REVIEW OF LITERATURE
CHAPTER 2
REVIEW OF LITERATURE

This review is an effort to consider the significant points of current knowledge including substantive findings, as well as theoretical and methodological contributions in terms of wastewater generated from pulp and paper industry for its reuse in agriculture.

2.1. Industrial Pollution

The term “water pollution” generally refers to human-induced changes to water quality or in other words, change in the chemical, physical, biological, and radiological quality of water that is injurious to its uses (Partha, 2009). Thus, the discharge of toxic chemicals from industries or the release of human or livestock waste is a serious environmental issue.

The contamination of ground water of water bodies like rivers, lakes, wetlands, estuaries and oceans can threaten the health of humans and aquatic life. Sources of water pollution may be divided into two categories (Clean, 2014). (i) Point-source pollution, in which contaminants are discharged from a discrete location. Sewage outfalls and oil spills are examples of point-source pollution. (ii) Non-point-source or diffuse pollution, referring to all of the other discharges that deliver contaminants to water bodies. Acid rain and unconfined runoff from agricultural or urban areas falls under this category. The principal contaminants of water include toxic chemicals, nutrients, biodegradable organics, and bacterial and
viral pathogens. Water pollution can affect human health when pollutants enter the body either via skin exposure or through the direct consumption of contaminated drinking water and contaminated food (Bina et al., 2013). Prime pollutants, including DDT and polychlorinated biphenyls (PCBs), persist in the natural environment and bioaccumulation occurs in the tissues of aquatic organisms. These prolonged and persistent organic pollutants are transferred up the food chain and they can reach levels of concern in fish species that are eaten by humans (Bina et al., 2013). Moreover, bacterial and viral pathogens can pose a public health risk for those who drink contaminated water or eat raw shellfish from polluted water bodies.

Contaminants have a significant impact on aquatic ecosystems. Enrichment of water bodies with nutrients (principally nitrogen and phosphorus) can result in the growth of algae and other aquatic plants that shade or clog streams (Merz, 2013). If wastewater containing biodegradable organic matter is discharged into a stream with inadequate dissolved oxygen, the water downstream of the point of discharge will become anaerobic and will be turbid and dark (Paul, 2011). Settleable solids will be deposited on the streambed, and anaerobic decomposition will occur. Over the reach of stream where the dissolved-oxygen concentration is zero, a zone of putrefaction will occur with the production of hydrogen sulfide (H₂S), ammonia (NH₃), and other odorous gases. Because many fish species require a minimum of 4–5 mg of dissolved oxygen per liter of water, they will be unable to survive in this portion of the stream. Direct exposures to toxic chemicals are also a health concern for individual aquatic plants and animals (Bina et al., 2013). Chemicals such as pesticides are frequently leached off to lakes and rivers via runoff, and they can have harmful effects on aquatic life. Toxic chemicals have been shown to reduce the growth, survival,
reproductive output, and disease resistance of exposed organisms. These effects can have important consequences for the viability of aquatic populations and communities.

Wastewater discharges are most commonly controlled through effluent standards and discharge permits. Under this system, discharge permits are issued with limits on the quantity and quality of effluents (Mugg, 1990 and Bina et al., 2013). Water quality standards are sets of qualitative and quantitative criteria designed to maintain or enhance the quality of receiving waters. Criteria can be developed and implemented to protect aquatic life against acute and chronic effects and to safeguard humans against deleterious health effects, including cancer.

Water pollution has many sources. The most polluting of them are the city sewage and industrial waste discharged into the rivers. Industrial waste is defined as waste generated by manufacturing or industrial processes (Hussain and Mukhtar, 2014). The types of industrial waste generated include cafeteria garbage, dirt and gravel, masonry and concrete, scrap metals, trash, oil, solvents, chemicals, weed grass and trees, wood and scrap lumber, and similar wastes. Industrial solid waste which may be solid, liquid or gases held in containers is divided into hazardous and non-hazardous waste. Hazardous waste may result from manufacturing or other industrial processes. Certain commercial products such as cleaning fluids, paints or pesticides discarded by commercial establishments or individuals can also be defined as hazardous waste (Watson, 2000). Non-hazardous industrial wastes are those that do not meet the EPA's definition of hazardous waste - and are not municipal waste. Industrial waste has been a problem since the industrial
revolution. Industrial waste may be toxic, ignitable, corrosive or reactive. If improperly managed, this waste can pose dangerous health and environmental consequences.

Water pollution is concentrated within a few subsectors, mainly in the form of toxic wastes and organic pollutants. Out of this a large portion can be traced to the processing of industrial chemicals and to the food products industry. Most major industries have treatment facilities for industrial effluents but this is not the case with small-scale industries, which cannot afford enormous investments in pollution control equipment as their profit margin is very slender. The effects of water pollution are not only devastating to people but also to animals, fish, and birds. Polluted water is unsuitable for drinking, recreation, agriculture, and industry. It diminishes the aesthetic quality of lakes and rivers. More seriously, contaminated water destroys aquatic life and reduces its reproductive ability. Eventually, it is a hazard to human health. Nobody can escape the effects of water pollution.

2.2. Pulp and Paper Industry

Paper industry in India is the 15th largest industry in the world. It provides employment to nearly 1.5 million people and contributes Rs 25 billion to the government's kitty. The government regards the paper industry as one of the 35 high priority industries of the country (Tripathi, 2014). Paper industry is primarily dependent upon forest-based raw materials. The first paper mill in India was set up at Sreerampur, West Bengal, in the year 1812. It was based on
grasses and jute as raw material (Chirayil, 2008). Large scale mechanized technology of papermaking was introduced in India in early 1905. Since then the raw material for the paper industry underwent a number of changes and over a period of time, besides wood and bamboo, other non-conventional raw materials have been developed for use in the papermaking. The Indian pulp and paper industry at present is very well developed and established. Now, the paper industry is categorized as forest-based, agro-based and others (waste paper, secondary fibre, bast fibers and market pulp). In 1951, there were 17 paper mills, and today there are about 515 units engaged in the manufacture of paper and paperboards and newsprint in India (CII, 2009). The pulp and paper industries in India have been categorized into large-scale and small-scale. Those paper industries, which have capacity above 24,000 tonnes per annum, are designated as large-scale paper industries. India is self-sufficient in manufacture of most varieties of paper and paperboards. Import is confined only to certain specialty papers. To meet part of its raw material needs the industry has to rely on imported wood pulp and waste paper.

Indian paper industry has been de-licensed under the Industries (Development and Regulation) Act, 1951 with effect from 17th July, 1997. The interested entrepreneurs are now required to file an Industrial Entrepreneurs' Memorandum (IEM) with the Secretariat for Industrial Assistance (SIA) for setting up a new paper unit or substantial expansion of the existing unit in permissible locations. Foreign Direct
Investment (FDI) up to 100% is allowed on automatic route on all activities except those requiring industrial licenses where prior governmental approval is required. Growth of paper industry in India has been constrained due to high cost of production caused by inadequate availability and high cost of raw materials, power cost and concentration of mills in one particular area. Government has taken several policy measures to remove the bottlenecks of availability of raw materials and infrastructure development. For example, to overcome short supply of raw materials, duty on pulp and waste paper and wood logs/chips has been reduced.

Based on raw material utilized the paper units can be classified in to three broad categories

- Wood based
- Agro based
- Waste paper based

The modern manufacture of paper evolved from an ancient art first developed in China, ca. 105 A.D. In principle, paper is made by: 1) pulping, to separate and clean the fibers; 2) beating and refining the fibers; 3) diluting. To form a thin fiber slurry, suspended in solution; 4) forming a web of fibers on a thin screen; 5) pressing the web to increase the density of the material; 6) drying to remove the remaining moisture; and 7) finishing, to provide a suitable surface for the intended end use.
Pulp and paper are made from cellulosic fibers (i.e., fibers from trees) and other plant materials, although some synthetic materials may be used to impart special qualities to the finished product. Most paper is made from wood fibers, but rags, flax, cotton linters, and bagasse (sugar cane residues) are also used in some papers. Used paper is also recycled, and after purifying and sometimes de-inking, it is often blended with virgin fibers and reformed again into paper. Other products made from wood pulp (cellulose) include diapers, rayon, cellulose acetate, and cellulose esters, which are used for cloth, packaging films, and explosives.

Wood is composed of: 1) cellulose, 2) lignin, 3) hemicellulose, and 4) extractives (e.g., resins, fats, pectins, etc.). Cellulose, the fibers of primary interest in papermaking, comprises about 50 percent of wood by oven dry weight. Lignin, which cements the wood fibers together, is a complex organic chemical the structure and properties of which are not fully understood. It is largely burned for the generation of energy used in pulp and paper mills. As the chemistry of lignin becomes better understood, what is now mostly a waste product used for fuel (some is converted to chemical products) could become a valuable feed stock for new chemical products.

The pulping process is aimed at removing as much lignin as possible without sacrificing fiber strength, thereby freeing the fibers and removing impurities that cause discoloration and possible future disintegration of the paper. Hemicellulose is similar to cellulose in composition and function. It plays an important role in fiber-to-
fiber bonding in papermaking. Several extractives (e.g., oleoresins and waxes) are contained in wood but do not contribute to its strength properties; these too are removed during the pulping process. The fiber from nearly any plant or tree can be used for paper. However, the strength and quality of fiber, and other factors that can complicate the pulping process, varies among tree species. In general, the softwoods (e.g., pines, firs, and spruces) yield long and strong fibers that impart strength to paper and are used for boxes and packaging. Hardwoods, on the other hand, generally have shorter fibers and therefore produce a weaker paper, but one that is smoother, more opaque, and better suited for printing. Both softwoods and hardwoods are used for papermaking and are sometimes mixed to provide both strength and printability to the finished product.

**Status of Paper Industry in Tamil Nadu**

Tamil Nadu is one of the well developed states in terms of industrial development. It has enjoyed a significant position in India’s geopolitical space and economic progress. Logistical advantages due to presence of three major seaports, an international airport and several domestic airports, quality of human resources, a peaceful industrial climate and a positive work culture have strengthened Tamil Nadu’s standing in the industrial world. The State’s business-friendly policies and proactive initiatives have played a key role in this resurgence.
Tamil Nadu continues to be one of the forerunners in the production of paper and paper products. There are 28 paper mills in operation in Tamil Nadu. The total paper production was 3.7 lakh tons in 2005 - 06, which accounts for 17.30 per cent share of the national production, next only to Andhra Pradesh. As the country’s forest cover is much below the desired level, the Government of Tamil Nadu established Tamil nadu news print limited in 1979 to manufacture newsprint and paper using bagasse (sugarcane waste) as the primary raw material. This is the largest paper mill in India with an installed capacity of 2,30,000 TPA (tons per annum). In 2005-2006, the company produced 230079 MTs of newsprint and printing and writing paper. Tamil Nadu is the largest producer of bagasse-based paper in the world especially at ‘Tamil nadu news print limited’

2.3. Manufacturing Process (Pulp and Paper Industry)

Manufacturing process in pulp and paper industry is divided into five steps (i) Wood preparation, (ii) Cooking, (iii) Pulping (iv) Paper making

(i) Hard wood logs are debarked by wet or dry process depending upon the size of the logs handled. Small diametric logs are debarked by dry process by friction. In wet process, debarking of larger logs of wood is done by drum or pocket barkers. Hydraulic barking uses high-pressure water jets to separate bark and log. Energy requirement for friction barking is lower than that for hydraulic barking. In India,
most of the mills are not doing debarking as they receive either debarked wood or use them with bark due to difficulty in debarking of some hardwoods. The logs are chipped to size suitable for pulping using chippers. Disc and drum chippers are used for chipping. The oversized chips are rechipped, as under sized chips are rejected.

(ii) The wood chips are heated in a solution of NaOH and Na$_2$S in a pressure cooker, during which time a lot of the lignin (the reinforcing substance that make tree cells wood hard and 'woody' rather than soft like those of other plants) is removed from the wood. The pressure is then released suddenly, causing the chips to fly apart into fibres.

(iii) Predominantly, pulp making is done either by mechanical or chemical means. In mechanical process, the wood is reduced to small particles by rubbing against huge grindstones revolving at high speeds. Ground wood mechanical process is the most commonly used and most of the Newsprint paper production is undertaken through ground wood pulp process. In India, chemi mechanical pulping (CMP) is done by only one newsprint paper mill. In CMP, the wood chips are subjected to a mild chemical treatment prior to mechanical separation using a refiner. In the chemical process, the cellulose fibers of the wood are separated from the non-cellulose components by chemical action.

Three primary chemical processes are in use, viz., Kraft or sulphate (alkaline), Sulphite (acidic) and Neutral Sulphite Semi Chemical (NSSC). As mentioned earlier,
all large Pulp and Paper mills in India use the Kraft sulphate chemical process for pulping. In this process, the raw material (almost any kind of wood - soft or hard) is cut and chipped to produce chips of 0.5-1" size. These chips are fed into digesters, reacted with white liquor (80:20 NaOH and NaS) and steamed for about two to three hours at high temperature and pressure (162 - 168 C and 7-8 kg / cm²). Digesters may be batch or continuous type, the latter offering advantages such as increased throughput, reduced labour and better energy utilization. Continuous digesters are also very useful in agro fiber pulping. The pulp is then washed to make the pulp free from soluble impurities and removal of black liquor through usual 3 or 4 stages of counter current washing using rotary drum filters. The washed pulp is sent for bleaching to increase the brightness of the pulp and the dilute black liquor is sent to evaporators. The treated pulp then goes for stock preparation. The black liquor after concentration is fired in recovery boilers. The residue "green liquor" is treated with lime to get white liquor for reuse.

In Soda process, which is mostly used for pulping of agricultural residues, Sodium Hydroxide (NaOH) is the main cooking chemical. Other cooking parameters are almost same as Kraft process.

(iv) Pulp when it comes from digester, contains residual coloring matter. This unbleached pulp may be used for making heavy wrapping paper or bags. However, paper to be used for printing, writing or paper which is to be dyed, must first be
bleached. The main object in bleaching is to remove residual lignin from the wood pulp fibers as well as to destroy or remove remaining coloring matter. Now days, various bleaching agents are used to bleach the pulp like chlorine, chlorine dioxide, hydrogen peroxide, oxygen and calcium hypo chlorite.

(v) The fibres are mechanically treated to make them bond better to each other (strengthening the paper), chemicals added to provide special properties such as colour or water resistance, and then the water is squeezed out and the pulp is rolled smooth and dried. The bleached or unbleached pulp may be further beaten and refined to cut the fibers and roughen the surface of the fibers (fibrillate) to improve formation and bonding of the fibers as they enter the paper machine. Before entering the paper machine, water is added to the pulp slurry to make a thin mixture normally containing less than 1 percent fiber. The dilute slurry is then cleaned in cyclone cleaners and screened in centrifugal screens before being fed into the ‘‘wet end of the paper-forming machine. In the paper making process, the dilute stock passes through a headbox that distributes the fiber slurry uniformly over the width of the paper sheet to be formed. The “web” of fiber that will make the new paper sheet is formed on a continuously moving bronze or polymer screen or between two such wire screens. Water drains from the slurry through the mesh of the screen, the wet paper web is consolidated and the paper sheet gains some strength through fiber bonding. The wet sheet of paper is continuously lifted from the screen (couched) and transferred to a
woven felt belt where additional water is squeezed from the paper sheet by pressure rollers; the remaining water is removed on steam-heated cylinders. When the paper is dry it may be treated with stabilizing materials and surface finishes improving durability or printability.

2.3. Problems Associated With Pulp and Paper Industry

There is great concern regarding the pollution generated at paper and pulp mills. While this industry discharges gaseous, liquid, and solid wastes, pollution of the aquatic ecosystem is the major problem as large volumes of wastewater is generated while producing paper (Bhattacharyya and Sharma, 1997 and Selvam et al., 2002). The characteristics of wastewater generated from various processes of the pulp and paper industry depend upon the type of process, wood material, process technology, recirculation of the wastewater for recovery of chemicals, and the amount of water to be used in each particular process. Parameters to be controlled before wastewater discharges into the environment include chemical and biological oxygen demand (COD and BOD), absorbable organic halides (AOX), and color.

**COD and BOD:** Pulp and paper mill wastewater discharges into freshwater, estuarine, and marine ecosystems. This in turn can alter aquatic habitats and adversely impact human health (Ghoreishi and Haghighi, 2007 and Jha et al., 2002). These wastewaters are loaded with organic matter that without adequate treatment can have high chemical and biological oxygen demand (COD and BOD) in the receiving waters
Impact of Treated Industrial Effluent on Crop Plants -
Jacob Varughese V.

(Ali and Sreekrishnan, 2001; Bhattacharyya and Sharma, 1997; Pellinen et al., 1988 and Vidal, 1999). Some components in the wastewater contributing to COD and BOD loads include lignin and its degradation product, fatty acids, resin acids, tannins, and sulfur containing compounds (Jantsch et al., 2002; Lacorte et al., 2003 and Sierra-Alvarez et al., 1994). Usually, most of the chemical compounds found in these effluents are naturally present in the environment. They tend to be slightly or non-toxic to the surrounding ecosystem. While several alternatives exist for controlling COD, BOD, and AOX, decolorization of wastewaters is usually overlooked. Color in water inhibits the process of photosynthesis as particles in solution will scatter and absorb light, reducing the photosynthetically available radiation (Kirk, 1994). In addition, brown color wastewaters increase water temperature leading to decreased levels of dissolved oxygen (Kringstad and Lindstroem 1984; Pellinen et al., 1988 and Selvam et al., 2002). As a consequence, the colored substances in aquatic systems have been associated with changes in primary productivity (Del and Peters 1994; Henebry and Cairns 1984 and Ilmavirta and Huttunen 1989), phytoplankton species composition (Beauchamp and Kerekes, 1989), and protozoan colonization rates. In addition, secondary production (Hessen, 1985), macro-invertebrate behavior (Juarez et al., 1986) and macro-invertebrate community structure (Kullberg 1992) can be affected.
2.5. Waste Release to Environment

No manufacturing process converts all of its inputs into final products. There is always some waste. The waste from pulp and paper manufacturing includes releases to air, land and water, as well as waste heat. In 1991, the pulp and paper industry discharged 2.25 billion tons of waste to the environment. This waste included about 2.5 million tons of air emissions from energy related and process sources and about 13.5 million tons of solid waste, leaving 2.23 billion tons of wastewater. Thus over 99% of the waste, measured by weight, was wastewater. A number of measures provide information about the consumption of natural resources and releases to the environment.

Adsorbable organic halogens (AOX) measures the quantity of chlorinated organic compounds in mill effluent and is an indirect indicator of the quantity of elemental chlorine present in the bleach plant and the amount of lignin in the unbleached pulp before it enters the bleach plant. The unit of measure is kilograms per metric ton of air-dried pulp.

- Biochemical oxygen demand (BOD) measures the amount of oxygen that microorganisms consume to degrade the organic material in the effluent. Discharging effluent with high levels of BOD can result in the reduction of dissolved oxygen in mills’ receiving waters, which may adversely affect fish and other organisms. The unit of measure is usually kilograms per metric ton of final product.
• Bleach plant effluent flow measures the quantity of bleach plant filtrates that the mill cannot recirculate to the chemical recovery system. This indicator provides direct information about a mill’s position on the minimum-impact mill technology pathway. For example, mills that recirculate the filtrates from the first bleaching and extraction stages have about 70-90% less bleach plant effluent than do mills with traditional bleaching processes. The unit of measure is gallons per ton of air-dried pulp.

• Chemical oxygen demand (COD) measures the amount of oxidizable organic matter in the mills’ effluent. It provides a measure of the performance of the spill prevention and control programs as well as the quantity of organic waste discharged from the bleach plant. The unit of measure is kilograms per metric ton of air-dried pulp.

• Color measures the amount of light that can penetrate the effluent. In certain situations, color can adversely affect the growth of algae and plants in mills’ receiving waters. It also provides information about the quantity of degraded lignin by-products in the effluent because these substances tend to be highly colored. Along with odor, the dark effluent is one of the obvious attributes of kraft pulp mills. The unit of measure is either color units per metric ton of final product or kilograms per metric ton of final product.

• Dioxins are a group of persistent, toxic substances, including furans that are produced in trace amounts when unbleached pulp is exposed to elemental chlorine.
The unit of measure for bleach plant filtrates is picograms of dioxin per liter of water (parts per quadrillion).

- Effluent flow measures the amount of water that is treated and discharged to a mill’s receiving waters. It is an indirect measure of fresh water consumption. The unit of measure is gallons per ton of final product.

- Total suspended solids (TSS) measure the amount of bark, wood fiber, dirt, grit and other debris that may be present in mill effluent. TSS can cause a range of effects from increasing the water turbidity to physically covering and smothering stationery or immobile bottom-dwelling plants and animals in freshwater, estuarine or marine ecosystems. The unit of measure is kilograms per air-dried metric ton of final product.

Waterborne wastes are often a focus of environmental concern for a number of reasons. Water based discharges have the greatest potential to introduce contaminants directly into the environment and the food chain. Water use also correlates with energy use, since it takes energy to pump, heat, evaporate and treat process water. The effluent from pulp mills contains a complex mixture of organic compounds. Effluent from mechanical pulp mills generally contains less organic waste than that of chemical pulp mills because most of the organic material stays with the pulp. Recovered paper processing systems can contain significant quantities of organic waste in their effluent. This material consists primarily of starches and other
compounds that are contained in the recovered paper that the mill uses. Kraft pulp mill effluent contains a mixture of degraded lignin compounds and wood extractives. Bleached kraft pulp mill effluent may also contain chlorinated organic compounds, depending on the amount of chlorine compounds used in the bleaching process.

2.6. Toxic Effect of Pulp and Paper Effluent

Toxicity of PAP industry effluent Toxic effects of the PAP industry effluent on the aquatic life of the receiving water bodies is very well documented. Also there are reports on the accumulation of some of the compounds from effluent in sediments and fishes. Salkinoja-Salonen and Sundman (1980) reported that some of the compounds in the PAP effluent are resistant to biodegradation Renberg et al., (1980) showed that these compounds can bioaccumulate in the aquatic food chain. Leuenberger et al., (1985) in their study on persistent chemicals in pulp mill effluents reported detection of tetrachlorophenol (TeCP) and pentachlorophenol (PCP) in the river Aare at Brugg, 70 km downstream of the pulp mill. According to Canadian Environmental Protection Act (Environment Canada and Health and Welfare Canada, 1991) PAP industry effluent has been defined as toxic. Berry et al., (1989) attributed acute and chronic toxicity of the effluent to the presence of chlorophenols especially polychlorinated phenols. They also showed that these compounds bioaccumulate in fish and are toxic and persistent. Liss and Allen (1992) reported that many of the chlorinated compounds present in
the effluent are toxic, persistent and may bioaccumulate. **Palm and Lammi, (1995)** reported that chlorinated guaiacols and catechols from the pulp mill effluents get preserved for a long time in the sediments. **Kahkonen et al., (1997)** showed that EOX (Extractable Organic Halides) accumulated in Lake Saimaa, Finland which received effluent PAP mill. The half life of EOX in the sediment was estimated to be 60-80 years by the authors. In another study on Lake Saimaa and a small pristine forest lake, **Suominen et al., (1997)** showed that the EOX concentration in the pristine lake ranged from 40-130 μg Cl (g d. w.)-1 whereas in Lake Saimaa, receiving effluent, it ranged from 770-4700 μg Cl (g d. w.)-1. The authors reported that the C:Cl (w/w) ratio ranged from 2000 to 5100 for pristine lake and 42 to 230 for Lake Saimaa. **Suominen, (1999)** reported that EOX in the sediment of Lake Vatavalkama had disturbed the ecological system of the sediment. In the layer with the highest organic halogen pollution (4-6 cm depth), ATP had virtually disappeared. The author also reported that the sediment was toxic to *Vibrio fischeri* and genotoxic to *E. coli* PQ37 and the population of *Aulacoseria subartica*, a diatom, decreased from 18-19% to 2% in the sediment.

**2.7. Wastewater Treatment**

*Treatment methodologies for pulp and paper industry effluent*

Due to severe toxic effects of the pulp and paper industry effluent it is necessary to treat the effluent, especially for the degradation of AOX, before it is discharged.
Different methods are available for the treatment of PAP industry effluent which includes physical, chemical, electrochemical and biological methods. 

Pokhrel and Viraraghavan (2004) and Savant et al., (2006) has extensively reviewed various treatment methodologies available for pulp and paper industry effluent.

2.7.1. Physical methods

Fly ash is known as an adsorbing medium and has shown removal of organochlorines and color using fly ash. Delayed petroleum coke is another material used for the removal of organochlorines by adsorption. Shawwa et al., (2001) reported removal of AOX at a concentration higher than 15000 mg/l by delayed petroleum coke. Use of photocatalytic treatment for the removal of organochlorines was described by Torrades et al., (2001). Ultrafiltration, nano-filtration and reverse osmosis are some of the other physical methods reported for the removal of organochlorines from effluent (Yao et al., 1994 and Siess et al., 2001).

2.7.2. Chemical methods

Milstein et al., (1988) in their study used a mixture of polyethylene and modified starches for the removal of AOX, COD and color with an efficiency of 75%, 59% and 80%, respectively. By neutralizing bleach plant effluent with lime mud followed by addition of alkaline sulfide process liquor, Milosevich and Hill (1992) could achieve
60-70% AOX removal. Ganjidoust et al., (1996) reported 90% and 70% reduction of color and total organic chloride (TOC) using chitosan as a coagulant.

2.7.3. Electrochemical methods

Khan, 2012 reported a novel method for AOX removal which they termed as supercritical water oxidation. In this method, the authors mixed oxidant with wastewater and heated the wastewater to a temperature above the critical point of water at a pressure of 250 kg/cm$^2$. The authors reported 100% oxidation of organic waste and tested the technology on mixtures of kraft bleaching effluents, pulp mill sludges and achieved 99.99% removal of organic waste.

2.7.4. Biological Methods

Bioremediation can be defined as any process that uses microorganisms or their enzymes to return the environment altered by contaminant to its original condition. Bioremediation may be employed in order to attack specific contaminants, such as chlorinated pesticides that degrade by bacteria, or more general approach may be taken such as oil spills that are broken down using multiple techniques including the addition of fertilizer to facilitate the decomposition of crude oil by bacteria. Not all contaminants are readily treated through the use of bioremediation; heavy metals such as cadmium and lead are not readily absorbed or captured by organisms (Vidali, 2001). The integration of metals such as mercury into food chain may make things worse as organisms bioaccumulate these metals. However there are number of
advantages to bioremediation, which may be employed in areas which cannot be reached easily without excavation. The foundation of bioremediation has been the natural ability of microorganisms to degrade organic compounds. Bioremediation is a natural process alternative to such methods as incineration, catalytic destruction and the physical removal of the pollutants (*Kumar et al., 2011*).

The cost of moving and incinerating pollutants is at least ten times that of in situ biological treatment. By integrating proper utilization of natural or modified microbial capabilities with appropriate engineering designs to provide suitable growth environments, bioremediation can be successful in the field. However, a gap exists between advances in laboratory research and commercial field applications. Two major factors responsible for this gap are lack of a sufficient knowledge base to accurately predict pollutant degradation rates and fates and sites designated as field research centers for bioremediation research and technology demonstrations. Laboratory and microcosm studies have documented the potential use of microorganisms for bioremediation. However, the physiological potential of microbial populations to remEDIATE environmental of relevant size, heterogeneity and variability has not been adequately tested (*Pradhan, 2012 and Kumar et al., 2011*).

Successful application of bioremediation techniques must address both the heterogeneous nature of many contaminated waste sites and the complexity of using living organisms. There has been progress in overcoming some of the barriers that
have impeded bioremediation from being successfully applied in the field. Scientist has to put their efforts to search for organisms with better biodegradation kinetics for a variety of contaminants within broad environmental habitats. Studies examining extremophiles could result in using organism’s insitu that have a high tolerance for organic solvents and alkaline soils or waters and that function at high temperatures for more efficient ex situ activity in bioreactors (Kumar et al., 2011).

2.7.4.1. Principle of Bioremediation

Bioremediation is defined as the process whereby organic wastes are biologically degraded under controlled conditions to an innocuous state, or to levels below concentration limits established by regulatory authorities (Mueller and Cerniglia, 1996). For bioremediation to be effective, microorganisms must enzymatically attack the pollutants and convert them to harmless products. As bioremediation can be effective only where environmental conditions permit microbial growth and activity, its application often involves the manipulation of environmental parameters to allow microbial growth and degradation to proceed at a faster rate. Bioremediation techniques are typically more economical than traditional methods such as incineration, and some pollutants can be treated on site, thus reducing exposure risks for clean-up personnel, or potentially wider exposure as a result of transportation accidents. Since bioremediation is based on natural attenuation the public considers it more acceptable than other technologies. Most bioremediation
systems are run under aerobic conditions, but running a system under anaerobic conditions may permit microbial organisms to degrade otherwise recalcitrant molecules (Colberg and Young, 1995).

Biological methods employ aerobic and anaerobic bacteria to bring about the degradation of organochlorines. Accordingly the treatment method is known as aerobic treatment and anaerobic treatment, respectively. Apart from bacteria, fungi are also employed for the treatment of effluent (Fuentes, 2010).

2.7.4.2. Aerobic treatment

Biological systems were studied for their pollutant removal efficiencies by Gergov et al., (1988) reported 48-65% AOX removal by the activated sludge process. Bryant et al., (1992) reported that with aerated stabilization basin, low molecular weight AOX could be effectively removed (43-63%) as compared to high molecular weight AOX (4-31%). Wilson and Holloran (1992) in their study with aerated stabilization basin, reported 15-60% AOX removal from bleach kraft mill effluent. Rovel et al., (1994), using a biofilter, showed 76%, 62%, 81% and 48% removal of BOD, COD, suspended solids and AOX, respectively.

2.7.4.3. Anaerobic treatment

Enso-Fenox process described by Hakulinen, (1982) was among the first anaerobic treatment processes for toxicity removal. The process consisted of an anaerobic fluidized bed reactor and an aerobic trickling filter. Approximately 64-94% reduction
in the level of chlorophenol toxicity and chloroform from bleaching effluent could be achieved using this process. **Raizer-Neto et al., (1989)** reported decrease in organochlorines from the bleaching effluents using a continuously fed fluidized bed reactor. Using a 36 hr anaerobic treatment process **Fitzsimons et al., (1990)** showed 35-40% COD and 42-45% AOX removal. **Ferguson et al., (1990)** reported higher AOX removal efficiency of anaerobic treatment compared to aerobic treatment using bench scale reactor. **Ali and Sreekrishanan (2001)** in their study on anaerobic treatment of black liquor and bleach effluent reported 73% and 66% reductions in AOX and COD, respectively by addition of 1% w/v glucose. **Chen et al., (2003)** developed a combined treatment process of coagulation, anaerobic acidification and aeration package reactor for the treatment of bleaching effluent. They reported 88.1%, 81%, 98.4% and 92% reduction in COD, BOD, AOX and toxicity levels.

### 2.7.4.4. Fungal treatment

Various fungal species have been reported for their capacity to treat pulp and paper industry effluent, most common being white rot fungi *Phanerochaete chrysosporium* and *Trametes versicolor* (**Vara et al., 2010**). Significant reduction in color and COD from effluent was reported by **Prasad and Gupta (1997)** using *P. chrysosporium* and *T. versicolor*. A *Penicillium sp* isolated by **Taseli and Gokcay (1999)** was able to remove 50% of AOX and color from bleach plant effluent. **Zhang et al., (1999)** have
reported efficient degradation of dissolved and colloidal substances by using *T. versicolor* and its culture filtrate.

### 2.7.4.5. Biological treatment

Though biological are known from a very long time, do not necessarily ensure complete removal of AOX. Aerobic treatment processes are feasible where sufficient molecular oxygen is available. These treatment processes demands large inputs of energy as the rate of degradation is directly proportional to the amount of dissolved oxygen. Therefore, these technologies are expensive and also there is sludge generation which needs additional treatment. Anaerobic treatments are sensitive to the variations in the environmental conditions and require longer time to establish. Moreover, methanogens in the anaerobic treatment system are sensitive to the toxic compounds present in the PAP industry effluent. Fungal treatment requires addition of extra substrate for growth and the biomass needs replenishment from time to time. Majority of the treatment technologies are concerned with the removal of COD, BOD and color form the effluent. Also the norm led by CPCB requires the PAP industry to reduce the quantity and not completely remove AOX from the effluent which is discharged in fresh water bodies or is used for irrigation. USEPA fact sheet (November 1997) on the PAP industry, the pulping process and pollutant releases to the environment has reported formation of a number of toxic chemicals in the pulping effluent. The report states that although the effluent is treated but the toxic chemicals
pass through the treatment, i.e., the treatment plant does not reduce the concentrations of the pollutants. The report also states that AOX exhibit toxicity and may bioaccumulate in fish which may present a risk to human health. Leuenberger et al., (1985) reported that chlorinated compounds, especially chlorophenols, were poorly eliminated in the activated sludge treatment plant in their study.

2.8. Issues and Trends in Wastewater Use in Agriculture

2.8.1. Wastewater use in agriculture: past and current practice

Wastewater, in its untreated form, is already widely used for agriculture, which has been the practice for centuries in countries all over the world. Where it is used in agriculture, and adequate treatment is not available, the challenge is therefore to identify practical and safe uses that do not threaten those communities which are dependent on waste-water, and take into account the importance that this resource plays in achieving food security in growing urban areas. It is important to note in this context that wastewater presents not only a challenge but also an opportunity. On the one hand, its nutrients can be applied for agriculture and other productive uses; on the other hand, municipalities are struggling, especially in large metropolitan areas, with limited space for land-based treatment and disposal. Furthermore, its use can both deliver positive benefits to farmers, society and municipalities, as well as create potential health risks for farmers, their families and consumers while impacting the
environment considerably. Although standards are set, these are not always strictly adhered to.

The use of domestic wastewater for agriculture is not new. The Minoans may have collected wastewater for reuse at Knossos, Crete, some 4000 years ago (Angelakis et al., 2005). In East Asia, human excreta have been used to fertilize crops and replenish depleted soil nutrients since ancient times. In his seminal treatise on traditional Asian agriculture, Farmers of Forty Centuries, King (1911) noted: One of the most remarkable agricultural practices adopted by any civilized people is the centuries-long and well nigh universal conservation and utilization of all human waste in China, Korea and Japan, turning it to marvelous account in the maintenance of soil fertility and in the production of food. The earliest documented sewage farms where wastewater is applied to land for disposal and for agricultural use were operated in the sixteenth and seventeenth centuries in Bunzlau, Germany and Edinburgh, Scotland (Shuval et al., 1986). With the advent of water-borne municipal sewage in the mid-nineteenth century, sewage farms were increasingly seen as a solution for the disposal of burgeoning volumes of wastewater from many rapidly growing cities of Europe and the United States including London, Paris, and Berlin. The benefits cited included the prevention of river pollution and the provision of water and nutrients to agriculture. With the development around 1913 of biological wastewater treatment processes, such as trickling filters and activated sludge, that require much less land,
sewage farms fell into decline in urbanized industrialized countries (Asano et al., 2007). Odors and concerns about public health, such as the possible transmission of disease from vegetables irrigated with raw sewage, also contributed to the decline of sewage farms and their almost complete abandonment in much of the western world (Shuval et al., 1986). In a few notable exceptions, including Melbourne, sewage farming was modernized, and wastewater irrigation continues to flourish today. After World War II scientific and engineering interest in wastewater treatment and disposal through land application grew in both industrialized and developing countries, particularly in the more arid regions. It was seen as a way to prevent river pollution and to increase the supply of water resources for agricultural development. Jiménez and Asano, (2008) report that globally about 20 million hectares of agricultural land is irrigated with polluted water (i.e., direct use of raw or untreated wastewater, direct use of treated wastewater, as well as indirect use of untreated wastewater). According to Pearce, (2004), “a tenth of the world's irrigated crops everything from lettuce and tomatoes to mangoes and coconuts are watered by sewage, and much of that sewage is raw and untreated, gushing direct from sewer pipes into fields at the fringes of the developing world's great megacities”. The estimates suggest that the extent of unplanned wastewater irrigation (with direct and indirect use of untreated wastewater) is an order of magnitude greater than planned wastewater use (with direct use of treated water and some indirect use of untreated
water) (Scott et al., 2010). In lower income countries, wastewater irrigation is predominantly unplanned and either involves the direct use of untreated wastewater or the indirect use of highly polluted waters from rivers and streams. Farmers seldom have other water sources, and unplanned wastewater use is their only means to irrigate when investments in wastewater treatment do not keep pace with urban growth, and/or no other measures are undertaken for a more controlled use of wastewater. In higher income countries where wastewater irrigation occurs, it is normally planned use with treated wastewater.

2.9. Risk and Benefits of Wastewater Use in Agriculture

Wastewater use in agriculture has substantial benefits for agriculture and water resources management, but can also pose substantial risks to public health especially when used untreated for crop irrigation (Pham-Duc et al., 2014; Hanjar, 2001). There can also be chemical risks to plant health, and risks to the environment in the form of soil and groundwater pollution. Countries seeking to improve wastewater use in agriculture must reduce the risks, in particular those to public health, and maximize the benefits through properly planned, implemented and managed wastewater irrigation practices (Boischio, 2006). Epidemiological studies carried out over the past four decades have linked the uncontrolled use of untreated or partially treated wastewater for edible crop irrigation to the transmission of endemic and epidemic diseases to farmers and crop consumers. Actual risks of using untreated wastewater
for irrigation include the increased prevalence of helminthic diseases (such as ascariasis and hookworm) in field workers and consumers of uncooked vegetables, and bacterial and viral diseases (such as diarrhea, typhoid, and cholera) in those consuming salad crops and raw vegetables. Chemical risks to public health. Chemical risks are greater for middle- and high-income countries where industrial wastewaters may be discharged to public sewers and contaminate municipal wastewaters. Chemical risks to human health may be caused by heavy metals (such as cadmium, lead, and mercury) and by many organic compounds (such as pesticides). There is also increasing concern in high-income countries about an emerging class of “anthropogenic” chemical compounds, which include pharmaceuticals, hormones and endocrine disruptors, antibiotics, and personal care products although their long-term health effects are less clearly understood.

2.9.1.Risks to plant health

The principal risk to plants is reduced crop yields if the physicochemical quality of wastewater used for irrigation is unsuitable for example by being too saline or having excessive concentrations of boron, heavy metals or other industrial toxicants, nitrogen, and/or sodium (Adamu, 2013). Risks to plant health are reduced if there is little industrial effluent in the wastewater, but in all cases five parameters should be monitored during the irrigation season: electrical conductivity, the sodium adsorption ratio, boron, total nitrogen, and pH (Pescod, 1996 and Debus, 2003).
2.9.2. Environmental risks

Soil and groundwater pollution is the main risk of using wastewater in agriculture; the microbiological pollution of groundwater is a lesser risk as most soils will retain pathogens in the top few meters of soil except in certain hydrogeological situations like limestone formations (ETWWA, 2010). Chemical risks include, among others, nitrates in groundwater from sewage irrigation, salination of soils and aquifers, and changes in soil structure from, for example, boron compounds common in industrial and domestic detergents. The key to controlling many of the chemical risks to humans, plants and the environment is to put in place effective industrial wastewater pretreatment and control programs (Scheierling et al., 2011 and ETWWA, 2010). Of course, effective programs are not the norm in developing countries, so special attention has to be paid to chemical risks in such circumstances. Benefits of wastewater use in agriculture when properly planned, implemented and managed, wastewater irrigation schemes can have several benefits that accrue to the agricultural, water resources management, and environmental sectors (Bartone et al., 2001 and Cairo, 2003).

2.9.3. Agricultural benefits

Agricultural benefits may include: reliable, and possibly less costly irrigation water supply; increased crop yields, often with larger increases than with freshwater due to the wastewater’s nutrient content; more secure and higher urban agricultural
production, and contribution to food security; income and employment generation in urban areas; and improved livelihoods for urban agriculturalists, many of whom are poor subsistence farmers, including a large share of women. Water resources management benefits (Mukherjee and Schwabe, 2010). In terms of water resources management, the benefits may include: additional drought-proof water supply, often with lower cost than expanding supplies through storage, transfers, or desalinization; more local sourcing of water; inclusion of wastewater in the broader water resources management context; and more integrated urban water resources management (ETWAA, 2010).

2.9.4. Environmental benefits

Among the environmental benefits that may accrue to well-managed wastewater irrigation schemes are: avoidance of surface water pollution, which would occur if the wastewater were not used but discharged into rivers or lakes – major environmental pollution problems, such as dissolved oxygen depletion, eutrophication, foaming, and fish kills, can thereby be avoided; conservation or more rational use of freshwater resources, especially in arid and semi-arid areas that is, freshwater for urban demand, wastewater for agricultural use; reduced requirements for artificial fertilizers, with a concomitant reduction in energy expenditure and industrial pollution elsewhere; soil conservation through humus build-up and through the prevention of land erosion; and
desertification control and desert reclamation, through irrigation and fertilization of tree belts (ETWWA, 2010 and Scheierling et al., 2011).

2.10. Effect of Treated Effluent on Germination

In recent years, considerable attention has been paid to industrial wastes which are usually discharged on land or into sources of water. It is anticipated that the industrial activities will accelerate with the pace of development. This would have adverse impact on agriculture and would cause environmental degradation. On the other hand, huge amount of wastewater generated from pulp and paper industries has an important role to play in the context of scarcity of fresh water resources for irrigating agriculture land. Besides being useful source of plant nutrients, these effluents often contain high amounts of various organic and inorganic materials as well as toxic trace elements. Now a days, treated wastewater is considered as a potential water resource because it contains considerable amount of nutrients, which may prove beneficial for plants growth (Sahai et al., 1985; Mishra and Behera, 1991) and hence the use of wastewater in agriculture is gaining importance rapidly. Generally, the quality of discharged effluent differs from industry to industry, which may or may not be suitable for the irrigation of crops. So, the effluent should be assessed properly prior to its application for irrigation. However, indiscriminate use of industrial effluent may reduce crop growth and contaminants may interfere with natural characteristics of soil.

The paper industry is one of the largest industries in India, consuming large amount of water (Trivedy and Raj, 1992). Nearly 75 to 95% of the water was discharged by the industries as effluent containing organic, inorganic pollutants and colouring materials.
Presence of these chemicals may affect soil and in turn the growth and development of plants (Baruah et al., 1996). Studies on the effect of paper mill effluent on various crops have been carried out by various investigators (Choudhury et al., 1987; Mishra and Behera, 1991 and Dutta and Boissya, 1996, 1999, 2000). Baruah and Das (1997) reported that there is delay, retarded and declined germination of rice seeds and seedling growth with paper mill effluent treatment in comparison to control. Rajannan and Oblismai, (1979) reported that paper mill effluent had drastically affected the germination of rice, black gram and tomato seeds, however, the diluted form of effluent (25 and 50%) enhance the growth. Karande and Ghanvat (1994) observed that dilute effluent showed negligible effect on the overall growth characteristics in pigeon pea seedling treated with paper mill effluent. Mishra et al., (1989, 1991) conducted the study of physiotoxicity of the paper mill effluents on Elusine coracana and Oryza sativa crops. Further, Mishra and Behera, (1991) observed the same effect on rice seedlings. Narwal et al., (2005) reported that paper mill effluent increased sodium and potassium contents and disturbed the anionic-cationic balance in plants, thereby reducing the yield and quality of crops.

The diluted form of paper mill effluent could be used for irrigation purpose to enhance production of agricultural crops (Rajannan and Oblisami, 1979; Karnde and Ghanvat, 1994 and Baruah and Das, 1997). The concentration of dilution is varied depending upon the crops. Distillery waste water creates toxic conditions in the receiving streams and results in the massive destruction of aquatic flora and fauna (Lee et al., 1999; Kadirvelu et al., 2000; Kadirvelu et al., 2003 and Vasanthy, 2004). Distillery effluent is a rich source of organic carbon and plant
nutrients particularly potassium, sulphur and nitrogen, but at higher concentration, the ions present in effluent may have detrimental effect on metabolic functions adversely affecting seed germination and plant growth (Singh et al., 1995), whereas lower concentration increased seed germination of wheat, rice, sorghum, cowpea and soybean (Mukherjee and Sahai, 1988; Pandey et al., 1994 and Singh et al., 1995). The utilization of industrial effluent for irrigation of agricultural crops is one of the highly beneficial propositions of waste water disposal. Many workers have also reported beneficial effect of paper mill effluent on rice (Dutta and Boissy, 2000), green gram (Malla and Mohanty 2005), maize (Choudhary et al., 1987) and lentil (Raina and Aggarwal, 2003).

In India (Tamil Nadu), the main contributors to the surface and ground water pollution are the by-products of a variety of industries such as textile, dying and pulp and paper (industrial wastewater) (Kaushik et al., 2005), tannery, groundnut (Indira et al., 2012; Ravi Mycin et al., 2012) sugar (Thamizhiniyan et al., 2009); processing, chemicals, pesticides, fertilizer, pulp and paper (Malla and Mohanty, 2005), distilleries, food processing Dairy and Sago (Dhanam, 2009), mining, electroplating and others (Sah et al., 2000). The discharge of industrial effluents, municipal sewage, farm and urban wastes carried by drains and canals to rivers worsen and broadens water pollution. High levels of pollutants in river water causes an increase in Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Dissolved Solids (TDS), Total Suspended Solids (TSS), toxic metals such as Cd, Cr, Ni and Pb and fecal coliform and the presence of heavy metals in the environment causes deleterious effects to plants and human beings, particularly at certain levels of exposure and absorption. Among the heavy metals (processes whereas others) like cadmium, nickel and
chromium have no physiological function but often results in harmful disorders at a higher concentration of effluent (Kavitha, 2010). Hence such water becomes unsuitable for drinking, irrigation and all aquatic life.

The pulp and paper mill effluent contains chemicals of organic and inorganic substances (Baruha et al., 1996) which are harmful for the components of environment including soil and plants. Presence of these chemicals affects the growth and development of seedlings. The pulp and paper effluent is used for the growth of various plants (Dutta and Boissya, 1996, 2000; Choudhary et al., 1987; Mishra and Behra, 1991; 2000; Choudhary et al., 1987, Raina and Aggarwal 2003 and Mishra et al., 1991). Baruha and Das (1997) reported that there is delay, retard and decline of germination of oryza seeds and seedlings growth with paper mill effluent treatment in comparison to control. Ranjannan and Oblismai, (1979), reported that paper mill effluent has drastically affected the germination of rice, black gram and tomato seeds, but dilute effluent (25% and 50%) however, enhance the growth. Karnde and Ghanvat (1994), observed that dilute effluent show negligible effect on the overall growth characteristic in pigeon pea seedling treated with paper mill effluent.

Taking leads from the aforesaid literature review and based on the requirement of utilization of effluents after efficient remediation, especially using bacteria and fungi, the present work was taken up in order to give efficient treatment to the effluent of pulp and paper board effluent. Afterwards application of the treated effluent was tested on the Maize Crop.