A Comprehensive Assessment of Heavy Metal Pollution in Iron and Paper–Pulp Industrial Effluents and The Potential of Microalgae for Sustainable Bioremediation in Nashik District, Maharashtra, India

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***Abstract*—The pulp and paper industry are a major consumer of water and chemicals and is recognized as one of the most polluting industrial sectors due to the discharge of large volumes of wastewater enriched with organic matter, nutrients, and toxic heavy metals. The present study aimed to assess the physico-chemical characteristics and heavy metal contamination of combined iron, paper and pulp industrial effluents from Nashik District, Maharashtra, India, and to evaluate the efficiency of algal-based phycoremediation under laboratory conditions. A total of twelve grab samples (I-1 to I-12) were collected from Satpur and Ambad MIDC industrial areas and analyzed for key water quality parameters including pH, temperature, electrical conductivity, turbidity, total dissolved solids (TDS), total suspended solids (TSS), chemical oxygen demand (COD), nutrients, and selected heavy metals using standard analytical methods. Pre-treatment analysis revealed that the effluents were highly polluted, exhibiting slightly acidic pH (5.7–6.7), high COD (735–1470 mg/L), elevated EC (1500–2500 mS/cm), substantial TDS and TSS, excessive nutrients (nitrate, ammonia and phosphate), and considerable concentrations of heavy metals such as Fe, Zn, Cu, Ni, Cr, Cd and Pb, indicating severe environmental risk if discharged untreated. Phycoremediation experiments were conducted using six aquatic algal and cyanobacterial species *Chlorella vulgaris*, *Spirulina platensis*, *Scenedesmus quadricauda*, *Oscillatoria terebriformis*, *Chroococcus turgidus* and other cyanobacteria grown in untreated effluent for 20–25 days under controlled laboratory conditions. Post-treatment results demonstrated significant improvement in effluent quality, with a marked reduction in COD (0.6–35.6 mg/L), nutrients, and heavy metals. Complete removal of cadmium and substantial reductions in copper, chromium, lead, zinc, nickel and iron were observed, attributed to algal uptake, biosorption and pH-induced precipitation. The pH of the treated effluent shifted towards neutral to alkaline conditions, enhancing metal immobilization and reducing toxicity. the study confirms that algal-based phycoremediation is an effective, eco-friendly and sustainable approach for the treatment of complex industrial effluents from iron, paper and pulp industries. The technique shows strong potential as a tertiary or polishing treatment option for reducing organic load, nutrient enrichment and heavy metal contamination, thereby contributing to environmental protection and sustainable wastewater management.**

***Index Terms*—Algae, water quality, water treatment, waste water, effluent, statistical assessment, paper-pulp industry.**

I. INTRODUCTION

Each person in Thailand consumes roughly 40 kg of paper annually, and this number is rising every year. For many years to come, pulp and paper production is expected to be a growing sector in Thailand (Szabó et al., 2009). Furthermore, the pulp and paper sector has historically been regarded as a large contributor to pollutant discharges as well as a big consumer of energy and natural resources (Gupta, G. K., & Shukla, P. 2020). The pulping and bleaching operations have a significant influence on the environment. Air emissions, liquid effluents, and solid wastes are the three primary categories of pollutants produced (Gupta et al., 2019). Even though bacteria are in charge of the biochemical breakdown of organic materials, earthworms play a significant role in the process by modifying the substrate and changing the biological activity (Aira et al., 2009). According to Loehr et al. (1985), earthworms create favourable circumstances for the decomposition of waste subsystems, consume organic solids, transform some of the organics into worm biomass and respiration products, and eject worm-cast as partially stabilized materials with low concentrations of dangerous compounds. The production of pulp and paper uses a lot of water. A significant amount of waste water sludge and other solids is produced throughout the entire process. About 45% of wastewater sludge is produced during the manufacturing of paper (Zambrano et al., 2003).

The pulp mill sludge may be a useful resource for soil amendments because of its chemical characteristics (high organic matter content, pH, buffer capacity, nitrogen and phosphorous level) (Zhang et al., 2004). Several sophisticated industrial processes are carried out. Rapid advancements in industrial processes result in the production of hazardous solid waste and discharge effluents that pose a risk to the environment. Large amounts of water are used in industrial activities, and the nearby locations receive effluents tainted with heavy metals. The third-biggest industrial polluter of land, water, and air is the pulp and paper sector (Rout 2008). High levels of phosphorus, chemical oxygen demand (COD), and biological oxygen demand (BOD) are present in paper mill effluent, along with rising conductivity, colour, and temperature (Gaete et al. 2000). Terpens, alcohols, phenols, methanol, acetone, chloroform, methyl ethyl ketone, surfactants, dyes and pigments, acids and alkaline solutions, and heavy metals like mercury, copper, iron, zinc, and aluminum are among the volatile organic compounds and toxic chemicals that are added to the effluent water (Nikhileshwar 1992). Thus, the wastewater from pulp and paper mills These dangerous compounds deteriorate the quality of the water and have a number of detrimental consequences on nearby agricultural areas, cattle, and aquatic ecosystems (flora and fauna) (Garg et al. 2004). Regular monitoring of pollutant indicators such total suspended solids (TSS), BOD, COD, chlorophenols, dioxins, and colour in these effluents is crucial for maintaining environmental safety (Raj et al. 2005). a sophisticated, environmentally acceptable, and successful Phyto technological strategy must be used to attenuate these harmful xenobiotic chemicals in light of the different deleterious consequences of paper mill effluents. The burden of heavy metals (Cu and Hg) from paper mill effluents has been reduced through the use of an efficient in situ phytoremediation technology. Several researchers have demonstrated this experimentally by using plants such as Brassica juncea, Datura metal, Lycopersicon esculentum, and Pteris vittata to clean up soil contaminated with lead and arsenic (Arthur et al. 2003; Selvarathi and Ramasubramanian 2010; Kumar et al. 2010; Ndimele and Jimoh 2011). In order to improve the treatment, variables including pH, wastewater composition, retention duration, and microbial activity are essential. Although other substrates like clay soil, zeolite, shale, and industrial wastes (furnace slag, steel slag, and sludge from waste treatment plants) have also been found to be effective filter materials, the majority of CWs use crushed stones, sand, and gravel as substrates to support the plant growth (Drizo et al. 1999; Haynes 2015; Hua et al. 2015). In their studies on feeding type and substrate appropriateness, Yalcuk and Ugurlu (2009) found that the horizontal system was superior for organic removal, whereas the zeolite-based bed material worked well in vertical flow systems for ammonium removal.

According to Nagajyoti et al. (2010) and Rahman et al. (2012), heavy metals are known to be dangerous pollutants in industrial effluents, and their discharge into aquatic environments is likely to endanger human populations as well as flora and fauna. Heavy metals like copper (Cu), cadmium (Cd), zinc (Zn), lead (Pb), nickel (Ni), and iron (Fe) have been linked to industrial effluent in both edible and inedible vegetable sections (Sharma et al. 2006). Significant levels of trace hazardous metals are present in wastewater, which frequently cause soil health to deteriorate and contaminate a food chain, primarily through vegetables cultivated on such soils (Rattan et al. 2002). Growing plants absorb the harmful components that have accumulated in the organic matter in soils, ultimately exposing humans to this contamination (Khan et al. 2008). Bioaccumulation may result from toxic heavy metals entering the ecosystem, especially through consumption of fruits and vegetables (Kashif et al. 2009). An excessive accumulation of heavy metals in the body could result from this. Pb, Cd, Cr, Co, and Ni are a few heavy metals that are frequently linked to detrimental effects on people (Gupta et al. 2008). The body needs certain heavy metals, like copper, iron, zinc, and manganese, but excessive exposure can cause signs of heavy metal toxicity.

Vegetables have varying quantities of heavy metals, which could be explained by their varying ability to absorb certain heavy metals (Singh et al. 2010). One of the main pollutants in vegetables is heavy metals. They have extended biological half-lives, are not biodegradable, and may accumulate in many human organs to cause undesirable effects (Nabulo et al. 2011). These days, a vast amount of wastewater containing heavy metals and other chemical pollutants is produced by a variety of businesses, including paper mills, mining, pharmaceuticals, sugar mills, electroplating, steel, textiles, tanneries, and paint. Due to their increased toxicity, industrial wastewater control is quite strict (Wuana and Okieimen 2011; Rajasulochana and Preethy 2016). India's paper industry is not as advanced as that of Western nations. In general, a wide range of cellulosic and noncellulosic raw materials are used by Indian paper mills to produce paper. About 43% of the cellulosic-based resources used in India's pulp and paper mills come from forest wood, 28% come from agricultural products, and 29% come from recycling waste paper (Balakrishanan 1999). Approximately 20% of industries in India have incomplete treatment facilities, while over 55% lack appropriate treatment procedures. Without any prior treatment, all of these industrial effluents are discharged into the environment (Srivastava et al. 1990). A complex colloidal solution of several inorganic components and organic polymeric compounds, such as lignin, carbohydrates, and their complexes, makes up the black liquor effluent of pulp and paper mills. The majority of our freshwater ecosystems have been ruined by the direct release of these effluents into aquatic systems (Kumar et al. 2000). Direct contact with solid wastes, leachate, or sludge, as well as precipitation of airborne emissions, can pollute soil, an essential part of the biosphere. According to Liyun et al. (2014), soil is both a source and a sink of heavy metals (HMs). The underlying chemical characteristics of the soil, such as pH, electrical conductivity (EC), and soil organic carbon (SOC), have a significant impact on the metal solubility. Because soil clearly reflects the HM profiles resulting from anthropogenic activities, it is a great medium for monitoring HM contamination and environmental quality (Li et al. 2009). Cu mobility in soils is strongly controlled by the compounds and species of the metal. Between pH 7 and pH 8, both cationic and anionic forms of Cu become less soluble. The bioavailability and mobility of copper in soils are controlled by its affinity for organic complexing (McBride and Blasiak 1979). Because it contains a number of heavy metals and other unidentified organic contaminants, the sludge produced by different sectors is regarded as a source of potentially harmful substances, and disposing of it poses a risk to human health. Sludge production is currently rising daily due to waste water treatment; it is still bulky and has a high moisture content, and depending on where it comes from, its composition can vary from a high organic content to minerals and heavy metals. In several nations, the sludge is occasionally utilized as fertilizer following composting and vermicomposting (Lim et al., 2016). The goal of the current study was to evaluate the amounts of heavy metals and other harmful loads in the industrial waste of iron, paper, and pulp in the Nashik District of Maharashtra, India. The potential phytoremediation ability of four aquatic macrophytes (Chlorella vulgaris, Scenedesmus obliques, Oscillatoria, and spirulina) grown for 20–25 days in reducing fe, cu, cd, zn, ni, and cr in iron, paper, and pulp industrial effluent through bioremediation under laboratory conditions by phytovolatilization and phytoextraction mechanisms is compared. Compared to traditional chemical treatment procedures used by enterprises, the present phytoremediation strategy is determined to be beneficial and successful.

II. STUDY AREA:

The paper and pulp industry in Nashik district of Maharashtra plays a significant role in the region's industrial development, offering a broad range of paper products that support sectors such as packaging, printing, education, and manufacturing. The industry is predominantly composed of small to medium-scale enterprises that adopt sustainable production practices and serve both domestic and export markets. Nashik's strategic location in northwestern Maharashtra, approximately 180 kilometers northeast of Mumbai, enhances its industrial importance. The district is well-connected by national highways, railways, and proximity to ports, allowing efficient movement of raw materials and finished goods. Its geographical features, including undulating terrain and the presence of rivers such as the Godavari, Darna, and Kadwa, provide a moderately favourable setting for waterintensive industries, although water availability remains a critical factor in dry seasons. Fig.1 shows map of study area

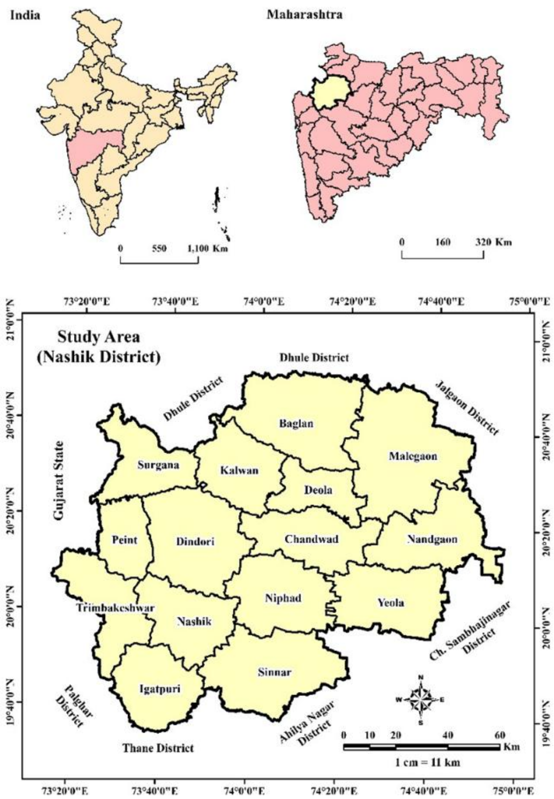

FIG. 1. MAP OF STUDY AREA

The major industrial clusters for paper and pulp manufacturing in Nashik are found in the Maharashtra Industrial Development Corporation (MIDC) areas such as Ambad, Sinnar, and Malegaon, as well as in peri-urban and rural belts like Dindori and Igatpuri. These locations have been chosen for their relatively low land costs, access to labor, and logistical proximity to both supply and consumer markets. Many of these clusters are situated at elevations that prevent waterlogging and provide suitable conditions for factory construction and wastewater treatment infrastructure. The climate of Nashik is generally moderate with hot summers, mild winters, and monsoon rainfall, which can influence both the availability of water resources and the condition of paper stock during storage and transport. The district's paper and pulp sector produce a diverse array of paper products. Kraft paper, used extensively in packaging, is one of the most commonly manufactured materials. It is generally made using recycled paper and agricultural residues, which not only lower production costs but also align with sustainability goals. Other products include writing and printing paper, such as copier and notepad paper, which are typically produced using eco-friendly methods that avoid the use of virgin wood pulp. In addition, some units focus on specialized products like filter paper, cellulose extraction pads, and industrial paper for use in chemical processing, pharmaceuticals, and food production. The rise in demand for environmentally sustainable packaging has also led to the production of corrugated boards and coated paper alternatives to plastic-based materials. In terms of raw materials, the industry predominantly uses recycled paper, agro-residues, and imported pulp. The adoption of circular economy principles is evident, as many units have established systems for waste collection, reuse, and treatment. Water is an essential input in paper production, and while Nashik's River systems offer a certain level of availability, sustainable water use remains a key concern. Many enterprises have installed Effluent Treatment Plants (etps) and adopted closed-loop water recycling systems to comply with environmental norms and reduce water consumption.

III. MATERIALS AND METHODS

3.1 SAMPLING AND PHYSICO-CHEMICAL ANALYSIS OF IRON, PAPER AND PULP INDUSTRIAL EFFLUENT

Waste water samples of Iron, Paper and pulp industrial Effluent were collected from different sites in Satpur MIDC industrial area and Ambad MIDC industrial area of Nashik District, Maharashtra, India. 12 grab samples were collected from these sites and transferred to the laboratory immediately. In this way, 12 samples were collected and analyzed for different water quality parameters. The samples were analyzed for pH, EC, Turbidity, TSS, TDS, BOD, COD, TAN, Sulphate, phosphate, Nitrite, calcium, chloride, Fluoride, etc, and heavy metals according to standard methods. The effluent was collected in clean plastic containers (5-L volume) from the inlet (untreated effluent) and outlet (treated effluent) of effluent treatment plant (ETP). Water quality Parameters and their method of analysis shown in table 1.

TABLE 1. WATER QUALITY PARAMETERS AND THEIR METHOD OF ANALYSIS

Sr No.	Parameters	Methods
1.	Ph	pH meter-Electrometric method
2.	Temp	Temperature meter
3.	EC	EC meter
4.	Total suspended solids	Oven drying method
5.	Total dissolved solids	Gravimetric analysis by oven drying method
6.	Turbidity	Nephelometric method
7.	COD	Open Reflux method
8.	Chloride	Titration
9.	Fluoride	Spectrophotometric method
10.	Phosphate	UV Spectrophotometer
11.	Sulphate	UV spectrophotometer
12.	Fluoride	Spectrophotometric method
13.	Calcium	EDTA method
14.	Total hardness	EDTA Titrimetric method
15.	Sodium	Flame photometric method
16.	Potassium	Flame photometric method
17.	Nitrate	U.V. spectrophotometric method
18.	Phosphate	Spectrophotometric method
19.	Ammonia	Colorimetric method/ TAN method
20.	Boron	Spectrophotometer-colorimetric measurement
21.	Iron	AAS
22.	Nickel	AAS (Atomic Absorption Spectroscopy)
23.	Cadmium	AAS
24.	Zinc	AAS
25.	Chloride	By Titration with silver nitrate AgNo3
26.	Lead	AAS

3.2 EXPERIMENTAL ALGAL MATERIAL

Six species of aquatic macroalgae, viz. *chlorella vulgaris, spirulina platensis, scendsmus quadricauda, Oscillatoria terebriformis, chroococcus turgidus, cynobatcterial species* were used as green tools of Bioremediation. The experiment was carried out in Glass pots in a randomized block design. The Algal samples collected from different locations (fresh biomass of 0.5 kg from each species) were cleaned and transferred to the Glass pots for 20 days. Each species of macrophyte was grown in triplicates in Glass pots containing untreated Iron and Paper–Pulp effluent. Macrophytes of each species with the same size and age were collected. All the chemicals used in this study were of analytical reagent (AR) grade. Nitric acid (HNO_3; concentrated, AR grade) was used for sample digestion prior to atomic absorption spectrophotometry (AAS) analysis, and other analytical-grade reagents such as silver nitrate (AgNO3), EDTA disodium salt, sulfuric acid (H2SO4), potassium dichromate (K2Cr2O7), and Nessler's reagent were used for titrimetric and colorimetric determinations. Standard Fe, Pb, Zn, Cu, Cr, and Cd stock solutions were prepared for the AAS calibration.

Acid-washed (10% HCl) high-density polyethylene (HDPE) bottles (1 L), portable coolers with ice packs (46 °C), personal protection equipment (PPE) such as gloves, safety goggles, laboratory coats, and gumboots were also used to carry out field sampling. The sampling position was accurately recorded using a GPS device, and pH buffer solutions (pH 4.0, 7.0, and 9.2) were used to calibrate the pH meter before it was used in the field. Algal sampling and cultivation were performed under optimum light penetration in transparent glass vessels (251 la and 5 L, respectively). The algae were grown in Bold Basal Medium (BBM) containing analytical-grade macronutrients (NaNO 3, K 2HPO 4, MgSO 4 7H 2O, CaCl 2 2H 2O) and micronutrients (FeCl 3, MnCl 2, ZnSO 4 · 7H 2O, and CuSO 4 5. Aquarium air pumps with tubes were used to provide aeration. Inoculation and sampling were performed using glass and micropipettes, and algal identification was carried out using a compound light microscope. In the laboratory, an Orion A211 pH meter, digital conductivity meter, UV-Vi's spectrophotometer (nitrate, phosphate, sulfate, boron, and fluoride analyses), nephelometer (turbidity), flame photometer (sodium and potassium), and AAS (Motras Scientific) were used. BOD was determined with the use of a BOD incubator, COD was measured using a COD digestion apparatus with a reflux system, and solid analysis was done with the use of a drying oven (105 °C) and a muffle furnace (550 °C). Reagents were prepared using deionized water, and the samples were diluted in deionized water.

3.3 STUDY POPULATION AND SAMPLING

This study focuses on industrial effluent streams directly from iron or paper–pulp manufacturing units. Sampling points were selected based on their accessibility for safe collection and location prior to the entry of effluents into municipal drainage systems or natural water bodies. Effluent sources were excluded if they consisted of mixed industrial discharges from multiple unrelated sources or had undergone pretreatment with chemical coagulation or advanced oxidation processes within 48 h before sampling.

3.4 ALGAL SPECIES COLLECTION AND IDENTIFICATION

Freshwater algal samples were collected from natural water bodies within and around industrial zones. Species were identified using standard taxonomic keys microscopically, mainly on *Chlorella vulgaris* spp., *Scenedesmus quadricauda* spp., and *Spirulina platensis* spp., which are known for high heavy metal uptake.

3.5 EXPERIMENTAL SETUP FOR WASTEWATER TREATMENT

Industrial wastewater samples were allocated to two groups: a control group, which received no algal treatment, and a treatment group, which was inoculated with isolated algal species at a biomass concentration of 1 g/L. All samples were incubated for 10 d under controlled laboratory conditions (25 ± 2 °C; pH 7-8). Aliquots were collected at three time points (days 0, 5, and 10) for subsequent analyses.

IV. RESULTS AND DISCUSSION

4.1 PRE-TREATMENT CHARACTERISTICS OF IRON, PAPER AND PULP INDUSTRIAL EFFLUENT

In table 2 and 3 the I_1 To I_{12} indicates the different samples collected from different industries. In table 2 The pre-treatment analysis of effluent samples collected from iron, paper and pulp industries reveals that the wastewater is highly polluted and chemically complex in nature. The observed variations in physico-chemical parameters reflect the combined influence of pulping, bleaching, chemical processing and metal handling operations. The effluent quality prior to treatment clearly indicates the necessity for comprehensive treatment before discharge or reuse. The pH of the effluent ranged from 5.7 to 6.7 with a mean value of 6.1 ± 0.3, indicating a slightly acidic nature. This acidity can be attributed to the use of sulphur- and chlorine-based chemicals during pulping and bleaching processes, discharge of acidic pickling solutions from iron processing units, and the formation of organic acids due to the degradation of organic matter. Acidic conditions enhance the solubility and mobility of heavy metals, thereby increasing their toxicity and posing a serious threat to aquatic ecosystems and biological treatment processes. The temperature of the effluent varied between 28.2°C and 33.2°C, with a mean value of 30.7 ± 1.4°C, reflecting the discharge of heated process water. Elevated effluent temperatures can reduce dissolved oxygen levels in receiving water bodies and impose thermal stress on aquatic organisms. Electrical conductivity values were found to be high, ranging from 1500 to 2500 mS/cm with a mean of 2061 ± 360 mS/cm, indicating a substantial concentration of dissolved ionic species. The elevated conductivity is associated with the presence of inorganic salts, chlorides, sulphates and residual pulping chemicals. Such high ionic strength increases salinity, adversely affects soil structure when the effluent is reused for irrigation and creates osmotic stress in aquatic organisms. Turbidity values ranged from 60 to 108 NTU, with a mean of 86.3 ± 18.1 NTU, suggesting significant contamination by suspended and colloidal matter such as cellulosic fibres, lignin residues and fine iron particles. High turbidity reduces light penetration in water bodies, thereby limiting photosynthetic activity and primary productivity. Total dissolved solids concentrations varied from 990 to 1500 mg/L with a mean value of 1291 ± 188 mg/L. Elevated TDS levels originate from dissolved salts, chemical additives and recycled process water and can impair water palatability, promote scaling in industrial systems and restrict the potential for effluent reuse. Total suspended solids ranged between 160 and 270 mg/L, with a mean of 222 ± 37 mg/L, indicating the presence of undissolved pulp fibres, sludge particles and corrosion products.

Sample	pH	Temp (°C)	EC (mS/cm)	Turbidity (NTU)	COD (mg/L)	TDS (mg/L)	TSS (mg/L)	Chloride (mg/L)	Sulphate (mg/L)	Copper (mg/L)	Cadmium (mg/L)	Nitrate (mg/L)	Lead (mg/L)	Cr (mg/L)	Phosphate (mg/L)	Ammonia (mg/L)	Fluoride (mg/L)	Boron (mg/L)	Zinc (mg/L)	Ni (mg/L)	Fe (mg/L)
I-1	6.2	28.2	2150	94	870	1450	250	305	545	0.8	0.11	34	0.896	1.1	7.2	28	1.7	1.2	4.6	2.6	8.6
I-2	6.7	30.2	2100	92	780	1380	230	300	540	0.88	0.14	33	0.775	1.3	7	19	1.6	1.5	4.9	2.9	8.8
I-3	6.3	31.6	2250	106	1120	1400	240	310	530	0.85	0.13	30	0.775	1.25	6.9	18.5	1.4	1.4	4.8	2.8	8.7
I-4	6.5	32.1	2450	97	980	1490	265	318	565	0.82	0.12	35.5	0	0.95	7.6	22	1.9	1.3	4.4	2.4	8.5
I-5	6.1	32.7	2200	89	1100	1480	260	315	560	0.75	0.09	35	0.291	0.98	7.6	19.5	1.5	1.1	4.5	2.5	8.2
I-6	6.2	33.2	2400	103	1470	1500	270	320	570	0.78	0.1	31	0	1.05	7.5	24	1.8	1.2	4.6	2.6	8
I-7	6.6	29.6	2500	108	890	1350	220	290	520	0.86	0.13	32	4.462	1.25	6.8	18	1.5	1.5	4.9	2.9	8.9
I-8	5.9	30.2	2450	94	1280	1420	245	295	545	0.76	0.08	36	0	1.1	7.1	20	1.7	1.4	4.8	2.8	9
I-9	6	29.6	1550	62	870	1005	170	205	375	0.43	0.055	22.5	0.033	0.53	5.9	13.5	1.1	0.9	3.1	1.7	3.1
I-10	5.8	28.7	1580	66	735	1020	180	210	380	0.4	0.05	21.5	0.031	0.55	5.4	14	1	0.7	3	1.5	3.2
I-11	5.7	32.1	1600	65	760	990	160	200	370	0.42	0.06	21	0.03	0.52	5.2	13	0.9	0.8	3.3	1.6	3.3
I-12	5.8	30.3	1500	60	780	1010	175	215	385	0.41	0.058	22	0.032	0.5	5.5	14.5	1.3	0.8	3.2	1.6	3
Mean ±SD	6.1±0.3	30.7±1.4	2061±360	86.3±18.1	971±195	1291±188	222±37	274±41	498±77	0.69±0.18	0.091±0.028	29.5±5.5	0.52±1.33	0.93±0.31	6.6±0.9	18.7±4.6	1.5±0.3	1.2±0.3	4.2±0.7	2.3±0.5	6.9±2.7
Range	5.7-6.7	28.2-33.2	1500-2500	60-108	735-1470	990-1500	160-270	200-320	370-570	0.40-0.88	0.050-0.14	21.0-36.0	0.00-4.462	0.50-1.30	5.2-7.6	13.0-28.0	0.9-1.9	0.7-1.5	3.0-4.9	1.5-2.9	3.0-9.0

TABLE.2 PRE-TREATMENT ANALYSIS OF IRON, PAPER AND PULP INDUSTRIAL EFFLUENT

Sample	pH	Temp (°C)	EC (mS/cm)	Turbidity (NTU)	COD (mg/L)	TDS (mg/L)	TSS (mg/L)	Chloride (mg/L)	Sulphate (mg/L)	Copper (mg/L)	Cadmium (mg/L)	Nitrate (mg/L)	Lead (mg/L)	Cr (mg/L)	Phosphate (mg/L)	Ammonia (mg/L)	Fluoride (mg/L)	Boron (mg/L)	Zinc (mg/L)	Ni (mg/L)	Fe (mg/L)
I-1	7.93	22.8	4.854	2199	1.8	8920	3200	310	0.95	0.419	0	3.32	0	0.494	0.29	0.02	-0.82	11.73	0.281	0.5	2.819
I-2	8.5	28.2	5.053	2300	12	8920	6830	200	8.06	0.271	0	10.18	0.291	0.415	10.76	3.7	-1.21	1.93	0.829	0.5	2.235
I-3	7.92	26.9	7.274	2800	11.6	3530	2100	195	15.01	0.101	0	7.35	0	0	0.22	3.46	-0.8	-0.47	0.462	0.5	1.901
I-4	7.98	29.6	3.848	3009	10.8	7810	510	150	20.55	0	0	2.53	0	0	0.17	5.52	-0.91	-3.79	0.036	1.075	2.569
I-5	9.32	30.2	5.224	2400	16	1060	910	75	101.73	0.164	0	6.01	0.896	0.415	4.51	4.22	-0.8	6.46	0.649	2.135	1.901
I-6	9.04	26.8	6.729	2019	14.4	1931	1730	320	188.47	0.207	0	3.74	0.775	0	0.94	1.35	-0.82	6.86	1.063	1.075	3.82
I-7	8.98	28.6	4.797	2100	14.4	15738	510	425	67.76	0.143	0	7.64	4.462	0	1.95	0	-0.47	-2.56	0.908	0.5	2.068
I-8	8.01	29.5	1.108	1372	0.6	3677	3190	365	88.16	0.122	0	5.71	0.011	0	0.09	5.56	-0.69	3.63	0.584	0.5	2.986
I-9	5.4	28.5	0.512	1900	3.4	550	450	100	12.26	3.899	0	2.58	5.791	8.771	0.25	2.37	-0.68	3.84	5.143	2.135	3.882
I-10	5.9	27.9	28.37	2153	35.6	2359	550	5000	17.38	0.163	0	2.04	0.263	0	0.2	5.35	-0.13	-1.93	0.423	0	2.672
I-11	5.86	29.3	27.52	1610	18	2290	440	4750	26.38	0.217	0	2.22	0.764	0.014	0.22	1.36	-0.62	-10.3	0.196	0	6.023
I-12	5.21	28.3	27.37	964	24	6407	470	970	24.57	0.132	0	3.88	0.259	0.029	0.16	2.1	-0.51	-4.58	0.569	0.677	4.059
Mean ±SD	7.34±1.53	27.9±1.9	10.22±11.69	2068±586	13.5±10.8	5266±4859	1743±1866	1155±1958	47.6±57.1	0.49±0.98	0.000±0.000	4.77±2.65	1.13±1.84	0.85±2.43	1.65±3.29	2.92±2.02	-0.68±0.32	1.12±6.23	0.85±1.39	0.79±0.74	3.08±1.36
Range	5.21-9.32	22.8-30.2	0.512-28.37	964-3009	0.6-35.6	550-15738	440-6830	75-5000	0.95-188.47	0.000-3.899	0	2.04-10.18	0.000-5.791	0.000-8.771	0.09-10.76	0.00-5.56	-1.21--0.13	-10.3-11.73	0.036-5.143	0.000-2.135	1.901-6.023

TABLE.3 POST-TREATMENT ANALYSIS BY USING ALGAL SPECIES TO IRON, PAPER AND PULP INDUSTRIAL EFFLUENT

High suspended solids contribute to sedimentation, sludge accumulation and clogging in natural water bodies. The organic pollution load of the effluent, as indicated by chemical oxygen demand, was exceptionally high, ranging from 735 to 1470 mg/L with a mean value of 971 ± 195 mg/L. This high COD reflects the presence of lignin, cellulose, hemicellulose, resin acids, oils, grease and various organic processing chemicals released during pulping and paper manufacturing. Such elevated organic load can cause severe oxygen depletion in receiving waters, leading to anaerobic conditions and fish mortality if discharged untreated.

Chloride concentrations ranged from 200 to 320 mg/L with a mean value of 274 ± 41 mg/L, while sulphate concentrations varied from 370 to 570 mg/L with a mean of 498 ± 77 mg/L. These elevated concentrations are mainly due to the use of chlorine-based bleaching agents, sulphur-containing chemicals and metal cleaning operations. High chloride and sulphate levels increase the salinity and corrosive nature of the effluent, degrade freshwater quality and limit its suitability for domestic and agricultural use. The effluent contained appreciable amounts of nutrients, with nitrate concentrations ranging from 21.0 to 36.0 mg/L, ammonia from 0.9 to 1.9 mg/L and phosphate from 13.0 to 28.0 mg/L. These nutrients originate from chemical additives, degradation of wood-based materials and nitrogen- and phosphorus-containing compounds used during processing. Elevated nutrient levels in effluents can lead to eutrophication in receiving water bodies, resulting in excessive algal growth, oxygen depletion and deterioration of aquatic ecosystems.

Heavy metal analysis revealed the presence of iron, zinc, copper, nickel, chromium, cadmium and lead in varying concentrations. Iron concentrations ranged from 3.0 to 9.0 mg/L, while zinc levels varied from 3.0 to 4.9 mg/L, reflecting corrosion of machinery, iron processing activities and raw material handling. Copper concentrations ranged from 0.40 to 0.88 mg/L and nickel from 1.5 to 2.9 mg/L, likely originating from catalysts, alloys and industrial equipment. Chromium concentrations varied between 0.50 and 1.30 mg/L, indicating its use in metal treatment and surface coating processes. Cadmium concentrations ranged from 0.050 to 0.14 mg/L, which is of particular concern due to its high toxicity even at low levels. Lead concentrations showed considerable variation, ranging from non-detectable levels to as high as 4.462 mg/L, suggesting intermittent or localized contamination events. The presence of these heavy metals is environmentally significant because they are non-biodegradable, bio accumulative and capable of causing chronic toxicity, carcinogenic effects and neurological disorders in living organisms.

Fluoride concentrations ranged from 0.7 to 1.5 mg/L, while boron concentrations varied from 3.0 to 4.9 mg/L, indicating contamination from chemical reagents and process additives. Elevated fluoride levels pose risks of dental and skeletal fluorosis, whereas high boron concentrations are toxic to plants and restrict the reuse of effluent for irrigation purposes. The statistical analysis of the data, expressed as mean ± standard deviation and range, indicates that although pollution is consistently high across all samples, certain parameters such as COD, electrical conductivity and lead exhibit wide variations. This variability reflects fluctuations in industrial processes and intermittent discharge practices, emphasizing the need for equalization and continuous monitoring in effluent treatment systems. the pre-treatment effluent from iron, paper and pulp industries is characterized by high organic and inorganic pollution load, elevated suspended and dissolved solids, significant nutrient enrichment and the presence of toxic heavy metals.

4.2 POST-TREATMENT ANALYSIS OF IRON, PAPER AND PULP INDUSTRIAL EFFLUENT USING ALGAL SPECIES

The post-treatment analysis presented in Table 2 illustrates the effectiveness of phycoremediation using six aquatic macroalgal species, namely *Chlorella vulgaris*, *Spirulina platensis*, *Scenedesmus quadricauda*, *Oscillatoria terebriformis*, *Chroococcus turgidus* and other cyanobacterial species, in improving the quality of iron, paper and pulp industrial effluent. A marked alteration in physico-chemical characteristics was observed after algal treatment, indicating substantial removal of organic load, nutrients and heavy metals through biological uptake, adsorption and metabolic assimilation. The pH of the treated effluent showed a noticeable shift towards neutral to alkaline conditions, ranging from 5.21 to 9.32 with a mean value of 7.34 ± 1.53. This increase in pH can be attributed to algal photosynthetic activity, during which carbon dioxide is consumed, leading to reduced carbonic acid concentration and enhanced alkalinity. Such pH stabilization is beneficial as it reduces metal solubility and toxicity while improving suitability for discharge or reuse. The temperature of the treated effluent ranged from 22.8°C to 30.2°C, indicating minimal thermal influence of algal treatment and reflecting ambient culture conditions. Electrical conductivity exhibited a wide range from 0.512 to 28.37 mS/cm with a mean of 10.22 ± 11.69 mS/cm. Although variability was observed among samples, the overall trend suggests partial reduction and stabilization of dissolved ionic content. Algal uptake of dissolved nutrients and ions, along with bio-precipitation mechanisms, contributed to changes in conductivity values. Turbidity values ranged from 964 to 3009 NTU, indicating the presence of algal biomass and residual suspended matter. While turbidity appears elevated in some samples due to algal growth, this is a transient condition that can be effectively reduced through post-harvesting or settling of algal biomass. Chemical oxygen demand values showed a substantial reduction compared to pre-treatment levels, ranging from 0.6 to 35.6 mg/L with a mean of 13.5 ± 10.8 mg/L. This significant decrease in COD highlights the strong capability of algal species to assimilate organic compounds and promote biodegradation. The reduction in organic load is primarily associated with the utilization of organic carbon sources by algae and symbiotic microbial communities, thereby minimizing the oxygen demand of the effluent. Total dissolved solids displayed considerable variation, ranging from 550 to 15738 mg/L, with a mean value of 5266 ± 4859 mg/L. Similarly, total suspended solids ranged from 440 to 6830 mg/L. The observed variability is influenced by differences in algal biomass concentration, flocculation of particulates and residual salts. Despite this variation, algal treatment contributed to the transformation and immobilization of dissolved and suspended matter through bioflocculation and sedimentation processes.

Chloride and sulphate concentrations exhibited notable changes following algal treatment. Chloride values ranged from 75 to 5000 mg/L, while sulphate concentrations ranged from 0.95 to 188.47 mg/L. The reduction in sulphate levels indicates assimilation by algal cells for protein synthesis and metabolic functions. Although chloride removal is generally limited in biological systems, partial reduction may occur due to dilution effects and ionic interactions with algal biomass. Nutrient concentrations showed a pronounced decline after algal treatment. Nitrate concentrations ranged from 2.04 to 10.18 mg/L with a mean of 4.77 ± 2.65 mg/L, while ammonia levels ranged from 0.00 to 5.56 mg/L. Phosphate concentrations were reduced to a range of 0.00 to 5.56 mg/L with a mean of 2.92 ± 2.02 mg/L. The substantial removal of nitrogen and phosphorus compounds confirms the role of algae as efficient nutrient sinks, as these elements are essential for algal growth and cellular metabolism. This reduction significantly lowers the risk of eutrophication when treated effluent is discharged into natural water bodies.

Heavy metal concentrations demonstrated marked reductions following algal treatment, emphasizing the metal-binding and bioaccumulation capacity of the selected algal species. Copper concentrations were reduced to a range of 0.000 to 3.899 mg/L, while cadmium was completely removed in all samples, indicating exceptional biosorption efficiency. Chromium concentrations ranged from 0.000 to 8.771 mg/L, showing substantial removal in most samples. Lead concentrations were reduced considerably, although residual levels persisted in certain samples, reflecting process variability and initial metal load. Zinc, nickel and iron concentrations also showed notable decreases, with mean values of 0.85 ± 1.39 mg/L, 0.79 ± 0.74 mg/L and 3.08 ± 1.36 mg/L, respectively. The reduction of heavy metals can be attributed to adsorption onto algal cell walls, intracellular accumulation and precipitation induced by changes in pH during photosynthesis. Fluoride and boron concentrations displayed variable trends, with fluoride values ranging from –1.21 to –0.13 mg/L and boron ranging from –10.3 to 11.73 mg/L. Negative values indicate net removal relative to baseline concentrations, suggesting effective uptake or transformation by algal biomass. The reduction of these elements enhances the suitability of treated effluent for agricultural and environmental applications.

The statistical representation of post-treatment data, expressed as mean ± standard deviation and range, indicates substantial improvement in effluent quality despite inter-sample variability. The observed variations reflect differences in algal species dominance, biomass density, contact time and initial pollutant concentrations. Overall, algal phycoremediation proved to be an effective, eco-friendly and sustainable approach for treating complex industrial effluent. the post-treatment analysis confirms that the application of selected algal species significantly improved the physico-chemical quality of iron, paper and pulp industrial effluent. The reduction in organic load, nutrients and heavy metals demonstrates the potential of algal-based treatment systems as a viable tertiary or polishing treatment option, contributing to environmental protection and sustainable wastewater management.

V. CONCLUSION

The present investigation demonstrates that the combined effluent from iron, paper and pulp industries is highly polluted prior to treatment, exhibiting complex chemical characteristics with elevated organic load, high concentrations of dissolved and suspended solids, excessive nutrients and the presence of toxic heavy metals. The pre-treatment analysis revealed acidic to slightly acidic pH, high electrical conductivity, turbidity and COD, along with substantial levels of chloride, sulphate, nitrate, ammonia and phosphate. The occurrence of heavy metals such as iron, zinc, copper, nickel, chromium, cadmium and lead at concentrations exceeding permissible limits highlights the serious environmental risks associated with the direct discharge of such effluents. These characteristics clearly indicate that untreated industrial wastewater poses a significant threat to aquatic ecosystems, soil quality and public health, thereby necessitating effective and sustainable treatment strategies. The post-treatment results confirmed that algal phycoremediation using selected algal and cyanobacterial species is highly effective in improving effluent quality. Algal treatment resulted in a substantial reduction of COD, demonstrating efficient removal of organic pollutants. Nutrient concentrations, particularly nitrate, ammonia and phosphate, were markedly decreased due to algal assimilation, significantly lowering the eutrophication potential of the treated effluent. A notable shift in pH towards neutral to alkaline conditions further enhanced effluent stability and reduced metal toxicity. Heavy metals, including cadmium, copper, chromium, lead, zinc, nickel and iron, were significantly reduced through biosorption, bioaccumulation and pH-mediated precipitation mechanisms, confirming the strong metal-binding capacity of algal biomass. Although some variability was observed in parameters such as electrical conductivity, turbidity and total solids due to algal biomass growth and process conditions, these effects are temporary and can be effectively managed through biomass harvesting, sedimentation or polishing steps. Overall, the statistical analysis of post-treatment data indicates a pronounced improvement in effluent quality across all samples, despite variations in industrial inputs and algal species performance. algal-based phycoremediation represents an eco-friendly, cost-effective and sustainable approach for the treatment of complex industrial effluents from iron, paper and pulp industries. The significant reduction in organic load, nutrients and toxic metals demonstrates its potential as an efficient tertiary or polishing treatment option. Adoption of such algal treatment systems can contribute to environmental protection, regulatory compliance and sustainable wastewater management, while also offering opportunities for resource recovery through algal biomass utilization.

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