Review Article

Paper Mill Effluent is an Alternate for Irrigation and Nutrient Sources in Improving Soil Health and Agricultural Productivity

ABSTRACT

The two most important environmental concerns related to the pulp and paper industries are the high consumption of fresh water and the generation of a huge volume of toxic wastewater. Hence, it is necessary to study the impact of these effluents on soil and crop before they recommended for agricultural purpose. This effluent is rich in dissolved solids as well as varying amounts of suspended organic materials. In addition to these constituents, effluents also contain some trace metals like Hg, Pb, and Cr. Most of the Indian paper and pulp mills discharge their effluents, which contain bleach and black liquor, directly into the receiving water bodies, thus causing serious environmental concerns. The paper mill effluent contains high concentrations of recalcitrant dissolved organic matter and when aquatic systems are overloaded, it can induce a high biochemical oxygen demand. On the other hand, treated paper mill effluent or wastewater is considered a resource that can be applied for productive uses since it contains nutrients that have the potential for use in agriculture and other activities. So we can use this wastewater efficiently for agricultural crops as a source of fertilizer as well as irrigation water.

Keywords**:** Paper mill effluent; toxic elements; treatment; nutrient source; crop yield

1.INTRODUCTION

Water is the most valuable resources in the world. Nowadays, in many places water resources are gradually becoming polluted by the addition of huge amounts of sewage, industrial waste, and effluents. These waste and effluents contain materials with varying properties, from simple nutrients to highly toxic substances. The discharge of industrial effluents with varying amounts of pollutants has altered the land and water quality. Among the different major industries, the paper industry is one of the polluter of the environment. There are nearly 700 paper mills in India, with an installed capacity of 701.4 lakh metric tonnes. During paper production, the mills release a large amount of wastewater containing various physical and chemical agents. They are discharged into land or nearby water bodies. The polluted water is being used for irrigation by nearby farmers. Nowadays, treated wastewater is considered a potential water and nutrient resource because it contains a considerable amount of nutrients, which may prove beneficial for plant growth. These effluents fall in borderline as saline water, but they can be considered as potential source for irrigation [1].The treated paper mill effluent had higher BOD and COD values with low NPK, while the contents of sodium, calcium, sulphate, and chloride were higher[2]. Paper mill effluent irrigation has the greatest potential in increasing yields of crops with significant savings in water and nutrients as compared to other conventional methods. In the present paper, an attempt has been made to evaluate both the beneficial and adverse effects of using paper mill effluent as irrigation water on the physio-chemical properties of soil.

1.1 Pulp and paper industry history

The technique of paper making is believed to have originated in China, from where it spread to the rest of the world, including India. The first handmade paper mill in India was set up in Kashmir in the 14th century. Much later, in 1832, the first mechanised paper mill based on jute and grass was established in Serampore, West Bengal. After a slow start, the growth was encouraged by the Bamboo Protection Act (1925) and the Indian Finance Act (1931). More than 10 paper mills were commissioned in this period, and by 1931, the production capacity had reached 45,600 metric tonnes[3].

1.2 Classification of paper mills

The categorization of pulp and paper mills is based on the raw material used, plant size, and end products manufactured. Based on the raw materials used, the paper mills are classified as follows:

Wood or forest-based mills: These mills use imported pulp as well as indigenous hardwood pulp from bamboo, eucalyptus, etc. The Indian paper industries, on average, consume about 3–4% of the total wood in India. **Agro-residue-based mills**: These mills use agricultural residues such as rice straw, wheat, sarkanda grass, bagasse, jute, etc. as raw materials. The use of agricultural residue by these mills has grown since the early 1970s, partly due to the dwindling bamboo resources and partly due to the government's industrial policy encouraging investments in agro-based paper production. However, seasonal availability, transportation costs, and investments in pollution control equipment are seen as limiting factors. **Wastepaper-based mills**: These mills use imported and indigenous wastepaper, corrugated waste paper, kraft paper, and waste cuttings as raw materials. The recovery of wastepaper by these mills for paper production has increased from 65 000 metric tonnes in 1995 to 850000 metric tonnes in 2000. However, the 20% rate of recovery is still one of the lowest internationally [4].

1.3 Chemical constituents of Raw materials and wastewater

Discharge of large amount of wastewater as effluent from pulp and paper industries in the surrounding streams result in serious health and environmental problems. These large quantities of effluents need to be characterized for evolving proper treatment strategy prior to their disposal[5]. Pulp and paper are manufactured from raw materials containing cellulose fibers, generally wood, recycled paper, and non-wood raw materials such as bagass, cereal straw, bamboo, reeds, esparto grass, jute, flax, and sisal. The manufacturing process uses a large amount of fresh water, most of which is thrown out as wastewater. The pulp and paper industry is one of the largest and most notorious sources of industrial pollution. The Ministry of Environment and Forests, Government of India, has categorized the pulp and paper industry as one of the twenty most polluting industries[6]). The wastewater from the pulp and paper industries contains stray wood chips, bits of bark, cellulose fibres, dissolved ligneous material (30–45%), saccharinic acid (25–35%), formic acid and acetic acid (10%), and extractives (3-5%). The exact chemical composition of pulp and paper mill effluent is complex and unclear. The chemical compounds found in pulp and paper mill effluent are mostly degrading products of lignin, cellulose, hemicellulose, and wood extractives. The lignin degradation products found in the pulp and paper mill effluent include a wide variety of compounds such as manomeric phenols, enol ethers, mercaptides, stilbene, quinone derivatives, chlorinated phenols, acetic acid, formic acid, acetaldehyde, methanol, furfural, and methyl glyoxal. About 300 organochlorine compounds have been identified in effluent, while hundreds more remain unidentified. The most dangerous of these compounds are chlorophenols such as guaicols and catechols and their transformation products, anisoles and verathroles. The most common chlorophenols are the extremely toxic and persistant trichlorophenol (TCP) and pentachlorophenol (PCP). Dioxins (polychlorodibenzo-p-dioxin, or PCDD) and furans (PCDF), which are the most dangerous chlorinated compounds reported, Apart from dioxins and furans, the other chlorinated compounds found in pulp and paper mill effluent include chloroforms, chloroacetones, aldehydes, and acetic acids [7].

Table 1. The organic composition and COD characteristics of pulp and papermill effluents [8]

S.No.	Wastewater	COD (mg/L)	Organic composition % COD	Potential inhibitory compounds
1.	Wet debarking	1300-1400	Tannins 30-35, monomeric phenols 10-20, simple carbohydrates 30-40, resin compounds 5,	Tannins ,resin acids
2.	Sulphite spent liquor	120000-220000	lignosulphates 50-60, carbohydrates 15-25	-
3.	Sulphur evaporator condensate SEC	7500-50000	Acetic acid 33-60, methanol 10 -25, fatty acids < 10	Sulphur, organic sulphur
4.	Chlorine bleaching	900-2000	Chlorine lignin polymers 65 -75, Methanol 1 -27	Chlorinated phenols, resin acids
5.	Kraft evaporator condensate KEC	1000-33600	Methanol 60-90	Sulphur,resinacids,fattyacids,volatile terpenes
6.	TMP effluent	1000-5600	Carbohydrates 25-40	Resin acids
7.	CTMP effluent	2300-13000	Polysaccharides 10-15, carbohydrates 25-45, Organic acids 35-40	Sulphur,fatty acids

1.4 PAPER PRODUCTION PROCESS

The pulp and paper industry converts fibrous lingo-cellulosic raw material into pulp and paper. The typical pulp and paper manufacturing processes involved and different waste waters generated are shown in Figure 1.

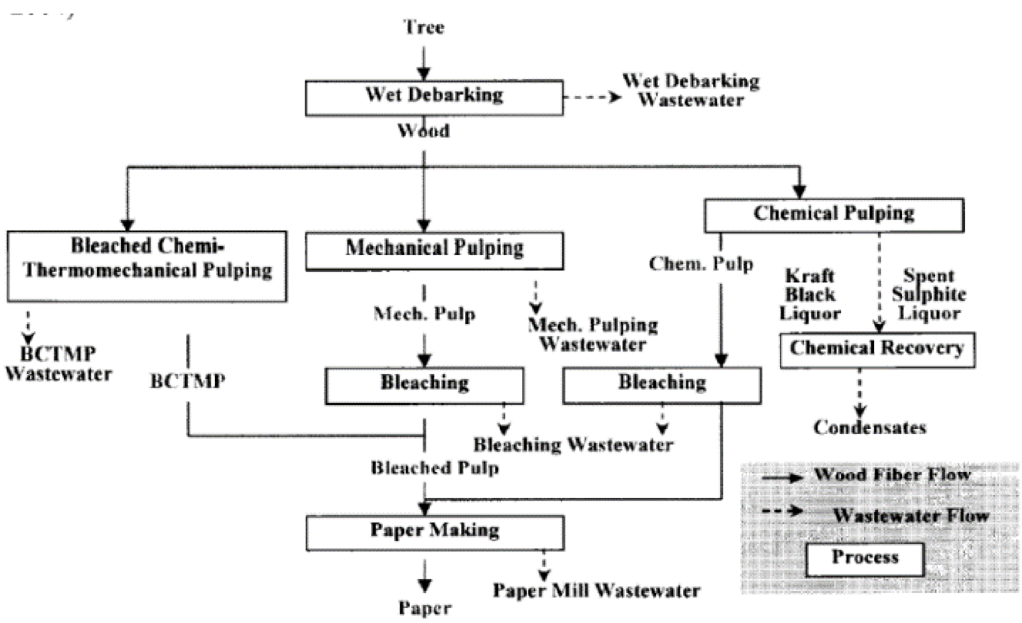

Figure 1. Different processes involved in pulp and paper production and corresponding waste waters generated [4].

Wastewater treatment methods

Agro-residue-based pulp and paper mills generally treat combined effluent. The treatment sequence involves equalization, primary settling, and clari-flocculation, followed by secondary biological treatment (anaerobic and/or aerobic). This is followed by the activated sludge process and secondary clarification. Most of the large and a few medium and small paper mills have chemical recovery plants to recover spent pulping chemicals. The treated effluent is disposed of on land, in surface water (rivers), or in drains. The primary sludge is dried in sludge drying beds or lagoons depending upon land availability and is generally sold to board manufacturers. The waste water treatments are broadly categorised into physicochemical and biological methods. Effluent discharge standards for pulp and paper mills under E (P) Act 1986 is given in Table 2.

Physiochemical methods:

- Several physicochemical colour removal methods, such as adsorption, rapid sand filtration, chemical precipitation, membrane processes, and electrochemical methods, have been developed and reported in the literature in the past [8].

- Adsorption methods are increasingly being considered for the removal of synthetic organic chemicals, colour-forming organics, and disinfection byproducts. The different adsorbates commonly used in effluent treatment include activated carbon, processed bone, char powder, activated alumina, magnesia, activated bauxite, fly ash, alum, lime, etc. [8].Activated carbon is the main adsorbent in full-scale effluent treatment. Other naturally occurring adsorbents are used in special cases. Activated alumina is widely used for the removal of fluoride. Silica gel is used for the separation of hydrocarbons. Polymeric resins and carbonised resins are often employed for improved removal of organic compounds from effluent.
- The membrane techniques require pre-treatment and a large capital investment. Membrane fouling is another problem associated with this method. Adsorption and membrane processes are efficient but expensive [9]. The application of the electrochemical method is another way to treat the wastewater from cellulose paper production [10]. This method guarantees high treatment efficiency, but its effectiveness depends on the type of electrodes, the construction of electro-coagulators, and the conditions under which the process is run.
- Chemical precipitation using alum, ferric chloride, and lime has been extensively studied [11]. Despite the short detention time and low capital cost, there are some drawbacks reported, such as the high cost of chemicals for precipitation and pH adjustment, voluminous sludge production due to heavy dosages, dewatering and disposing of generated sludge, and high residual cation levels. The chemical precipitation methods are cheap but produce a large quantity of sludge and do not completely remove toxicity.
- The chemical aspect of colour removal from effluent from the pulp and paper industry is very important. The use of calcium hypochlorite (1–2% of available chlorine) during alkaline extraction reduced the colour of effluent by 84% without affecting the quality of pulp. The use of chlorinated backwater (having 0.8% residual chlorine) during brown stock washing reduced the colour of effluent by 60% without affecting the quality of pulp. The combination of alum, lime, and magnesium sulphate in the presence of ferric acid chloride reduced the colour, BOD, and COD by 97%, 68%, and 52%, respectively. The combination of alum, calcium hypochlorite, and ferrous sulphate in the presence of chlorine water was most effective and reduced the colour, BOD, and COD by 97, 71, and 64%, respectively. The treatment options that have been explored till now are not cost-effective at the plant level, and no completely efficient method is currently available.

Biological methods

- Biological methods have the potential to eliminate or reduce the problems associated with physicochemical methods. Several studies have been carried out concerning the decolorization and treatment of such wastewaters by biological methods. The colour of paper mill effluent is largely due to lignin and lignin derivatives and polymerized tannins, which are resistant to degradation due to the presence of carbon-to-carbon biphenyl linkages. It is reported that lignin and lignin derivatives are biodegradable by some microorganisms under proper environmental conditions. Numerous bacteria have been reported to decompose lignins and lignin derivatives, some of which include Pseudomonas spp., Flavobacteria, Xanthomonas spp., Bacillus spp., Aeromonas spp., Cellulomonas spp., Chromobacteria, etc. [12]. Although numerous bacteria can decompose monomeric lignin structure models, only a few strains are able to attach lignin derivatives obtained from different pulping processes.
- Many of the past studies have focused on screening, identifying, and evaluating the ability and effectiveness of fungi in degrading lignins in situ and in vitro. A variety of fungi have been proven to be lignin degraders and are classified into white-rot, soft-rot, and brown-rot fungi based on the type of wood decay carried out by these organisms [12].
- The white rot fungi are a group of basidiomycetes that possess an active lignolytic enzyme system, which is the most efficient of the microorganisms that degrade lignin and its modified forms ([13]. These fungi do not use lignin as a carbon source for their growth but use it as a secondary metabolite, which is not required for their growth. The lignin degradation by white rot fungi is extensively studied, and degradation is caused by three extracellular phenol oxidases, namely lignin peroxidases (LiP), manganese peroxidases (MnP), and laccases (Lac) (Peng Wang et al. 2008). In addition to degrading lignin, these fungi are also capable of degrading a variety of environmentally persistent pollutants, such as chlorinated aromatic compounds, heterocyclic aromatic hydrocarbons, synthetic high polymers, and various dyes[14].
- Several authors reported on the capacity of different fungal species to remove color from kraft mill effluent [15,16,17]. [18] reported on a substantial reduction of colour and COD by the use of the white-rot fungi, T. versicolor and P. chysosporium. [19] showed that the white-rot fungi P. chysosporium, in combination with other white-rot fungi (P. sanguineus, P. ostreatus, and H. annosum), and with the use of surfactants, were able to remove color, COD, and lignin content. Further, it was found that lignin, BOD, COD, and colour removal were achieved to the extent of 77%, 76.8%, 60%, and 80%, respectively, by the fungal species Pleurotusostreatus. [20] isolated a fungal species (Pencillium sp.) that was able to remove 50% of the AOX and colour

from the soft-wood bleachery effluents in a contact time of 2 days. [21] showed that fungi such as T. versicolor and fungal culture filtrate (FCF) obtained from these organisms were able to efficiently degrade the dissolved and colloidal substances. The other white-rot fungi reported to degrade effluent colour under optimum conditions include Tinctoporiaborbonica, Schizophyllum commune, Aspergillus fumigatus, and Pleurotusostreatus, among others [22].

Table 2. Effluent discharge standards for pulp and paper mills under E (P) Act 1986

S.No.	Category	Standard	Note
1.	Large (writing & printing) pulp and paper mills	200 m³/tonne of paper 150 m³/T	Standards of discharge for the large pulp & paper mills established from 1992 onward to meet standard of 100 m³/tonne of paper
2.	Agro-residue based	200 m³/ tonne of paper	Agro-residue based mills established from January 1992 onward to meet the standards of 150 m³/tonne of paper
3.	Wastepaper based mill	75 m³/tonne of paper	Wastewater based mills established from January 1992 onward to meet the standards of 50 m³/tonne of paper

1.5 Effect of untreated effluent on land quality

General physico chemical properties of effluent is given in table 3. Elements such as magnesium, sodium chloride, and sulphur, which are also common in pulp mill wastewater, can cause nutrient imbalances in crops, increase soil salinity, deteriorate soil structure, and ultimately lower crop productivity in the long run [23]. The paper mill effluent contains toxic trace elements that may accumulate in soils in excessive quantities; these toxic elements may cause severe problems to humans and animals by entering the food chain. Untreated industrial effluents contain high concentrations of heavy metals. Pulp mill effluents disturb soil quality by, among other things: increasing pH of soil, changing soil colour and texture, imbalance of macro- and micronutrients in soil, negative effect on soil microbial activities and disturbing all natural cycles, increasing organic load, and depletion of oxygen supply in soil. Untreated paper mill effluents contain higher amounts of Cd, Pb, Zn, Cu, Mn, and Fe and enhance the concentration of the heavy metals in irrigated surface soils (Xiog et al. 2001). Significantly higher values of EC, organic carbon, available K, exchangeable cations (Ca^{2+}, Mg^{2+}), exchangeable anion (Cl^-, HCO_3^-), and micronutrient cation (Cu^{2+}) have been reported in soils being irrigated by paper and pulp industry effluents. The biochar formed due to the slow pyrolysis of paper effluent affected the agronomic performance and soil fertility of some soils

Table 3. Physio chemical analysis of pulp and paper mill effluent

Parameters	Mean value
BOD	32000± (577.35)
COD	45000 (±946.48)
Nitrogen	299 (±9.46)
Phenolic compounds	5.1 (±0.06
Phosphorus	767.66 (±26.26)
Sulphate	3800 (±57.73)
Total suspended solids (TSS)	97686.66 (±566.10)
Total dissolved solids (TDS)	9,566.66 (±88.19)
Chlorine	2800(±26.83)
Total organic carbon	2880(±22.30)
K	481.33 (±28.93)
Na	498 (±16.83)
Cu	0.31 (±0.03)
Fe	72.07 (±12.76)
Mn	3.68 (±0.64)
Ni	0.86 (±0.01)
Zn	3.781 (±0.06)

All the values are in ppm means (n=3) ± standard error.

1.6 Effect of untreated effluent on Crops

Pulp and paper mill effluent is also responsible for affecting the quality of crops due to irrigation with polluted water, which damages the soil, growth, quality, and yield of the crop (Table 3).

Table 4. Negative impact of untreated effluent on Crops

S.No.	Negative impact
1.	Decrease germination percentage and seedling growth in crops [23]
2.	Inhibiting effect on the germination of crops [24]
3.	Reduces crop growth and gives severe adverse effect on soil properties [25]
4.	Seed germination in Sunflower and maize [26]
5.	Germination of seeds in paddy [28]
6.	Reduction in shoot weight (44%) in paddy [29]
7.	Germination percentage and yield in paddy [30]

1.7 Effects of untreated effluent on water bodies

Studies demonstrated a variety of responses in fish populations living downstream of bleached kraft pulp mills. These included delayed sexual maturity, smaller gonads, changes in fish reproduction, and a depression in secondary sexual characteristics. The main problem that occurred due to pulp and paper mills was the growth of sewage fungus in the river receiving effluents. The dark colour and high turbidity due to suspended solids can cause problems with both water opacity and blanketing of river or lakebeds. Severe blanketing may result in anaerobic decomposition under the blanket, releasing hydrogen sulphide into aquatic ecosystems. The dark colour and blanketing can reduce photosynthetic activity in aquatic plants [28]. This leads to a chain of adverse effects on the aquatic ecosystem as the growth of primary consumers as well as secondary and tertiary consumers is adversely affected. Therefore, it becomes necessary to remove colour and toxicity before they can be accepted into surface waters.

1.8 Effect of untreated effluent on Soil Biology

Soil biological properties as affected by wastewater application have been investigated, with variable results depending on the experimental design and measurements monitored. For example, traditionally, microbiological counts have been reported, whereas in more recent studies, molecular biological approaches concentrating on gene expression and enzymatic activities are employed.

The paper mill effluents adversely affect the germination of rice seeds[28]. [30] reported that the germination of rice seeds showed a gradual decline at 50% and above concentrations of the effluent throughout the experimental period in comparison to control seeds. [29] have shown a 44% reduction in shoot weight in 100% wastewater-treated soil. Other deleterious effect on water bodies is given in table 5.

Table 5. Effect of untreated effluent on water bodies

S.No.	Impact on water bodies
1.	Accumulate metal (loid)s, salts, and organic compounds such as pesticides in soils that might be toxic to soil fauna and flora [30]
2.	Antibiotics are bioactive compounds and can reach soils through wastewater irrigation, thereby affecting soil biological activity [31]
3.	Wastewater-borne microorganisms might compete with indigenous microbial communities [32]
4.	Microbiological population from aerobic to anaerobic microorganisms due to short-term oxygen depletion of the topsoil resulting from wastewater irrigation, as seen by a

	decrease in oxygen diffusion rate [33]
5.	The stimulation of copiotrophic bacteria was observed in the same long-term wastewater irrigation area [34,35]

1.9 Effect of treated effluent on soil properties

The soil has both inherent and dynamic properties. In India, a tropical country, drought conditions and the depletion of groundwater sources necessitate an alternate irrigation source and the positive impact of treated paper mill effluent is given table 6. . The various irrigation sources can be augmented by using the effluent from the pulp and paper industry.

Table 6. Effect of treated effluent application on improvement in soil physical and chemical properties

S.No.	Effect of treated effluent application on improvement in soil physical and chemical properties
1.	Soil physical and hydraulic properties [36]
2.	Soil aggregate stability [37]
3.	Bulk density and porosity induced [38]
4.	Lower bulk density and increase soil porosity [38]
5.	Total porosity [39]
6.	Actinomycetes and fungi population [40]
7.	Soil nutrients status [41]
8.	N, PO4, Na, K, Mg, and Ca ([42]
9.	Na, and extractable S, Zn, Fe, Mn, Pb, and Ni [43]
10.	Soil pH and organic C, N, P, and K. [44]
11.	Organic carbon (3.2–5.9 gkg1), and concentrations of N, P, K, and Na [45]
12.	Long-term wastewater irrigation affects total microbial biomass and/or soil enzyme activities in different soils [46]
13.	Increase in bacterial counts and bacterial activity [47]
14.	Increased the soil bacteria, actinomycetes, fungi, rhizobia, and yeasts, and the populations of soil microorganisms [44])

The reuse of industrial effluents for irrigation purposes is an alternate and effective waste disposal method commonly called "agro-recycling" where wastewater and plant nutrients could be recycled to diminish pollution and accomplish additional income (Table 7). The use of industrial effluents for agricultural purposes involves two main principles: the use of soil as a treatment system to reduce pollution of surface water and the use of wastewater as a supplementary source of irrigation. In certain cases, thus, the lack of nutrients can also perhaps be compensated to a limited extent by industrial effluent irrigation.

Table 7. Effect of treated effluent on crop growth

S.No.	Effect of paper mill effluent irrigation on crop growth
1.	Germination percentage, plant height, crop growth rate (CGR), and relative growth rate (RGR), of sorghum, maize, and sunflower [47]
2.	Pod yield and oil content of the groundnut [48]
3.	Yield parameters of tomato, viz., number of fruiting clusters, fruit weight, and fruit yield, were higher [49]
4.	Quality traits of bhendi and amaranthus[50]
5.	Cowpea yield by up to 28 percent and the nodule formation [51]
6.	Higher chlorophyll, protein content, root length, shoot length, leaf area, and total biomass in black grammes at a 10% concentration of paper mill effluent irrigation. [42]
7.	Bacterial, fungal, and nodule counts had also increased in black gramme up to 50% concentration[52]
8.	Germination and growth of peas[53]
9.	Pod (2608 kg ha-1) and kernel yield (1534 kg ha^{-1}) [54]
10.	Length of seedlings after germination in vegetable crops [55]
11.	Yield and biominerals viz., Ca and Fe, of banana[56]
12.	Paper mill effluent on germination, seedling growth and chlorophyll content in Zea mays L [57]
13.	Increase in chlorophyll content, plant height, shoot and root biomass, grain yield etc. in Triticum aestivum L. [28]

Subsequent research on paper mill waste utilisation in agriculture [49] has revealed numerous benefits with no deterioration in crop produce (Figure 2). The adverse effects of effluent irrigation from paper factories could be alleviated by resorting to the application of N, P, and K along with organic and inorganic amendments such as press mud, farmyard manure, and gypsum [48].

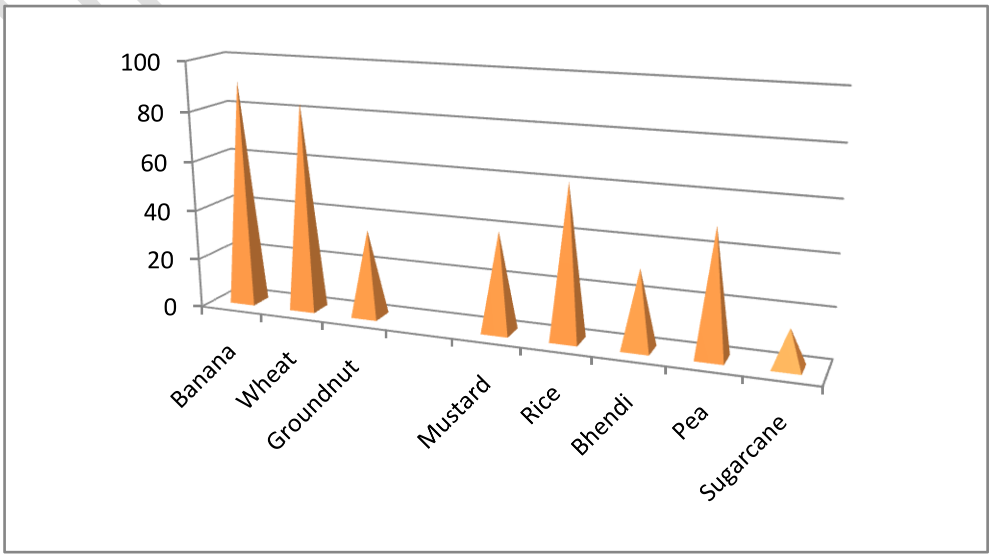

Figure 2. Effect of paper mill effluent on yield in various crops (%)

2. CONCLUSION

Several studies have been done on the impact of various industrial effluents on various crops. Paper mill effluent is reported to be rich in mineral nutrition which could improve growth and yield. Maintaining good soil quality and minimizing soil pollution and degradation are of fundamental importance to preserving agriculture and developing the economy of the country. For enhancing food production, proper and effective use of available land, water and fertilizer resources are essential. Now a days, treated wastewater is considered a potential water and nutrient resource because it contains a considerable amount of nutrients, which may prove beneficial for plant growth. Raw paper mill effluent has an adverse effect on the growth and development of crops and soil, but treated paper mill effluent in lower concentrations is no toxic on crop and also in soil. The beneficial effects of effluent on crops are proved by many studies. Hence, it can be recommended for appropriate dilution of the effluent of a paper mill for agricultural crops and it could be used for irrigation in agricultural fields to enhance crop productivity. Thus, from the foregone review, it could be concluded that the treated paperboard mill effluent and solid wastes could be used for crop production without any adverse effect on yield and quality of produce.

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