.1 NTU (Nephelometric Turbidity Unit) and the chromium of RO permeate was less than 15 PCU. As the result, the treated water by the integrated membrane process could be reused in paper manufacturing process perfectly [80].

2.3. Drug Industry

2.3.1. An Owerview of Drug Production Industry

Pharmaceutical industry produces a wide variety of products. It uses both inorganics and organics as raw materials; the latter is either of synthetic or of plant and animal origin [88]. Medicines are produced by mixing the active ingredient substance according to a standart recipe. Solid form drugs are powders, granules, lozenges, tablets, capsules and their manufacturing process flow diagram shown in Figure 5 (Guide, Pharm. Ind.; 2013).

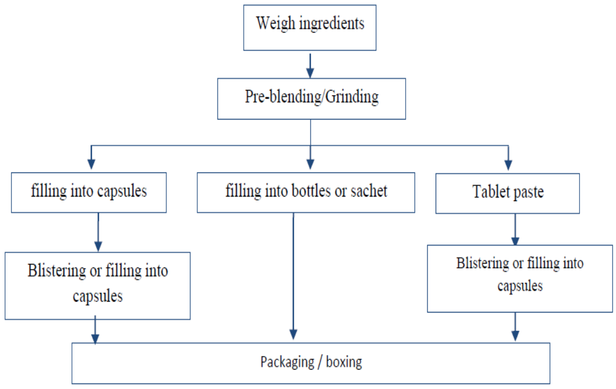

Figure 5. Tablet manufacturing process flow diagram [89].

General process flow diagram is shown at Figure 5. Pharmaceuticals can also be semi-solid form; semi-solid form drugs pomade, ointment, suppository, cream, gel, production flow diagram is shown in Figure 6.

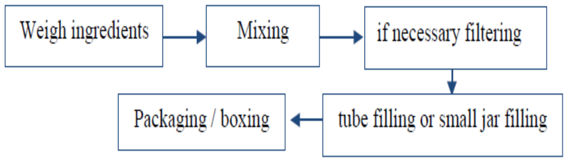

Figure 6. Semi-solid form drug production flowchart [89].

Sterile medicines in liquid form (bulb, drops and serum) and nonsterile (syrups and other solutions) are divided into two groups. Liquid form drug production flowchart is shown at Fig. 7.

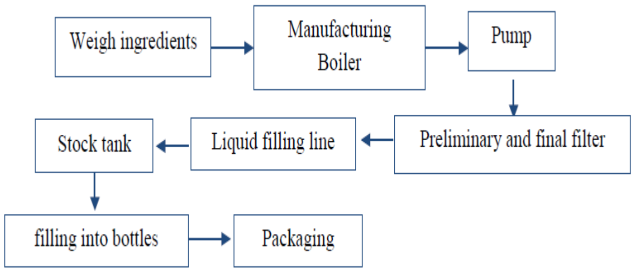

Figure 7. Liquid form drug production flowchart [89].

2.3.2. Water Consumption and Water Quality Used in Drug Industry

Water is used widely in the pharnaceutical industry as the main ingredient, a raw material, reaction member and a cleaning agent at formulation and manufacturing steps. Microbiological quality of the water is important because microorganisms can multiply rapidly during purification, storage, transport,and handling. Many different quality water is available in the drug industry and this water is used at different stages of drug production. Depending on intented use despite of changing of water quality, water, used for drug manufacturing, can be divided into three main groups as;

- Drinking water,
- Pure water and
- Injectable water

To obtain pure water, its storage, usage preserving physical, chemical and microbial quality is considered as part of the pharmaceutical manufacturing.

Drinking water may be used for cleaning the first step of the chemical synthesis and pharmaceutical production equipment. Drinking water is also used in the manufacture of pure water used in the pharmaceutical industry. Drinking water can be obtained by specific sources or combination of these sources such as tap water and well water and e.g. On drinking water quality, in Turkey TSE 266 (1997), World Health Organization (WHO) (1999), the US Environmental Protection Agency (EPA) (2002) and the European Union (EC) (1998) dated standards are available. According to these standarts, drinking water must not contain coliform bacteria in 100 ml and its pH must be in the range of 6,5-9,5. In drug manufacturing pure water is used as intermediate or for cleaning certain equipment at different stages or for production of some pharmaceutical chemicals in the scope of semi-finished products. The water, used for this purpose, must be pure and protected gainst microbial growth. Pure water quality characteristics, defined as clear, colorless, odorless in the European and US Pharmacopeia Standarts applied in Turkey, are given in the Table 4.

Table 4. Pure water quality characteristics defined in Pharmacopeia Standarts [90].

Quality Criteria	EU Pharmacopeia Standarts (EP)	US Pharmacopeia Standarts (USP)
Nitrate (ppb)	200	-
Heavy Metals (ppb)	100	-
TOC (mg/L)	0,5	0,5
Conductivity (µS/cm)	4,3 (20^{o}C)	1,3 (25^{o}C)
pH	(5-7)	(5-7)
Bacteria (CFU/mL)	100	100

Conductivity of pure water is calculated as 0,055 µS/cm (25^{o}C) or electrical resistance is as 18,2 Mega ohm/cm. İf drinking water is taken as a source, pure water is produced by using deionization, distillation, ion exchange, reverse osmosis, filtration or other suitable methods.

Injectable water is used for prepation of medicines to be injected into the body as a carrier, for cleaning critical equipment and prepation of some drug components. For this pupose water is further purified via distillation after pre-treatment or reverse osmoz. In order to prevent biofilm formation in storage equipments inner surface must be very smooth and must be found washing ball to be sprayed to all inside and the tank must be completely closed. To minimizing corrosion effect AISI 316 L quality stainless steel tank is used for chemical and thermal sanitization.

Distribution piping system must be allow to circulate whole water contstantly and to discharge periodically to prevent microbial growth. Microbial levels in water systems are mainly kept under control with the sanitization process. 254 nm emitting ultraviolet light lamps, connected to the distribution line in constant circulation of the water system, are used as auxiliary sanitization elements.

A preventive maintenance program is created to control the water system. This program includes system operating procedures, the critical quality values, critical operating conditions and calibration of critical measuring instruments, periodical sanitization plan, preventive care of devices and system components, systematic of the amendments to the mechanical systems and operating conditions [90].

2.3.3. Waste Resources and Wastewater Characterization of Drug Industry

Waste water formation and characterization vary depends on product type and quantity. Generally, waste water form pharmaceutical industry is toxic to biological lifei lethal toxic to aquatic species and are usually have high BOD_5, COD values and a low BOD_5/COD ratio, which is the main problem causing the failure of biological treatment [88].

Waste waters generated from pharmaceutical company contain high loads of organic pollutants represented by COD, BOD_5 values, suspended solids, oil and grease, phenol, sulfate, sulphide, TKN (Total Kjeldahl Nitrogen), Ammonia (NH_3), Tot-P (Total phosphorus) and high concentration of refractory and priority compounds such as diclofenac, chloramphenicol, paracetamol drugs and their byproducts p-aminophenol, phenol, benzoic acid, nitrobenzene and salicylic acid were detected in all waste water samples. Generally, the final waste water from the company is not complying with the National Environmental Laws and its regulations [88].

Taking into account raw material, process, production, waste water characterizaton and treatability factors, USEPA (Environmental Protection Agency) has been classified drug industry in 5 different catoegories as shown below;

- Fermentation
- Extraction and Distillation,
- Chemical Synthesis
- Formulation - Pharmaceutical research

or by different combinations of the above methods [91].

Fermentation; is a large scale batch process used for production antibiotics and stereoids such as penicillin, teramycin and streptomycin. Waste waters form fermentation have high BOD_5, COD and SS. pH varies between 4-8. During fermentation process and solvent extraction solvents can be recovered and reused. Waste water resources in fermentation proces;

- Ground and equipment cleaning waters
- Solvents from extraction
- Cooling waters

Usually steam and occasionally chemical disinfectants such as phenol are used for equipment sterilization in fermentation process. In some cases fermentation tank is infected. Therefore, the process being early discharge and impurity concentration, resulting from nutrients in process, is further increased.

Flow rate of the waste water resulting from the extraction process is low. A large part of the waste water occurs as a result of cleaning. Some of the solvent residue miscible in waste water. Recirculation of the solvent is not possible to plant discharge channel. Many of the drugs are produced by chemical synthesis. Solvents, in chemical synthesis, employed n reaction and purification intensively. Benzene and toluene are most commonly used organic solvents. Solvents can be recovered by releasing them pollution. The recovery process is achieved by column distillation. However, the solvent may be the loss during storage. The majority of waste water is result form this process. Chemical synthesis effluents is complex and extremely difficult to treatment[91].

Effluent resources comprising chemical synthesis processing are provided below;

- Waste solvents, filter waste
- Ground and equipment cleaning water
- Spills, pump water filtrate

Chemical synthesis waste water can be characterized by high BOD_5, COD and SS values. pH value varies between 1 to 11. Wastes, because of being complex structure, can show inhibitor effect in biological waste treatment systems [91].

Drug formulation waste water sources are listed below.

- Ground and equipment cleaning water
- Accidental spills
- Laboratory waste

Waste water flow rate is low since processes, to be used water for formulation, are less. Water is used for cooling and in-plant cleaning rather than formulation. Water is used also for cleaning ventilation system filters. During washing mixing tanks waste water goes to the waste water treatment plant in different quantities and concentrations. These type waste water may contain some pollutants such as inorganic salts, sugars where biological waste water treatment is applied to treat. Waste water from formulation department has lower BOD_5, COD and SS concentrations, pH value varies between 6 to 8 [91].

Chemical, microbiological, pharmacological research are conducted in pharmaceutical industry. Waste water coming form drug research processes are less than drug production facilities, however it is irregular in terms of quality, quantity and discharge time since different solvents and radioactive chemicals could be used and removed from the laboratories. Waste water resources generated during pharmaceutical research are given below.

- Ground and equipment cleaning water
- Animal cages cleaning water
- Laboratory-scale production waste water

Waste water from pharmaceutical research processes takes similar values to municipal waste water in terms of BOD_5 and COD concentrations and pH value varies between 6 to 8 [91]. Waste water characterics, obtained form production processes in Fako pharmaceutical company, are presented in Table 5.

Table 5. Waste water characteristics, obtained form production processes in Fako pharmaceutical company [91].

Parameter	Value
pH	8,2
COD (mg/L)	572
NH_3 (mg/L)	2
TKN (mg/L)	25
Conductivity (µs/cm)	4420
SS (mg/L)	153
VSS (mg/L)	140
TSS (mg/L)	3353
T-P (mg/L)	3,6
T-Fe (µg/L)	0,4
Color 436 nm (m^{-1})	90,5
Color 525 nm (m^{-1})	43.2
Color 620 nm (m^{-1})	29.2

2.3.2. Applications about Wastewater Treatment and Reuse of Drug Industry

Pharmaceutical industry waste water has been treated conventional methods so far. However conventional waste water treatment methods were insufficient due to their limited effectiveness [92]. In case conventional biological waste water treatments have limited degradation efficacy, chemical oxidative treatment technologies and the advanced oxidation processes can be helpful for their known capacity of oxidising and partially mineralising many organic contaminants [93;94]. In Salerno university G. Mascolo, L. Balest *et al.* investigated that the biodegradability of different waste water samples originated from the industrial production of three pharmaceuticals (naproxen, acyclovir, and nalidixic acid) by Zahn–Wellens test. As the result of this study realized in 2010, the biodegradation of high concentrations of organic solvents and other biodegradable compound tended to ‘‘hide” the lack of removal of the target compound. In this study it is offered to adopt of more efficient biplogical treatments such as MBR technology and /or the integration with an advanced oxidation process, either to enhance the biodegradability or to mineralize the refractory and recalcitrant compounds [95].

The reuse of waste water has two fold benefits through not only the reduction of discharged effluent to the environment but also a potential reduction of pressure on existing water resources.

Pharmaceutical compounds, in particular antibiotics, have been recognized and used in the ecosystem for almost 30 years. In recent years, the use of antibiotics in veterinary and human medicine has become widespread (annual consumption of 100,000-200,000 tons), thus increasing the likelihood of water contamination with such compounds [96]. Disposal of these compounds through anthropogenic sources has become a potential risk source for aquatic and land organisms [97;98]. Due to the most WWTPs are not designed to be suitable for the treatment of high-pole micro-pollutants such as antibiotics may mix into surface waters, reach groundwater after leaching and thus can enter in the DWTPs (Drinking Water Treatment Plants) as the contaminated surface waters [96]. The direct release of veterinary antibiotics through application in aquaculture is another important source of contamination [2;99;100].

The pollutant type and concentration in the effluent and the cost of the process are important criterias to choose treatment method at the feasibility stage. Chemical and physical tereatment can be applied for organic compounds removal such as chemical oxidation and biodegradation (destructive methods).

In the conventional waste water treatment plants often use biological processes, filtration and coagulation / flocculation / precipitation processes. [101; 102; 103;104; 105]. Activated sludge is a widely used technology in biological systems, especially in industrial waste water treatment. This method uses coagulation / agglomeration / precipitation, solid precipitation, precipitation of pollutants and colloid formation and subsequent precipitation, and continuous temperature and chemical oxygen demand (COD) is followed by decomposition of organic compounds into activated sludge tanks by aerobic or anaerobic systems. [2]. Lime, alum, iron salts and polymers are the most used chemicals for this method used when the pollutants toxicity is low, this method continues to be applicable.

A wide variety of conventional techniques have been used to remove antibiotics to date. The study of the application of anaerobic processes in the removal of macrolides and tetracyclines was described by Chelliapan *et al.* (2006) and Arikan in 2008. Although not always such results were obtained; 90% reduction for macrolides and 75% reduction for tetracyclines. [106;105]. Göbel *et al.*, were studied the traditional primary and secondary treatments for macrolides, sulphonamides and trimethoprim verifying slight eliminations (20%) in this case in 2007 [102] [2]. Adams *et al.* (2002), Stackelberg *et al.* (2007) and Vieno *et al.* (2007) investigated the efficiency of some physicochemical methods, such as clarification, coagulation/ flocculation/sedimentation and filtration applied to macrolides, sulphonamides, quinolones, quinoxaline derivatives and trimethoprim, resulting in low removals (maximum removal of about 30%). [101;103;104]. Finally new alternative techniques have emerged due to the low efficiencies of these methodologies and sometimes the inability of their use [2].

Due to its low cost, chlorination have been frequently applied in the disinfection of drinking water treatment plants by using chlorine gas or hypochlorite at oxidation processes. In the distribution systems, advanced oxidation processes are used as a post-treatment, in order to maintain a disinfectant residual level. [107]. This technique is also applied to oxidize to less toxic compounds which are readily biodegradable during treatment of drugs prior to application of biological processes. During waste water treatment in this technique, the major reactive is hypochlorous acid which can react with organic compounds through oxidation reactions. In addition, some of these substances reacting to aromatic rings, neutral amines and double bonds may react by producing halogenated organic compounds with potentially dangerous carcinogenic activity (halogen and acid acids) [107;108]. Since it does not form trihalomethane in its reactions with organic compounds, chlorine dioxide has been used as an alternative to other chlorine species [108].

Due to the recalcitrant nature of the effluents containing antibiotics residues interferes in the elimination of these compounds by traditional biological treatments afterwards advanced oxidation processes (AOPs) such as Fenton, photo-Fenton, photolysis, semiconductor photocatalysis and electrochemical processes are applied for alternative [2].

Ozonation process is used for the removal of a strong oxidant to act direct or indirectly (molecular ozone is used to obtaine direct oxidation). The studied-compounds must have. carbone carbon double bonds, aromatic bonds or nitrogen, phosphorous, oxygen or sulphur atoms [109]. Otherwise, the decomposition of ozone in water to form hydroxyl radicals occurs [110]. This technique has the advantage of being applied while the flow rate and/or composition of the effluents are fluctuating. However, it has some disadvantages such as the high cost of equipment and maintenance, as well as energy required to supply the process. [2].

In addition to all, the presence of organic matter, suspended solids, carbonate, bicarbonate and chlorine ions and also pH and temperature affects the ozonation performance [110; 111]. This case is realized by by researchers studies for example, Andreozzi *et al.* (2005), Balcioglu and Ötker (2003), Arslan-Alaton *et al.* (2004), Cokgor *et al.* (2004) and Arslan-Alaton and Caglayan (2005, 2006) [112;113;114;115;116;117]. Beta-lactams have been degradated by using this technique in their studies. Results of these studies were revealed that even for long treatment times, although high removal efficiencies were achieved (COD removals> 50%), the degree of mineralisation was low (~ 20%). pH influence was critical for the ozonation process. They were determined that decreasing of pH cause the accumulation of carboxylic acids [118], macrolides [119;120;121;122;123], quinolones [113;124], sulfonamides [120;121;119;125;123] and tetracyclines [126]. During the process occurred degradation was above 76%. To improve the performance of such treatment techniques, a combination of UV radiation, hydrogen peroxide or ozone used in combination with catalysts is applied [113]. Studies revealed that the degradation, by perozonation of beta-lactams and quinolones antibiotics, broughts no advantage over the ozonation.

As a result of these studies have shown that ozonation is suitable for fluctuating flow rates and compositions.

It it requires a greater amount of oxidant to treat the same pollutant load. The results show that although high degradation efficiencies are achieved, the mineralisation degree is low and the ecotoxicity of effluents remains or even increase. On the other hand, this methodology is extremely pH-dependent, requiring a control over the work range. For these reasons and due to the high cost of equipment and the energy required to supply the process, this methodology does not seem to be adequate for the contaminated water treatment [2].

The Fenton's oxidation is another treatment methos applied for homogeneous or heterogeneous waste water. pH, temperature, catalyst, hydrogen peroxide and target-compound concentration are operation criterias. The pH value is very important for efficiency of Fenton and photo-Fenton processes. Hydrogen peroxide is more stable at low pH in order to prevent the sludge formation (oxyhydroxides precipitates) due to the formation of oxonium ions ($H_3O_2^+$), which improves its stability and, presumably, greatly reduces its reactivity with ferrous ions [116]. Since it is low cost, non-toxic, easy to operate and safe for environment fenton processes are perferred for pharmaceutical waste water including actams [114; 114-a;118-a;118-b;119], imidazoles [120], lincosamides [121], quinolones [122;123], sulphonamides [124;125;126], tetracyclines [121] with desired degradation efficiency above 53%, COD removal> 44%, TOC removal> 20% and a slightly increase in biodegradability, more efficient one is photo-Fenton with degradation efficiency above 74%, COD removal> 56%, TOC removal> 50%.

To remove toxic organic compounds as an an effective, versatile, cost-effective, ease and clean technology electrochemical treatments have been applied [127; 128;128-a]. Pollutants is destroyed electrochemically by a direct anodic oxidation, where pollutants are first adsorbed on the anode surface and then destroyed through the anodic electron exchange. Electrochemical oxidation is applied to antibiotics (epirubicin (anthracycline), bleomycin (glycopeptides) and mitomycin C) by Hirose et al. in 2005 [127]. Only epirubicin was mostly removed. Another study with lincomycin (lincosamide) and ofloxacin (quinolone) degredation is carried out by Jara et al. in 2007 [128]. Lincomycin was oxidized at the rate of %30, ofloxacin is totally removed at the rate of >99%. Electrochemical treatments may be appropriate for treatment of toxic waste water including high concentrates antibiotics and COD.

Adsorption processes (chemical adsorption or physical adsorption) are widely used in industry to remove organic contaminants. Adsorption efficiency depends on surface area, porosity and pore diameter of adsorbent [129]. The most used adsorbents are GACs (Granular Activated Carbons), but their high cost and difficulty of regeneration are disadvantages [130]. Chen and Huang (2010) studied the adsorption of three tetracyclines antibiotics on aluminium oxide which were adsorbed as >50% [131]. A study revealed that the adsorption capacity of activated carbon and bentonite, using amoxicillin (a beta-lactam antibiotic) was 95% for activated carbon and 88% for bentonite [132]. Adsorption of imidazoles and sulphonamides with trimethoprim respectively on activated carbon was studied [101; 133] in which about 90% removal was achieved. Batch or continuous adsorption of trimethoprim, with the removal of above %90, was investigated [134]. As a result, it can be considered that adsorption is an effective method to remove antibiotics from waste water.

The reverse osmosis constitutes one of the membrane processes [135;136;137] which is appropriate for removing large molecules and ions from effluents. Membranes should be resistant to chemical and microbial attack, mechanical and structural stable over long operating periods [138]. RO has disadvantages of being easily fouled or damaged and they are susceptible to be attacked by oxidizing agents, on the other hand it has advantageous to able to remove small molecules.

In order to remove antibiotics from waste water by using reverse osmosis, nano and ultrafiltration processes many studies have been realized. There are different studies about reverse osmosis, nano and ultrafiltration applied to the antibiotics removal with the succes of %90 for all the antibiotic classes [101;136;135;137]. Combination these processes with other methodologies helps the performance of treatment.

Three Australian waste water recycling schemes, two of which employ RO technology, the other applying ozonation and biological activated carbon filtration, have been studied for their ability to remove trace organic contaminants including 11 pharmaceutically active compounds and two non-steroidal estrogenic compounds. Contaminant concentrations were determined using a sensitive analytical method comprising solid phase extraction, derivatization and GC with MS using selected ion monitoring. In raw waste water, concentrations of analgesics and non-steroidal anti-inflammatory medications were comparable to those found in waste waters around the world. Remarkably, removal efficiencies for the three schemes were superior to literature values and RO was responsible for the greatest proportion of contaminant removal. The ability of RO membranes to concentrate many of the compounds was demonstrated and highlights the need for continued research into monitoring waste water treatment, concentrate disposal, improved water recycling schemes and ultimately, safer water and a cleaner environment [139].

The ion exchange systems have been used to improve water quality [2]. Ion exchange membranes can be prepared from inorganic materials such as zeolites, betonite or phosphate salts. However, these membranes are too expensive, have bad electrochemical properties and have frequently large pores [140;141]. The most used membranes are the polymeric (styrenic and acrylic resins) because they usually have both chemical and mechanical stability and great permselectivity [142].

Combined processes have developed to improve treatment perfromance of the processes. Reverse osmosis has been combined with AOPs by using carbon filters' adsorption as pre-treatment [143]. Ozon process and adsorption in the removal of imidazoles were combined by Sánchez-Polo *et al.*, in 2008 [144]. With only ozon process degradation perfromance was 90-100% and mineralization was 10-20%. At the result of this study it is mentioned that obtained by products were toxic. Activated carbon was helpful during ozon process increasimg the removal perfromance and decreasing toxic by-products [145]. AOPs have been applied as a pre-treatment step, in which the pollutants are oxidized to by-products that are easily biodegradable and less toxic, preventing the death of microorganisms that are present in the subsequent biological treatments [146]. Fenton was combined with reverse osmosis in 2006 by Zhang et al. After Fenton process achieved TOC removal was %38, with the combination of reverse osmosis removal was enhanced, the overall. TOC removal was %99[145].

Another combination was realized by Augugliaro et al. in 2005 in which lincomycin (lincosamide) was removed by semiconductor photocatalysis and nanofiltration together [147]. Lincomycin was completely oxidized, photocatalyst particles and the degradation products were separated by filtration. Ozon process is coupled with adsorption by Ötker and Akmehmet-Balcioglu in 2005 as an emerging techniques for the removal of enrofloxacin (quinolones). Absorption performance was 80%, ozon process was completely successful in degredation enrofloxacin adsorbed on zeolite [148]. Sirtori *et al.* (2009) studied the combination solar photo-Fenton with biological treatment for degradation of quinolones. Removal perfromance for organic carbon was 95%, for solar photo-Fenton was 33% and for biological treatment was 62% [149].

According to the information obtained from literature survey, combination processes should offered for the antibiotics removal from pharmaceutical waste water which has persistent and resistant compounds to biodegradation, accumulating in the environment. Mostly conventional treatment methods such as coagulation, flocculation, sedimentation and filtration are applied for the treatment of pharmaceutical waste water. Because of recalcitrant antibiotics the advanced oxidation processes (AOPs) have been preferred.

Ozonation and Fenton's oxidation are the most tested methodologies. Several studies report that this technique is effective in the antibiotics removal. [113;115; 112;125;125a;150]. This method has also been applied to the most prescribed class of antibiotics, obtaining the same conclusions [113;114; 115; 112;116;117].

Besides ozonation, Fenton's oxidation is one of most studied AOPs. This is another process often applied to the group of beta-lactam antibiotics, especially when combined with UV irradiation (photo-Fenton). In these cases, a complete degradation was achieved, accompanied by an increase in the TOC removal (mineralisation degree) and an improvement of the effluent biodegradability [118;118-a]. Therefore, this seems to be a promising method for antibiotic elimination.

Adsorption is another process that has been reported as an alternative to oxidation techniques, though not widely applied to the more prescribed antibiotics. In all studies, this technique was very efficient (removals above 80%). However, it has the disadvantage of producing a new residue. Most of the studies used activated carbon, a high cost adsorbent material. As previously indicated, an AOP followed by biological treatment or by a membrane or even by an adsorption process is the most usual combined process [147;148; 145].

2.4. Chemical Industry

2.4.1. An Owerview of Chemical Industry

The chemical industry creates an immense variety of products which impacts every aspect of our lives. The chemical industry is the essential partner for other industries such as automotive, construction, energy, pharmaceuticals, health & nutrition, communications, agriculture, and consumer goods. The chemical industry helps to develop products for today's resource-conscious environment.

There are five main sectors clustered in the chemicals industry: home and personal care, paints and coatings, fertilizer and pesticides, plastics and rubber and inorganic chemicals. Turkey's main value propositions for all these sub-sectors are the sustainability of growth in customer industries and a much more favorable business environment offered to foreign companies compared to other large investment destinations [151].

The chemical industry involves the use of chemical processes such as chemical reactions and refining methods to produce a wide variety of solid, liquid, and gaseous materials. Most of these products serve to manufacture other items, although a smaller number go directly to consumers. Solvents, pesticides, lye, washing soda, and portland cement provide a few examples of product used by consumers. The industry includes manufacturers of inorganic-and organic-industrial chemicals, ceramic products, petrochemicals, agrochemicals, polymers and rubber (elastomers), oleochemicals (oils, fats, and waxes), explosives, fragrances and flavors. Examples of these products are shown in the Table 6.

Table 6. Organic and inorganic industrial chemicals.

Product Type	Examples
Inorganic industrial	Ammonia, chlorine, sodium hydroxide, sulfuric acid, nitric acid
Organic industrial	Acrylonitrile, phenol, ethylene oxide, urea
Ceramic products	Silica brick, frit
Petrochemicals	Ethylene, propylene, benzene, styrene
Agrochemicals	Fertilizers, insecticides, herbicides
Polymers	Polyethylene, Bakelite, polyester
Elastomers	Polyisoprene, neoprene, polyurethane
Oleochemicals	Lard, soybean oil, stearic acid
Explosives	Nitroglycerin, ammonium nitrate, nitrocellulose
Fragrances and flavors	Benzyl benzoate, coumarin, vanillin
Industrial gases	Nitrogen, oxygen, acetylene, nitrous oxide

Although the pharmaceutical industry is often considered a chemical industry, it has many different characteristics that puts it in a separate category. Other closely related industries include petroleum, glass, paint, ink, sealant, adhesive, and food processing manufacturers. Chemical processes such as chemical reactions operate in chemical plants to form new substances in various types of reaction vessels. The products of these reactions are separated using a variety of techniques including distillation especially fractional distillation, precipitation, crystallization, adsorption, filtration, sublimation, and drying [152].

2.4.2. Water Consumption and Water Quality Used in Chemical Industry

Chemical industry requires huge quantities of water for industrial production process or / and need to be supplied by water with specific characteristics. Water is used for heating, cooling products and equipment, cleaning and product processing, for vacuum creation, steam production, preparation of solvents and reaction media, extractive or absoptive reagents, product rinsing, distillation and transport, as raw material, as a solvent, as part of product. Most of the technological processes take place at high temeratures and pressures, and this means that for such technologies demineralized high pure water is required. Water consumption in chemical and agrochemical industries is determined by production capacity, type of production and technological used, qualification of technique prosennel,water resources at the enterprise [153]. The chemical industry includes producers of commodity chemicals such as organic and inorganic chemicals and industrial gases, and speciality chemicals such as pharmaceutical products and essential oils. It also includes mixing, blending, diluting or converting basic chemicals to make chemical products and preparations, e.g. paints, pesticides, inks, detergents and cosmetics [154]. The chemical and refinement industries in Europe are responsible for 50% of all water used by the manufacturing industry and represents 6% of the total freshwater abstracted [155].

Water quality may impact seriously production units and quality of finished products. In chemical industry, like other industries such as pharmaceutical industry, food industry, pulp and paper, micro-electronics, metal-working industry – water is of an extreme importance and impacts directly production performances, operational costs and the sustainability. Problems linked to the development of microorganisms in process water are not always sanitary issues (for example proliferation of Legionella bacteria) but also Microbial Induced Corrosion (MIC), clogging, bio-fouling are phenomena described and studied. A more efficient microbial water management improves cost-effectiveness, reduces maintenance costs, water consumption and use of chemical disinfectants, reduces wear of equipments, and reduces risks of producing non-conpliant products. In most cases, water is treated by disinfection. Evaluation of efficiency of water treatments and optimization of their use is an important issue for reducing operational cost and improving sustainability of processes [156].

Process Water Quality Requirements for Chemical and Petrochemical Industry is illustrated in Table 7. Due to the huge water consumption cooling water is generally reused in order to save the acquisition cost and water resource. In order to improve the quiality of circulated cooling water, pH control and corrosion inhibiters are applied. The quality level of water for chemical industry must be quite high. Semiconductor processing water, in particular, requires the highest quality of water, so called "ultra-pure water", contains no contaminants and hazardous substances to humans and the environment.

Large technology-driven companies have both responsibilities and opportunities to use water resources wisely. The Dow Chemical Company is an example of a company that actively participates in each of these water-related activities. Dow is a significant user of water. Globally it uses about 900 billion pounds of fresh water per year (~300 million gallons per day). Approximately 90 percent of this water is pre-treated before use, and 70 percent is post-treated and discharged after being used only once.

Table 7. Industrial process water quality requirements for chemical and petrochemical industry [157].

Parameter	Chemical	Petrochemical & Coal
Cu	-	0,05
Fe	0,1	1
Mn	0,1	-
Ca	68	75
Mg	19	30
Cl	500	300
HCO_3	128	-
NO_3	5	-
SO_4	100	-
SiO_2	50	-
Hardness	250	350
Alkalinity	125	-
TDS	1000	1000
TSS	5	10
Color	20	-
pH	6,2-8,3	6-9
CCE	-	-

* All values in mg/L except color and pH.

2.4.3. Waste Resources and Waste water Characterization of Chemical Industry

A wide variety of products are made in the chemical and pharmaceutical manufacturing industries, typically requiring large volumes of chemicals, materials, and substances that are used throughout process operations. Waste streams generated in these industries can be heavily laden with contaminants, toxins, nutrients, and organic content, presenting unique challenges in terms of treatment, especially as regulations become more stringent [158].

Contaminants from chemical industry waste water may include organic and inorganic substances. Organic water pollutants include:

- Detergents
- Disinfection by-products found in chemically disinfected drinking water, such as chloroform
- Insecticides and herbicides, a huge range of organohalides and other chemical compounds
- Petroleum hydrocarbons, including fuels (gasoline, diesel fuel, jet fuels, and fuel oil) and lubricants (motor oil), and fuel combustion byproducts, from storm water runoff [159]
- Volatile organic compounds, such as industrial solvents, from improper storage.
- Chlorinated solvents, which are dense non-aqueous phase liquids, may fall to the bottom of reservoirs, since they don't mix well with water and are denser.
  - Polychlorinated biphenyl (PCBs)
  - Trichloroethylene
- Perchlorate
- Various chemical compounds found in personal hygiene and cosmetic products
- Drug pollution involving pharmaceutical drugs and their metabolites

Inorganic water pollutants include:

- Acidity caused by industrial discharges (especially sulfur dioxide from power plants)
- Ammonia from food processing waste
- Chemical waste as industrial by-products
- Fertilizers containing nutrients--nitrates and phosphates—which are found in storm water runoff from agriculture, as well as commercial and residential use [159] heavy metals from motor vehicles (via urban storm water runoff) [159;160] and acid mine drainage
- Silt (sediment) in runoff from construction sites, logging, slash and burn practices or land clearing sites.

While most chemicals are toxic, pathogens can produce water-borne diseases for humans or animals. Physicochemical changes such as pH change, electrical conductivity, temperature and eutrophication may occur in water. Eutrophication; is the increase in the concentration of a chemical nutrients to enhance the primary productivity of the ecosystem. Subsequent negative environmental effects such as anoxia (oxygen depletion) and severe reductions in water quality may occur depending on the degree of eutrophication affecting fish and other animal populations [161].

High levels of pathogens can be detected due to in situ sanitation systems (septic tanks, pit toilets) or inadequately treated wastewater discharges (EPA, 2009). This can be caused by a sewage plant designed with less than secondary treatment (more typical in less-developed countries). Sewer overflows are the problems of waste water collection systems (pipes, pumps, valves) of developed countries and old cities with aging infrastructure. In some cities, rain water is combined with sewage wastewater and in case of excessive rainfall, wastewater overflow occurs [162].

Especially in groundwater reservoirs, most chemicals are subject to reactive degradation or chemical change over a long period of time. Chlorinated hydrocarbons such as trichlorethylene (used in industrial metal degreasing and electronic production) and tetrachlorethylene used in the dry cleaning industry are among the most notable among such chemicals. Both groups of chemicals are carcinogenic and may undergo partial decomposition reactions into new hazardous chemicals (including dichloroethylene and vinyl chloride) [163].

Pesticides are used in farming to control weeds, insects and fungi. Run-offs of these pesticides can cause water pollution and poison aquatic life. Subsequently, birds, humans and other animals may be poisoned if they eat infected fish. Petroleum is another form of chemical pollutant that usually contaminates water through oil spills when a ship ruptures. Oil spills usually have only a localised affect on wildlife but can spread for miles. The oil can cause the death of many fish and stick to the feathers of seabirds causing them to lose the ability to fly [164].

2.4.4. Applications about Wastewater Treatment and Reuse of Chemical Industry

Waste water treatment in the chemical and petrochemical industry waste water; is difficult due to the complex chemical substance contained [165;166]. Waste water include high concentrations of COD, BOD_5, Toxic Substances, TSS and Color. The content of toxic waste water adversely affect the biological treatability. Therefore, for the treatment of waste water, in addition to the conventional treatment processes (anaerobic, aerobic) it is referred to the the pre-treatment and / or to the advanced treatment methods. Which treatment operations will be applied depends on the characterization, concentration, flow rate and discharge limits of the waste, properties, that can be varied according to each unit, such as reuse ability of the water and the presence of joint public treatment system.

The increasingly stringent regulations have enforced the application of advanced technologies for complying the discharge limits and allowing for water recycling. Among those technologies, Fenton oxidation has been gaining interest in the last two decades [167]. Fenton process is applied in the treatment of the waste waters from pesticides production in southern Poland. Most of the pesticides were completely degraded using a H_2O_2 dose of 2.5 g/L, corresponding to five times the stoichiometric amount on a COD basis. The best results were achieved for the organophosphorous pesticides, which degraded at 97–100%. The removal efficiency for organochlorinated was also fairly high (>90%), and the toxicity of the raw waste water towards the bioluminescent bacteria *Vibrio fischeri* was reduced [168].

Fenton process is studied for treating four types of industrial waste waters collected from two chemical factories in southern Poland. The waste waters from the production of maleic acid, maleic anhydride, 2-ethylhexyl alcohol, urea-formaldehyde adhesives and pesticides. Although high removal efficiencies were obtained in terms of COD, these were not always accompanied by a reduction of ecotoxicity (*Vibrio fischeri*) to sufficiently low levels unless frankly high H_2O_2 amounts and reaction times were used [169].

Waste water from a detergent manufacturing process was treated by coagulation–flocculation and filtration and in order to have high purification result fenton oxidation and neutralisation process, followed by flocculation and sedimentation was implemented [167].

Fenton process was applied for the waste water from petroleum extraction, refining and chemical processing. Testing the efficiency of the system one sample of waste water was taken from oil production process and second one was from a petrochemical plants. Contaminants in waste water were m-cresol, 2- chlorophenol, methyl-tertbutyl-ether (MTBE) and volatile aromatics (benzene, toluene, ethylbenzene and xylene) [168].

The efficiency of Fenton and photo-Fenton processes was evaluated or the treatment of waste waters from the leather industry to study the reduction of COD. COD degradation process was approximately 82% at initial fast step treatment, after that COD removal reached 94% followed by a slow step [170].

Waste water including pesticides is not compatible with classical biological treatment, due to their toxicity to the microorganisms involved in those processes [171]. Therefore other treatment methods are necessary. Advanced Oxidation Processes (AOPs) are among the most widely used technologies for industrial effluent treatment of water polluted by organic compounds characterized by their high chemical stability and low biodegradability [172]. An attractive option is a combination of a pretreatment with AOP, which makes the recalcitrant pollutants biodegradable intermediates that can then be degraded in a biological process [173]. Furthermore, the higher the pollutant concentration, the longer the AOP treatment time, and therefore, a combined AOP and biological oxidation system is even more suitable [172].

The effectiveness of combined treatment processes, coagulation/flocculation (C/F), electrooxidation (EO) and membrane (M) processes for tackling organic load in a segregated chemical industry waste water is reported to study the treatment of high strength chemical industry waste water [174].

The waste water is characterized by strong color, high concentrations of salinity, TKN and COD. Three different combined process; i) UF–RO (CP-I); ii) C/F–EO–UF–RO (CP-II) and iii) C/F–EO1–EO2–UF–RO (CP-III) were investigated. The overall COD and TDS removal efficiencies in that order were: CP-I, 73% and 82%; CP-II, 84% and 85%, and CP-III, 93% and 87%. The percent COD and TDS removals at each stage of the combined process were evaluated and the impact of EO process on the overall performance of the process schemes was discussed. It emerged that intermediate level EO process considerably reduces organic load in the effluent, while large part of TDS removal can be attributed to final RO treatment. Thus, the combined treatment processes appear to be promising for obtaining greater efficiency of organic and salinity load removals [174].

The performance of a carbon bed based TDR (Three-Dimensional Electrode Reactor) in terms of COD removal from recalcitrant chemical industry waste water was assessed. The pH and temperature changes in the TDR during electrolysis were correlated with COD removal efficiency. The carbon weight loss and particle size reduction due to erosion of carbon particles during electrolysis was also examined. Two cases of experiments were performed; 'case I' employed a high surface area Indcarb-60 GAC, whereas a low surface area carbon (GAC-10) was used for 'case II'. The other experimental variables are, initial COD concentration, HRT (Hydraulic Retention Time) and the duration of electrolysis. The experimental results showed that TDR could remove COD efficiently (49±7%). The apparent Faradic efficiency and specific electrical energy consumption were estimated to be 3.42% and 6.59 kW h/ kg COD for case I and 0.78% and 28.65 kW h/kg COD for case II [175].

High strength chemical industry waste water requires high degree of treatment before being discharged into the water bodies. The conventional treatment incorporating chemical and biological treatments alone is not adequate. More recently, advanced oxidation processes such as electrochemical oxidation (EO) treatment are being increasingly viewed as capable of providing necessary treatment [176;177;178;150].

The volatilization and biodegradation removal rates of VOCs (Volatile Organic Compounds) in a MBR (Membrane Bioreactor), and impacts of biomass and soluble organics characteristics on membrane fouling are investigated. A laboratoryscale MBR was operated to treat synthetic waste water containing acetaldehyde, butyraldehyde and vinyl acetate. In Phase I, the organic loading rates were varied from 1.06 to 2.98 kg COD m^3/ d. In Phase II, the DO (Dissolved Oxygen) concentrations were varied from 0.2 to 5.4 mg/L. Total VOC removal rates were greater than 99.8 percent at all organic loading rates. Volatilization removal rates were achieved as low as 0.78 percent for acetaldehdyde, 1.27 percent for butyraldehyde, and 0.59 percent for vinyl acetate. Biomass stabilization status had a significant effect on volatilization. Under unstable conditions, 85 percent of vinyl acetate was volatilized. Regardless of the DO concentrations, total and biodegradation removal rates were greater than 99.7 and 95.9 percent. When the DO concentrations were increased, the volatilization rate increased [179].

3. Conclusion

The need to conserve water is becoming a common concern throughout the world. Whether this is due to the cost of water, availahility of water, or environmental concerns, water conservation is becoming a major focal point, both in the public and private sector. In those areas where renewable water resources are limited, and in regions where there are significant environmental concerns and costs associated with waste water discharges, reuse of waste water may be a valid option to conserve valuable water resources and to reduce overall water-treatment costs.

Many industrial facilities around the world are dealing with water supply issues and are looking for alternate means of finding inexpensive water supplies. While reuse of waste water generated in these facilities is an admirable goal, there are potential technology and cost challenges associated with reusing waste water generated within these facilities. When considering the practicality and economics of reusing waste water, one must consider the following questions:

- Where is water used in the facility and what is the quality of water required at each point of use?
- Where is waste water generated in a facility, from what process areas; and what is the quality of each individual waste stream?
- What is the water reuse goal? Always select a reasonable goal. The higher the percentage of waste water reused, the higher the treatment and recovery costs.
- Are there specific waste streams within the facility that are potentially easier (less costly) to reuse?
- Can waste water be reused in areas that do not require a high level of treatment (like fire water or utility water)?
- Are there other sources of waste water, outside the facility, that can potentially be reused, at a lower cost?
- Can a pilot or bench-scale treatability study be undertaken to confirm the waste water can be treated for reuse?
- Does all the waste water need to be reused?
- How will the water residuals, or solids, be disposed of, and what are the associated costs?

While reusing waste water can be an economical alternative to internal or external fresh-water supplies, there are many factors that must be addressed that can impact the reliability of the reuse system and the associated cost of waste water reuse. Doing a proper evaluation of these factors can insure a well-operating water reuse system, as well as a continuous and economic stream of high quality water that is available for the facility.

In this study, detailed analysis were carried out on miscallenous industrial sectors such as metal, pulp and paper, pharmaceutical, chemicals industries, in terms of water consumption, process water quality, waste water sources, treatment, reuse of waste water and focused on re-use alternatives. As a result, each plant has to be designed and evaluated by considering its own production dynamics. In addition, similar studies should be carried out for different industrial effluents in order to select the most economical treatment & reuse option.

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