



Processing Technology and Wastewater Characterization of a Rice Mill in the District of Raipur Chhattisgarh India

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Abstract

A comprehensive investigation was performed to know the processing technology and salient features of the rice mill wastewater in the district of Raipur, Chhattisgarh. The production capacity of the rice mill was 240 million metric tons per day (MT/day). The characterization of the wastewater divulged a high concentration of biochemical oxygen demand (3,518 mg/L), chemical oxygen demand (5,265 mg/L), total hardness (2,240 mg/L as CaCO₃), total solids (3,928 mg/L), total organic solids (3,008 mg/L), and a chloride content (748 mg/L) as well as a moderate concentration of sulfate (71 mg/L), orthophosphate (76 mg/L), sodium (69 mg/L), volatile fatty acids (307 mg/L), total inorganic solids (921 mg/L) and total suspended solids (953 mg/L). The wastewater had an acidic pH (5.24) with low concentrations of oil and grease (17 mg/L), nitrate (21 mg/L), phenols (14.7 mg/L), and dissolved oxygen content (1.2 mg/L). Furthermore, the wastewater was enriched in sodium (69 mg/L), potassium (495 mg/L), lignin (148 mg/L), and calcium hardness (1,906 mg/L). The overall wastewater characteristics do not meet the norms of discharge standards for industrial effluents on the land surface for irrigating agricultural crops or into the surface water bodies.

Key Words: Hydrothermal treatment, Gelatinization, Soaking, Steaming, Rice bran

Introduction

Wastewaters emanating from various industrial activities include higher concentrations of organic and inorganic materials causing significant pollution scenarios. To sustain the continuity of our global water resources and water supply, many environmental operation programs have been established to address pollution problems. Many environmental regulations, legislations, and directives have been formulated aimed at defining effluent quality standards. The high biochemical oxygen demand, chemical oxygen demand, dissolved solids, alkalinity, and hardness still pose a financial problem for the stakeholders since these have been designated as primary parameters for effluent discharge (Ahmed et. al. 2005, Rodrigues et al. 2007). Waste may be categorized into three groups: solid, liquid, and gaseous. Liquid waste may be referred to as wastewater mainly comprised of utilized water blended with dissolved and suspended solids, human and animal excreta, culinary waste, and industrial sewage. When the wastewater is released untreated or undertreated in the environment, it causes severe damage to the environment and ecology. Various

industries' environmental, economic, and social impacts have led to foreseeable conflicts between industrial development and ecological sustainability. The wastewaters have adverse effects on biodiversity, due to their natural mobility. There can be severe adverse effects without appropriate ameliorations when they are disposed of into water bodies (Alderson et. al. 2015).

Food demand has been tremendously enhanced worldwide with the world's growing population. The prime foodgrain crops are- rice, wheat, maize, and millet. Rice, which is obtained from paddy by milling operations, is a paramount food staple of the earth, and 90% of the production and consumption of rice occur in Asian countries (Choudhary et al. 2015). India ranks first in areas sown under paddy crops and second in paddy production, followed by China in the world. The five-pioneer rice-producing countries of the world are- China, India, Indonesia, Bangladesh, and Vietnam. The apex ten paddy-cultivating countries including India are responsible for almost 85% of the world's rice production and all countries are located in Asia except Brazil, which is in South America. (World Economic Forum 2022). The contribution of India to the world's rice production is 21.5% in the financial year 2021-2022. In India, paddy acreage has increased from 43.66 million hectares (MHa) in 2019-2020 to 45.5 MHa in 2021-2022.

Rice production is a swiftly growing industry that plays a key role in the global economy. As a result, rice mill wastewater treatment is a consequential concern. The management practices of wastewater adopted in most rice mills are the disposal of a vast amount of wastewater through conduits or open drainage systems. They, sometimes use chemicals prior to wastewater discharge but mostly they don't bother environmental and ecological safety. They generally use chemicals for the safety of their boiler and the quality of the rice produced. Then, they discharge the wastewater along the roadside or into ponds and lakes, or in the municipal drains, which leads to a great threat to the environment. It causes a disagreeable odor promoting the mosquito's growth, degrades water quality, encourages pathogenic microorganisms resulting in the spread of waterborne diseases, and gradually fills the ponds and lakes. For proper living and sound health of citizens, it is essential to increase awareness about a hygienic environment. Consequently, this vast amount of wastewater originating from rice mills must be properly treated and managed so that it may not harm human and animal lives as well as the environment. For this, it is necessary to know the chemical ingredients of the wastewater.

Rice is the main diet of 40% of the population of India. India's top ten states producing rice are- West Bengal, Uttar Pradesh, Punjab, Tamil Nadu, Andhra Pradesh, Bihar, Chhattisgarh, Odisha, Assam, and Kerala. Chhattisgarh stands 7th in rice production in India and produces 6.0% of the net production of rice in the country. The area under rice in Chhattisgarh is 3.6 MHa. Chhattisgarh is divided into three climatological zones: the Chhattisgarh plains, the Bastar plateau, and the Northern Hill regions of Surguja. Rice is cultivated in almost all 33 districts of Chhattisgarh. The production of rice in Chhattisgarh in the financial year 2009-2010 was 4.1 million metric tons (MT), which increased to 7.1 MT in the year 2021-2022 registering an increase of 73.17%, which is a breakthrough achievement in this sector. Rice production in the state in the financial year 2020-2021 was 6.5 mt. (DACR, 2021-2022).

As a consequence of the massive production of paddy in Chhattisgarh and the demand for edible rice from the consumer market, the rice milling industry is gaining momentum in the state in the previous few years. Nowadays, there are more than 1,500 rice mills in Chhattisgarh and approximately 450 rice mills are situated in Raipur District including Nawapara town commonly known as the rice hub of Raipur District. The milling capacities of these rice mills vary from 10 mt/day to 250 mt/day (DCIC 2021-2022). However, the stakeholders in this agro-industrial sector do not release sufficient details on the chemical constituents of the wastewater. Furthermore, much information regarding the characteristics of rice mill wastewater is not available in the public domain to date. Though a handful of researchers have found some constituents of this wastewater, they are quite limited.

Giri et. al. 2016 analyzed 6 parameters of rice mill wastewater (RMWW) and found pH, BOD, COD, TDS, TSS, and nitrogen contents to be 4.67-4.90, 3968-4464 mg/L, 6400-7200 mg/L, 4187-5134 mg/L, 1386-2340 mg/L, and 62-80 mg/L respectively. Ramprakash and Muthukumar 2018 determined 5 parameters of RMWW and found pH, BOD, COD, TDS, TSS, and nitrogen contents to be 5.10, 6900 mg/L, 18600 mg/L, 4720 mg/L, and 31 mg/L respectively. Rambabu et. al. 2019 found 5 parameters of RMWW- pH, BOD, COD, TDS, TSS, and nitrogen contents to be 6.30, 9600 mg/L, 19800 mg/L, 8500 mg/L, and 39 mg/L respectively. Anuf et. al. 2022 also analyzed 5 parameters of RMWW- pH, BOD, COD, TDS, TSS, and nitrogen contents to be 5.30, 3435 mg/L, 5279 mg/L, 4327 mg/L, and 45 mg/L respectively. Raychoudhury and Behera 2022 determined 7 parameters of RMWW- pH, BOD, COD, TDS, TSS, lignin, and phenol contents to be 5.40, 1450 mg/L, 3150 mg/L, 3300 mg/L, 220 mg/L, 417 mg/L, and 4.97 mg/L respectively. Raychoudhury et. al. 2022 found 5 parameters of RMWW- pH, BOD, COD, TDS, and phenol contents to be 5.40, 1350 mg/L, 2800 mg/L, 3300 mg/L, and 4.95 mg/L respectively.

In the present study, the authors have executed an extensive investigation in the Raipur district of Chhattisgarh to visualize the processing technology of the rice mill industry and determined 27 physicochemical parameters after elaborative analyses in triplicates of the samples of wastewater emanating from this industry. The novelty of this research paper is that it incorporates a total of 27 physicochemical characteristics of the wastewater as well as a sufficient sample size of 15 viz., S1, S2, S3, S15 for analyses, that are not available in the public domain to date, and, consequently it will prove a milestone for the researchers, academicians, and stakeholders.

Processing Technology of the Rice Milling Industry

The paddy crop is harvested from the field and is threshed in a thresher to get paddy grains. Though it may be directly obtained from the field with the help of a combine harvester, in which reaping (harvesting), threshing and winnowing operations take place simultaneously and grains are directly collected in separate bags. The grains are thereafter transported to the rice mill, and cleaned by paddy cleaner to segregate the impurities like pebbles, stones, gravel, soil clods, etc. Then the paddy grains undergo a milling process if raw rice is to be produced. But if the stakeholder wants to produce the parboiled rice, it has to undergo three sequential processes: parboiling, drying, and ultimately milling.

Principle of parboiling

Parboiling is a hydrothermal treatment of paddy that promotes starch molecules within the rice kernels to gelatinize. It causes irreparable bump and bonding of starch molecules that transform the starch from a crystal structure to a shapeless one. By virtue of it, the precise prismatic structure of the starch molecules transforms into a consistent lump (Rao and Juliano 1970). The pertinent transformation due to parboiling is the starch-gelatinization and the decomposition of protein molecules in the rice grains. Consequently, the protein and starch enlarge and fill the intramural air voids. The starch molecules are meticulously squeezed to create indestructible cohesion among them, which seals the ruptures and fissures in the endosperm rendering the grains diaphanous and rigid enough to accommodate the forces imposed by the milling process. It enhances the net production of intact rice grains and minimizes the mass of brokens.

Paddy-parboiling comprises three distinct steps: soaking in a soaking tank, steaming from the boiler, and drying in sunlight or in a mechanical dryer. During the soaking of paddy in the soaking tank, water ingresses into the microscopic pores in the rice kernel and hull and the starch molecules, in turn, suck up water and expand, creating a significant volume increase in paddy grains (Ali and Pandya 1974). Steaming facilitates exposure of soaked paddy grains to the heat of steam for a fixed span of time, which enables gelatinization of the starch molecules in the rice grains. Eventually, the steamed paddy is wilted to a moisture content of 14 to 16% by drying, imparting the requisite harshness to the grains required for withstanding the milling stress.

Processing technology adopted for parboiled rice production in Chhattisgarh

The cleaned paddy devoid of impurities is soaked in hot water at a temperature of 70-80°C for 6 to 8 hours in a big soaking tank (handi), in which the paddy is taken with the help of a mechanized bucket conveyer. In the soaking tank, the stakeholders generally add urea (NH_2CONH_2) and table salt (NaCl) as additives to impart the glazing to rice and inhibit the boiling point of soaking water respectively. The soaking water is facilitated from the overhead tank, in which water is stored by pumping the groundwater from tube wells with the help of an electric motor. After proper soaking for the specified duration, the soaked paddy is drained, as a result of which, the wastewater comes out of the parboiling tank and is stored in artificial trenches made for wastewater collection.

When the draining of the soaked paddy is complete, the steaming of the drained soaked paddy is accomplished by superheated and saturated steam at 100°C temperatures pressurized at 10^5 to 5×10^5 Pa (N/m^2). The steam is supplied from the boiler, which makes use of rice husk (RH) as fuel, and groundwater for generating steam. The steaming time depends on the amount of paddy and varieties of paddy. Steaming generally takes 2-3 minutes for small batches whereas it takes about 20-30 minutes for larger batches of 6 to 8 metric tons. Splitting of the paddy husk is considered an indicator of the accomplishment of the steaming process. When the steaming is accomplished, the steamed paddy is conveyed to the mechanical dryer or to the open ground for drying. In the open ground, the steamed paddy is exposed to the ambient atmosphere and is kept for drying in direct sunlight. If the mechanical dryer is employed for drying the steamed paddy, RH is used as its fuel. When the paddy is dried up to a water content of about 14 to 16%, it is taken to the milling section for the milling of dried paddy.

The paddy is first cleaned in the milling section and then taken to the rubber roll shelling unit for de-husking. The de-husked paddy is then passed across the husk aspirator to segregate the husk from the brown unpolished rice. The brown unpolished rice is then taken to the polishing unit, where bran is separated from the brown rice, and polished rice is obtained. Ultimately, the polished rice is passed through the rice grading machine, which separates the brokens from the whole rice grains. Both the intact rice and the brokens are separately packed in bags after weighing properly. Finally, the packed whole rice and the brokens are transported to the consumer market via a proper food supply chain. From Chhattisgarh, the stakeholders directly export the graded whole rice grains and brokens in packed bags to foreign countries apart from marketing in the native country. China is a good importer country of brokens from Chhattisgarh. Chinese stakeholders produce noodles from broken rice, which is the primary food intake of the Chinese people.

Rice bran (RB) and RH are the two important byproducts of this industry. Bran is transported to the bran oil extraction industry for producing bran oil, which is popularly used in Chhattisgarh and adjoining states like Odisha, Madhya Pradesh, Maharashtra, etc. as an edible oil in the kitchen. RH is also a very good building material from an infrastructure point of view apart from its use at the point of generation itself. It is used in manufacturing high-density fiberboard (HDF) which is further applied to manufacture doors, roofs, partitions, furniture, etc. Rice husk ash (RHA) also called agro-silica is a very good admixture that enhances the workability of fresh concrete. RHA is also used in producing geopolymer binders.

Waste Generation from the Rice Milling Industry

The rice mill industry brings forth wastes primarily in liquid, solid and gaseous forms. A big or medium rice mill producing parboiled rice usually generates liquid in the form of wastewater from the following operations: paddy-soaked wastewater, parboiling wastewater, and boiler blowdown wastewater. The wastewater from these operations finally conveys through a common pipe drain to the outskirts of the rice mill periphery into an artificial trench and this is commonly referred to as rice mill wastewater or rice mill effluent. On the other hand, a small rice mill or a huller mill producing the parboiled rice generates wastewater from the open steaming process as parboiling is directly done in a number of metal containers having fresh tube well water in them and RH is used as fuel for boiling of water. The wastewater emanating from these metallic containers after the completion of the parboiling process is passed through a common drain to an artificial ditch made for wastewater collection. A flow diagram of the processing technology of a rice mill producing parboiled rice with origins of wastewater is given in Figure 1.

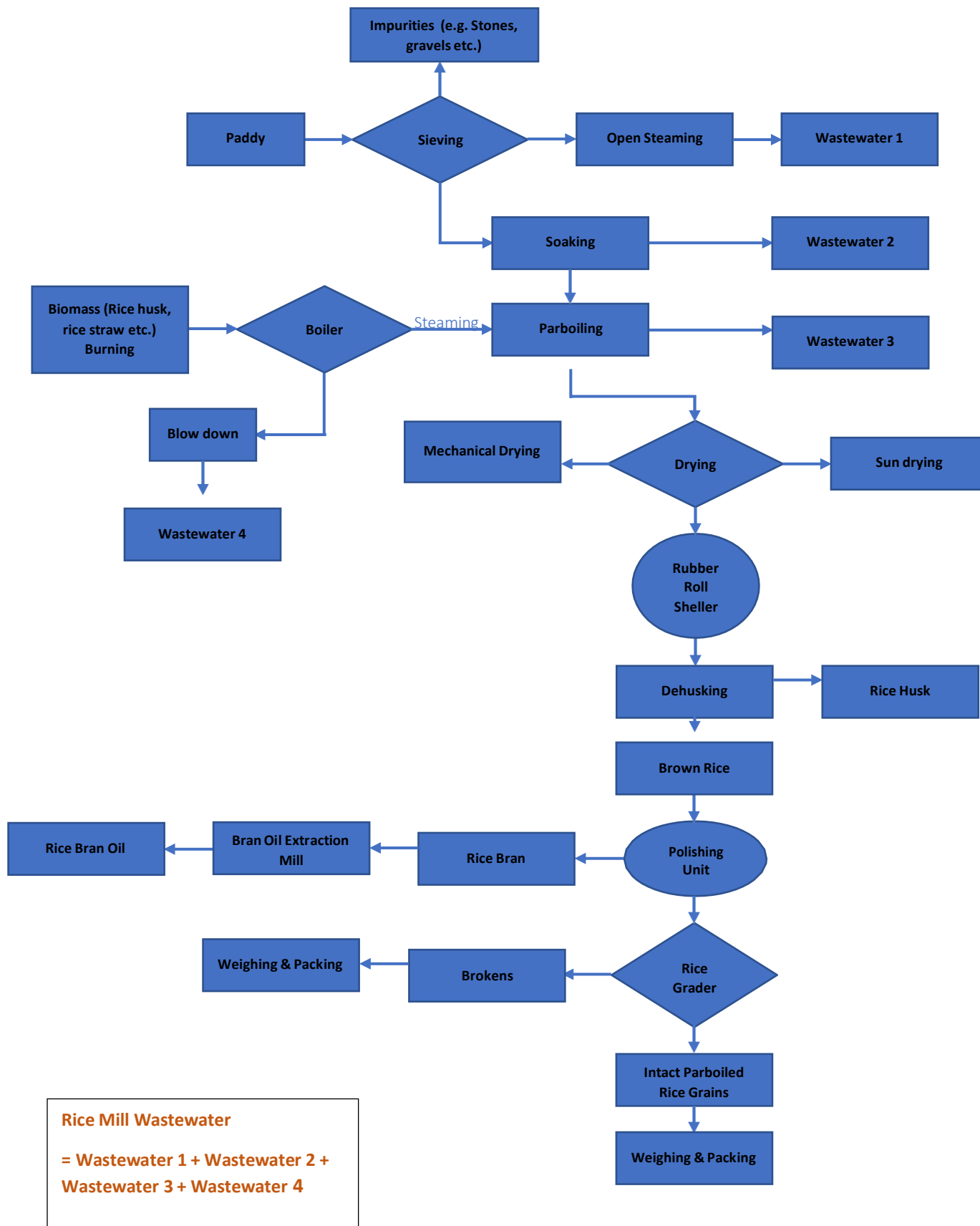


Figure 1. Flow diagram of processing technology of a parboiled rice mill with origins of wastewater

Apart from the liquid wastes, RH and ash obtained from the combustion of RH constitute the main volume of solid wastes. However, the major bulk of RH is reutilized in the rice mill for operating the boiler, and the remaining volume is purchased and transported by the manufacturers dealing with High-Density Fireboard/Hardboard (HDF) manufacturing. Thus, solid wastes emanating from a rice mill is ash left after the combustion of RH for the boiler operation. The gaseous pollutants primarily emitted from a rice mill are nitric oxide (NO), nitrogen dioxide (NO₂) sulfur oxide or sulfurous acid anhydride (SO₂), and carbon monoxide (CO).

Sampling of the Wastewater and its Analysis

The rice mill wastewater samples were taken from the parboiling unit of a rice mill, 45 kilometers distant from the National Institute of Technology Raipur premises, having a milling capacity of 240 MT/day. A total no. of fifteen samples viz. S₁, S₂, S₃, S₄, S₅.....S₁₅ were collected at different times on different days and in different seasons- monsoon, pre-monsoon, post-monsoon, summer, and winter starting from January 2022 to March 2023. The samples were taken in low-density polyethene (LDPE) bottles of 1.0 L capacity each. On each sampling occasion, the rice mill wastewater sample (RMWW) was collected in triplicate. The pH and dissolved oxygen (DO) content of each sample were determined at the wastewater collection site with the aid of the digital pH meter and DO meter having membrane-electrode technology respectively.

The biochemical oxygen demand (BOD) of each sample was determined immediately after arriving at the NIT Raipur campus in the Environmental Engineering Lab. A total of 27 parameters of each sample were determined for the physicochemical characterization of the wastewater, out of which two parameters- pH and DO were determined in the rice mill premises at the time of sampling. The remaining 25 parameters such as total alkalinity (TA), total hardness (TH), Ca- hardness, Mg-hardness, electrical conductivity (EC), turbidity, chemical oxygen demand (COD), biochemical oxygen demand (BOD), total solids (TS), total dissolved solids (TDS), total suspended solids (TSS), total organic solids (TOS), total inorganic solids (TIS), chloride, sulfate, nitrate, lignin, phenol, volatile fatty acids (VFA), etc. were determined within fifteen days in our Institute's lab after properly preserving the samples in the laboratory fridge at 4°C.

For each sampling, three LDPE bottles of 1.0 L capacity each were used. The first bottle was filled with absolute RMWW without acidification for determining BOD, TA, TH, Ca-hardness, Mg-hardness, VFA, sulfate, chloride, lignin, etc. The second bottle filled with RMWW was acidified with 2 mL of Conc. H₂SO₄ for determining COD, total Kjeldahl nitrogen (TKN), nitrate (NO₃), phosphate (PO₄), oil and grease, phenol (C₆H₅OH), etc. The third bottle filled with RMWW was acidified with 2 mL of Conc. HNO₃ for determining sodium (Na) and potassium (K). The procedure of taking RMWW in all three bottles is repeated during each sampling at the point of sample collection. All three bottles filled with wastewater samples during each sampling were preserved in the laboratory refrigerator at 4°C temperatures to maintain the integrity of the constituents of the sample.

Results and Discussion

The physicochemical characterization of the rice mill wastewater was performed by analyzing all 15 samples. A total number of 27 parameters were examined as per the methods incorporated in the Standard Methods for the Examination of Water and Wastewater by APHA, AWWA, and WWF (2017) 23rd Edition, which is mentioned as follows:

1. pH - It measures the hydrogen ion (H^+) content present in the wastewater and designates the severity of acidity or basicity of the wastewater sample. Mathematically, it is computed as, $pH = -\log [H^+]$. Its value generally ranges from 0 to 14. The pH value influences the chemical and biochemical reactions in wastewater. The favorable pH for anaerobic digestion is 6.5 to 8.5 because the methanogens cannot work beyond this limit. The H^+ content of water is affected by the disintegration of water molecules. It is also influenced by the relationship between the carbonic acid (H_2CO_3) concentration and its ions (H^+ , CO_3^{2-}) as well as by the production of these ions from the humic acids ($C_9H_9NO_6$). The pH analyses of the 15 RMWW samples show that the wastewater emanating from the rice mill is moderately acidic. The pH of the sample varied from 4.28 to 6.08 and the average pH value is 5.24. The pH of the sample S10 is 4.28 whereas that of S13 is 6.08. Thus, the pH of the RMWW was not within the permissible value of BIS (5.5 to 9.0) recommended for the disposal of industrial effluents into surface water bodies (BIS 1974) or on the land surface for irrigating agricultural crops (BIS 1977).

2. Color – The color of the RMWW samples was visualized by the naked eyes one by one. It was found to be faint yellow to faint brown. The color of samples S1 to S3 and S11 to S15 was faint yellow, whereas samples S4 to S10 were faint brown. The color of RMWW is seen due to the turbidity of the wastewater that is caused by the inorganic and organic substances as well as coloring materials present in the wastewater. The characteristics of the rice mill effluent (RME) including color depend upon the varieties of paddy to be soaked for parboiling, parboiling temperature, duration of parboiling as well as temperature and duration of steaming.

3. Electrical Conductivity (EC) - The electrical conductivity (EC) or simply conductivity of a wastewater or an aqueous solution is its capability to conduct electricity within it. It relies upon the presence of ions (cations and anions), the total concentration of ions, their mobility, and the valency of the ions, as well as on the temperature of the wastewater. The wastewater comprising inorganic compounds is a good conductor, whereas that having organic compounds which scarcely dissociate in an aqueous solution is a poor conductor of electricity. The SI unit of EC is milli siemens per meter (mS/m). $1 \text{ mS/m} = 10 \text{ } \mu\text{S/cm}$. The value of EC in $\mu\text{S/cm}$ is divided by 10 to express it in mS/m. The EC of RMWW samples comprising both inorganic and organic compounds was measured by the electrical conductivity meter. It directly gave EC of the wastewater in $\mu\text{S/cm}$, when the probe of the conductivity meter was dipped inside the wastewater sample. The EC of the RMWW samples varied from 4.05 $\mu\text{S/cm}$ to 7.50 $\mu\text{S/cm}$ and the average EC of the samples was 5.84 $\mu\text{S/cm}$. The EC of sample S10 was 4.05 $\mu\text{S/cm}$, whereas that of S13 was 7.50 $\mu\text{S/cm}$.

4. Turbidity - The turbidity of a wastewater sample is a declaration of the ocular property that motivates the light rays to be dispersed and soaked up rather than conveyed with no change in flux level or direction of the rays through the sample. It is caused due to the colloidal and suspended silt, clay, organic and inorganic materials, phytoplankton zooplankton, and other microorganisms present in the wastewater. It depends on the size, shape, and refractive index (RI) of the particulates. It hinders the penetration of the sunlight with a reduction in photosynthetic activity along with the depleted oxygen level and renders the water incongruous for use. It is measured by the Nephelometric Turbidity Meter and is expressed in Nephelometric Turbidity Unit (NTU). The least count (LC) of the instrument is 0.02 NTU. In our study, the turbidity of the RMWW samples ranged from 32.4 NTU to 38.5 NTU and the average turbidity of the samples was 38.5 NTU. The turbidity of the sample S10 was minimum (32.4 NTU), whereas that of S13 was maximum (43.8 NTU).

5. Dissolved Oxygen (DO) - Molecular oxygen present in water and wastewater in soluble forms is referred to as dissolved oxygen (DO). It is a key indicator of water quality. Its concentration depends upon the bio-physicochemical actions in water-both lentic and lotic. DO determination is a paramount test for knowing the strength of wastewater and accordingly, the organic loads to be imposed on the treatment plants. DO is necessary for the sustenance of underwater creatures including fish. Oxygen gets dissolved in inland waterbodies owing to the agitating activities of breezes, storms, and hurricanes. It is also enhanced due to the photosynthetic activities of aquatic plants. Oxygen solubility is less in salt-containing water in comparison with fresh and clean water. DO contents of the clean and fresh water at 0°C and 30°C are 14.6 mg/L and 7.6 mg/L respectively under 1 atm. pressure, whereas those of the marine water at 0°C and 30°C are 11.3 mg/L and 6.1 mg/L respectively at the same pressure. Oxygen solubility in water depends upon the temperature and pressure. The higher the temperature, the lower will be the solubility, and the higher the pressure, the higher will be the solubility of oxygen due to the increase in the collision frequency of oxygen molecules and vice-versa. In our study, the DO content of the RMWW samples varied from 0.9 mg/L to 2.2 mg/L and the average DO concentration of the samples was 1.5 mg/L. The DO content of the sample S13 was 0.9 mg/L whereas that of S10 was 2.2 mg/L.

6. Total Alkalinity (TA) – The alkalinity or total alkalinity (TA) of water or wastewater is its capability to counteract acids and is the sum total of all titratable bases (TB). It is recognized by the existence of hydroxide ions (OH^-) having the potential to amalgamate with the hydrogen ion (H^+) present in acids to form water (H_2O). TA in surface water is caused because of the free hydroxide ions. Furthermore, the weak acid and strong base salts viz. carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) also contribute to TA of surface water after being hydrolyzed. There are three forms of alkalinity in water or wastewater viz. hydroxide, carbonate, and bicarbonate alkalinity. Bicarbonate alkalinity is the prime form of alkalinity as it is created in significant quantity by the reaction of carbon dioxide (CO_2) on alkaline materials present in the earth's crust. Other weak acid salts such as silicate, borate, and phosphate as well as some volatile acids such as acetic acid, propionic acid, and butyric acid along with hydrogen sulfide (H_2S) may also contribute to TA. Alkalinity is expressed in mg/L as CaCO_3 . In our study, the TA of the RMWW samples ranged from 1,833 mg/L as CaCO_3 to 2,467 mg/L as CaCO_3 , and the average TA of the samples was

reported to be 2,156 mg/L as CaCO₃. TA of the sample S10 was minimum (1,833 mg/L as CaCO₃) and that of S13 was maximum (2,467 mg/L as CaCO₃).

7. Total Hardness (TH) - Total hardness (TH) of water is a principal feature to assess the water quality aimed at using it for household, agricultural, or industrial purposes. It is caused due to the presence of multivalent metallic cations in water/wastewater, principally due to the divalent calcium (Ca) and magnesium (Mg) ions. Though, other cations such as strontium (Sr), ferrous iron (Fe²⁺), aluminum (Al), barium (Ba), and manganese (Mn) also contribute to TH to some extent. The anions imparting TH are principally sulfate (SO₄²⁻) and chloride (Cl⁻) apart from carbonate, bicarbonate, and hydroxyl ions. TH is temporary and can be remediated merely by boiling the hard water if it is imparted due to bicarbonate and carbonate. On the contrary, if it is caused by sulfate and chloride of metals, it is permanent hardness and cannot be removed simply by boiling water rather it needs specific treatment like the Soda-lime process, Ion-exchange process, Calgon process, etc. TH of water/wastewater is also categorized as carbonate-hardness and non-carbonate hardness. When the TH of water is arithmetically more than the total of CO₃²⁻ and HCO₃⁻ alkalinities, that quantity of TH equal to the total alkalinity (TA) is referred to as carbonate hardness and the quantity of hardness surplus of this is termed non-carbonate hardness. Thus, non-carbonate hardness=TH-TA. When TH is arithmetically equivalent to or lower than the totality of carbonate and bicarbonate alkalinity, the whole of the hardness is carbonate-hardness and non-carbonate hardness is nil. In our experimental assay, the TH of the RMWW samples varied from 1,900 mg/L as CaCO₃ to 2,567 mg/L as CaCO₃ and the average hardness of the wastewater samples was 2,240 mg/L as CaCO₃. TH of the sample S10 was 1,900 mg/L as CaCO₃ and that of S13 was 2,567 mg/L as CaCO₃.

8. Calcium Hardness (Ca-Hardness) - Calcium hardness of water or wastewater is defined as the fraction of TH caused mainly due to the carbonate, bicarbonate, sulfate, and chloride of calcium. When Ca-hardness is due to the bicarbonate and carbonate of calcium it is called temporary Ca-hardness, whereas if it is imparted due to the sulfate and chloride of Ca it is called permanent Ca-hardness. It is expressed in mg/L as CaCO₃. In our study, the Ca-hardness of the RMWW samples varied from 1,633 mg/L as CaCO₃ to 2,233 mg/L as CaCO₃. The average Ca-hardness of the sample was found to be 1,906 mg/L as CaCO₃. Ca-hardness of the sample S10 was 1,633 mg/L as CaCO₃ whereas that of S13 was 2,233 mg/L as CaCO₃.

9. Magnesium Hardness (Mg-Hardness) - Magnesium hardness in water or wastewater is defined as the fraction of TH caused mainly due to the carbonate, bicarbonate, sulfate, and chloride of magnesium. When Mg-hardness is due to the bicarbonate and carbonate of magnesium, it is called temporary Mg-hardness, whereas if it is imparted due to the sulfate and chloride of Mg, it is called permanent Mg-hardness. It is expressed in mg/L as CaCO₃. In our study, the Mg-hardness of the RMWW samples ranged from 267 mg/L as CaCO₃ to 500 mg/L as CaCO₃. The average Mg-hardness of the wastewater samples was 334 mg/L as CaCO₃. Mg-hardness of the sample S10 was 267 mg/L as CaCO₃ whereas that of S5 was 500 mg/L as CaCO₃.

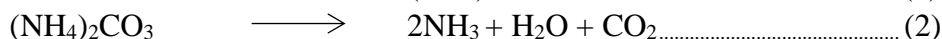
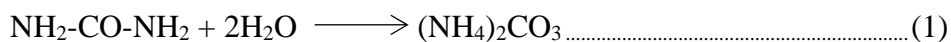
10. Chemical Oxygen Demand (COD) - It is the measurement of oxygen consumed by a strong oxidizing agent (potassium dichromate/K₂Cr₂O₇) during the oxidation of both bio-decomposable

and indecomposable organic materials existing in the wastewater sample under a restricted environment. The amount of the oxidizing agent ingested is revealed with regard to its oxygen compatibility. COD is always greater than BOD because in the COD test all organic materials including the bio-refractory organics like lignin, phenol, poly-chlorinated benzenes, etc. are oxidized and converted to carbon dioxide (CO_2) and water, whereas, in BOD test, only biodegradable organics are oxidized by the microorganisms. The main advantage of the COD test is that it takes only 3 hours, whereas the BOD test is completed in 5 days. Moreover, COD data can be expressed in terms of BOD values from the reliable correlation between COD and BOD after an intensive experience. The COD of a wastewater sample is determined by the reflux method and preferably by the closed reflux method. It is expressed in mg/L. In our study, the COD of the RMWW samples varied from 3,947 mg/L to 6,507 mg/L and the average COD of the sample was found to be 5,568 mg/L. The COD of sample S10 was minimum (3,947 mg/L), whereas that of S13 was maximum (6,507 mg/L).

11. Biochemical Oxygen Demand (BOD) – It is referred to as the quantity of oxygen needed by microscopic organisms, specifically bacteria to stabilize biodegradable organic materials existing in the wastewater sample. It is necessarily a bio-assay process, in which organic materials serve as food for living organisms. It is comprehensively used to assess the pollution potential of domestic and industrial effluents with regard to the molecular oxygen that they will necessitate if disposed of in surface water bodies, in which aerobic conditions prevail. The BOD test is of paramount importance in regulatory work and in evaluating the self-purification capacity of the watercourses. It is essentially a wet oxidation process, in which the living organisms act as the medium for the oxidation of the bio-decomposable organic substances to CO_2 , and H_2O in the presence of oxygen. The biochemical reaction involved in the BOD test is a first-order equation and the rate of reaction is proportional to the quantity of bio-degradable organics remaining at any time, as modified by the population of the active microorganisms. The BOD test is a cumbersome and slow procedure and takes 5 days to complete. BOD is expressed in mg/L. In our study, the BOD content of the RMWW samples varied from 2,890 mg/L to 4,223 mg/L and the average BOD content of the samples was 3,532 mg/L. The BOD content of the sample S10 was minimum (2,890 mg/L) and that of S13 was found to be maximum (4,223 mg/L).

12. Total Kjeldahl Nitrogen (TKN) - Nitrogen occurs in four forms in water and wastewater: nitrate (NO_3^-), nitrite (NO_2^-), ammonia/ammonium nitrogen ($\text{NH}_3\text{-N}/\text{NH}_4^+\text{-N}$), and organic nitrogen. The total of $\text{NH}_3\text{-N}/\text{NH}_4^+\text{-N}$ and organically bound nitrogen is called “Total Kjeldahl Nitrogen (TKN)”. On the other hand, the whole of NO_3^- -N and NO_2^- -N is called Total Oxidized Nitrogen (TON). Organic nitrogen is functionally referred to as organically bound nitrogen in the tri-negative oxidation state. It incorporates organic materials such as proteins, amino acids, peptides, nucleic acids, nucleotides, $\text{NH}_2\text{-CO-NH}_2$, and a number of synthetic organic substances. The concentration of organic nitrogen ranges from a few hundred $\mu\text{g/L}$ in lentic water bodies like lakes and ponds to greater than 25 mg/L in industrial wastewater. Ammonia/ammonium nitrogen is generally present in natural water and wastewater. Ammonia concentration is usually stunted in aquifer water, since it is a good adsorbate and is adsorbed onto clay particles, which is a good adsorbent for ammonia. Thus, ammonia is restricted from leaching easily to the soil profile aimed

at assimilating into groundwater. NH_3 is largely generated in nature by hydrolysis of urea that mainly contains urea with the help of urease enzyme as follows:

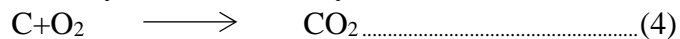
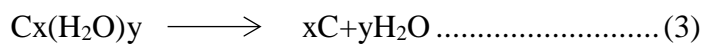


Ammonia (NH_3) is also released naturally by the deamination of organic compounds containing nitrogen such as proteins and amino acids. NH_3 is added at the time of disinfection in some water and wastewater remediation sites to combine with chlorine to form combined chlorine residuals aimed at producing fewer disinfection by-products (DBPs), which are suspected human and animal carcinogens. Ammonia nitrogen ($\text{NH}_3\text{-N}$) concentration varies from $\leq 10 \mu\text{g/L}$ in some surface water and groundwater to greater than 25 mg/L in some wastewaters. TKN is determined in the laboratory by the Kjeldahl Method, which was enunciated by Johan Kjeldahl in 1883 during the analysis of the crude protein content of foods. Kjeldahl Method comprises three apparatus: digestion apparatus, distillation- apparatus, and apparatus for ammonia determination. In our study, the TKN of the RMWW samples varied from 28 mg/L to 58 mg/L and the average TKN content of the samples was 42 mg/L . The TKN content of sample S10 was minimum (28 mg/L) and that of S13 was maximum (58 mg/L).

13. Total Solids (TS) - The residues left in a sample dish having water or wastewater sample after evaporation in a water bath succeeded by heating in an oven at 103°C to 105°C temperatures for a duration of ≥ 1 hour is called total solids (TS). The sample with a substantial quantity of Ca, Mg, Cl^- , and SO_4^{2-} may be moisture-absorbent due to its hygroscopicity and accordingly requires enlarged drying followed by well-organized desiccation, and quick weighing with the help of the analytical balance. The solid remains dried at 103°C to 105°C temperatures and can have crystallization water and some mechanically impeded water. There may be CO_2 depletion when HCO_3^- converts to CO_3^{2-} during drying. TS comprises both suspended and dissolved solids. Similarly, it also comprises both inorganic and organic solids present in the sample. In our study, the TS of the RMWW samples ranged from $3,437 \text{ mg/L}$ to $4,200 \text{ mg/L}$ and the average TS content of the samples was $3,928 \text{ mg/L}$. The TS of the sample S10 was minimum ($3,437 \text{ mg/L}$), whereas that of S13 was maximum ($4,200 \text{ mg/L}$).

14. Total Inorganic Solids (TIS) - The residues left in a sample dish after igniting the total solids of the water or wastewater sample in the muffle furnace at 550°C for a duration of ≥ 15 minutes is called TIS. The organic solids contained in the sample are completely oxidized at 550°C and the residues remaining in the dish are TIS. At this temperature, all mechanically occluded water as well as the water of crystallization are completely removed. TIS is expressed in mg/L . In our experimental assay, the TIS of the RMWW samples varied from 690 mg/L to $1,080 \text{ mg/L}$ and the average TIS content of the sample was 921 mg/L . The TIS content of sample S10 was minimum (690 mg/L) whereas that of sample S13 was maximum ($1,080 \text{ mg/L}$).

15. Total Organic Solids (TOS) - The fraction of TS of a water or wastewater sample that is completely volatilized and oxidized during its ignition in the muffle furnace at 550°C for a duration of ≥ 15 minutes, is referred to as TOS. The ignition of organic solids at 550°C is the lowest temperature at which the total organic materials including carbohydrates, lignin, etc. are completely oxidized at an appropriate speed caused by Pyrolysis. The chemical reactions involved during Pyrolysis are as follows:



TOS of a sample is numerically equivalent to the difference of TS and TIS i.e., $TOS = TS - TIS$. TOS is expressed in mg/L. In our study, the TOS of the RMWW samples ranged from 2,747 mg/L to 3,214 mg/L and the average TOS content of the sample was 3,008 mg/L. The TOS content of sample S10 was minimum (2,747 mg/L) whereas that of sample S4 was maximum (3,008 mg/L).

16. Total Dissolved Solids (TDS) – The fraction of total solids (TS) present in a water or wastewater sample that passes through the glass fiber filter with a nominal average pore size of 2.0 μm with the help of a vacuum pump, is referred to as TDS. When the sample undergoes vacuum filtration, TDS passes through the filter paper and persists in the filtrate. When the filtrate is evaporated in a water bath and thereafter heated in an oven at 180°C temperatures for a duration of ≥ 1 hour, the residues remaining in the sample dish are the TDS. The residues heated at 180°C lose approximately all mechanically impeded water but crystallization water may remain to some extent, specifically if sulfates are present. TDS is expressed in mg/L. In our experimental study, the TDS of RMWW samples ranged from 2,423 mg/L to 3,260 mg/L and the average TDS content of the RMWW samples was 2,975 mg/L. The TDS content of sample S10 was minimum (2,423 mg/L) and that of S13 was maximum (3,260 mg/L).

17. Total Suspended Solids (TSS) – The fraction of total solids in a water or wastewater sample that is retained on the glass fiber filter with a nominal average pore size of 2.0 μm during vacuum filtration of the sample, is called TSS. The solids remaining on the filter paper are dried at 103°C to 105°C in an oven and weighed with the help of the analytical balance, which gives TSS. It may also be obtained by subtracting TDS from TS i.e., $TSS = TS - TDS$. It is also expressed in mg/L. In our examination, the TSS of the wastewater samples emerging from rice mills ranged from 845 mg/L to 1,123 mg/L and the average TSS content of the samples was 953 mg/L. The TSS content of sample S3 was minimum (845 mg/L) whereas that of S8 was maximum (1,123 mg/L).

18. Lignin – Lignin is an ingredient of plants and vegetation that is generally discharged in substantial amounts in the wastewater emanating from the paper and pulp industry. Tannin also called tannic acid is a similar complex polyphenol that is generally present in many plant foods and vegetables and is generally present in the wastewater emerging from the vegetable processing and tanning industry. Lignin is an organic compound of complex phenolic polymers that constitutes the vital constructional materials in the reinforcement tissues of most vegetations. It is

remarkably indispensable in the construction of cell walls and imparts rigidity to the various supporting organs of plants. It is an organic polymer made by cross-linking of phenolic precursors **monolignols** which are aromatic alcohols. It is constituted by the oxidative coupling of three monolignols: p-coumaryl, coniferyl, and sinapyl alcohols (Grabber et. al. 2004). Lignin is the second most copious organically bound polymer on the earth followed by cellulose and constitutes approximately 30% of the non-fossilized organic carbon. It is accountable for intercepting carbon present in the atmosphere and preserving it in the tissues of various organs of plants imparting structural stringency. It degrades very slowly and increases soil moisture content. It is more resistant to insects and pests compared to other constituents of plants. After post-harvest processing of the paddy crop, lignin is generally present in significant amounts in paddy straw as well as in rice husk covering the rice kernel. Rice straw comprises 32-47% cellulose, 19-27% hemicellulose, and 5-26% lignin (Lo et. al. 2021) whereas rice husk contains 55-60% cellulose inclusive of hemicellulose, 20-25% lignin, and 15-20% silica (Liou 2004, Bazargan et. al. 2020, Novia et. al. 2022). The parboiled rice is produced from the paddy grains by milling process. In a parboiled rice mill, paddy is partially boiled at 70-80°C temperatures for 6-8 hours in the parboiling unit, as a result of which part of the lignin present in the rice husk is squeezed and assimilates with the hot water present in the parboiling handi (container). After the accomplishment of the parboiling process, the wastewater comprising lignin is drained from the handi, which ultimately is stored in the wastewater collection trench. In the laboratory, lignin is determined by Colorimetric Method with the help of a UV Spectrophotometer. It acts on the principle that lignin and tannin react with the Folin Phenol Reagent (tungsto-phosphoric and molybdo-phosphoric acids) to form a blue color dye suitable for detection of lignin content up to 9 mg/L. In our study, the lignin content of the RMWW samples varied from 122 mg/L to 171 mg/L and the average lignin content of the samples was 148 mg/L. The lignin content of sample S10 was minimum (122 mg/L) whereas that of sample S13 was maximum (171 mg/L).

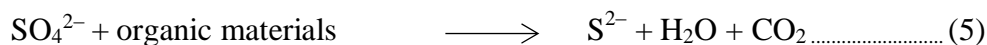
19. Phenol (C₆H₅-OH) – Phenol is an aromatic organic compound defined as hydroxy derivatives of benzene. It is a white solid having a crystal-like structure. Its chemical formula is C₆H₅OH and is volatile in nature. It is mildly acidic and hence needs cautious handling. It is also called carbolic acid, phenylic acid, phenic acid, and hydroxy-benzene. Phenol is soluble in water and may exist in water supplies, natural water, and wastewater. Chlorination of water contaminated with phenol produces an obnoxious odor and taste due to the formation of **chlorophenol**. Phenol may be removed from water/wastewater by ozonation, super-chlorination, or adsorption by activated carbon or chlorine dioxide (ClO₂) treatment. It may also be removed to some extent by biodegradation with the aid of **Cryptanaerobacter phenolicus** and **Rhodococcus phenolicus** bacteria. **Phanerochaete chrysosporium** fungus also removes phenol from the industrial wastewater to some extent along with lignin. Phenol in rice mill wastewater comes from the parboiling process. Actually, rice kernels comprise antioxidants: oryzanol, **phenolic acids**, proanthocyanidins, flavonoids, anthocyanins, tocopherols, tocotrienols, and phytic acid (Goufo & Trindade 2014). Phenolic acid, also called phenol carboxylic acid is a type of aromatic acid that contains a benzene ring and an organic carboxylic acid function. Salicylic acid is a common phenolic acid. Phenolic acid is a common antioxidant found in almost all rice varieties of the world (Sanghamitra et. al. 2022, Tyagi et. al. 2022, Priyanthi & Sivakanesan 2021). In the parboiling

tank, a little amount of phenol is secreted from rice kernels at a high soaking temperature of 70-80°C and is assimilated with the hot water of the tank. After the completion of the parboiling process, it comes out with the wastewater when the parboiled paddy is drained and is conveyed to the drying yard for sun-drying. Phenol imparts an unpleasant odor to rice mill wastewater. In the laboratory, phenol in wastewater is determined by Colorimetric Method with the help of a UV spectrophotometer. It acts on the principle that phenol reacts with 4-amino antipyrine (dye) to give a bright-red coloration for the detection of concentrations up to 1.0 mg/L or less. In our experimental assay, the phenol content of the RMWW samples varied from 14.0 mg/L to 15.4 mg/L; the average phenol content was 14.7 mg/L. The phenol content of the sample S10 was minimum (14.0 mg/L) whereas that of S13 was maximum (15.4 mg/L).

20. Chloride – Chloride (Cl^-) is a paramount inorganic anion in natural waters and wastewater. It exists in all natural waters- both surface and ground waters, municipal and industrial wastewaters in different concentrations. Its concentration depends upon the mineral contents of the soil strata. The higher the number of chloride minerals in the soil strata, the higher will be the chloride concentrations of groundwater due to the geogenic process and vice versa. Some of the common chloride minerals found in Earth's crust are sylvite (KCl), halite (NaCl), bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), kainite ($\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$), and carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$). The chloride contents of water found in upland and mountain regions are generally low, whereas river and ground waters have comparatively high chloride concentrations. The chloride levels of sea and ocean are very high due to the partial evaporation of natural waters that flow into them. The taste of water having 250 mg/L of chloride is salty, if one of the major cations is sodium ion (Na^+). The salty taste of water, on the other hand, is absent even if it contains 1000 mg/L of chloride of calcium and magnesium ions that predominate in cations. Municipal wastewater (sewage) has higher chloride content than tap water as sodium chloride (NaCl) is an essential dietary ingredient and undergoes unaltered through the excretory organ of humans and animals. Human urine contains chloride in the same quantity as it is taken with food and water. This quantity approximately equals 6.0 g of chloride (Cl^-) per person per day and consequently enhances the chloride content of municipal wastewater to nearly 15.0 mg/L above that of the carriage water. Thus, municipal and domestic wastewaters add considerable chloride to the receiving water bodies. Similarly, industrial wastewaters have remarkable concentrations of chloride due to the chloride content of the intake water as well as the processing techniques adopted in various industries. Water with high chloride concentration may hamper metallic pipes and other metallic frameworks. The wastewater emerging from a rice mill also has a substantial chloride content. In a laboratory, the chloride content of the water or wastewater is usually determined by Argentometric Method. In our study, chloride contents of the RMWW samples varied from 583 mg/L to 950 mg/L and the average chloride content of the samples was 748 mg/L. The chloride content of sample S10 was minimum (583 mg/L) whereas that of S13 was maximum (950 mg/L).

21. Sulfate (SO_4^{2-}) – Sulfate ion (SO_4^{2-}) is one of the prime anions existing in natural water. Its concentration in the domestic water supply scheme is of paramount importance when it is on the higher side due to its cathartic effect on human beings. The permissible concentration of SO_4^{2-} ion in potable water should be 250 mg/L as per the United States Environmental Protection Agency's

(USEPA) secondary standard (SDW-EPA, 810). SO_4^{2-} content in industrial water supplies is also of prime importance owing to the tendency of sulfate-rich water to form hard scales in heat exchangers and boilers. Moreover, SO_4^{2-} concentration in municipal and industrial wastewater is of major concern in the storage, convenience, and treatment of wastewater. The main problems associated with sulfate are- sewer corrosion and odor which results from the reduction of sulfate to H_2S by sulfate-reducing bacteria (SRB) in the anaerobic condition as given below:



Sulfate concentration of water and wastewater is determined by **Gravimetric Method with Drying of Residues** in the laboratory, in which barium chloride (BaCl_2) is used as a precipitant in an acidic medium of hydrochloric acid (HCl). The SO_4^{2-} present in water/wastewater reacts with BaCl_2 to give a precipitate of Barium sulfate (BaSO_4). In rice mill wastewater, SO_4^{2-} concentration is caused by the groundwater having sulfate contamination, used for the parboiling process as well as the partial boiling of paddy at 70-80°C for 6 to 8 hours in the parboiling tank. Actually, rice kernels comprise a little amount of sulfur in the form of protein sulfur (Hagan et. al. 2003, Naskar et. al. 2021). In our study, sulfate contents of the RMWW samples ranged from 51 mg/L to 88 mg/L and the average sulfate content of the samples was 71.2 mg/L. The sulfate content of sample S10 was minimum (51 mg/L), whereas that of S13 was maximum (88 mg/L).

22. Oil & grease - The oil and grease content of municipal and industrial wastewater is a key concern in the management and amelioration of these substances for final discharge. They may disrupt the microbial processes in the absence and presence of oxygen, resulting in diminished wastewater remediation output. Thus, an appropriate understanding of the quantity of oil and grease is quite beneficial in the operation and maintenance of wastewater remediation plants. The **grease** encompasses a broad spectrum of organic substances like waxes, esters, oils, hydrocarbons, fats, and long-chain volatile fatty acids (VFAs), which are soluble in the organic solvent n-hexane. In rice mill wastewater, oil is encountered due to a little erosion of the upper brown layer of the rice kernels called the **rice bran** during the parboiling process of the raw paddy. Oil and grease content in municipal/industrial wastewater is determined by Soxhlet Extraction Method in which n-hexane is used as the solvent for oil and grease. Therefore, this method is also referred to as Solvent Extraction Method. In our experimental assay, the oil and grease contents of the RMWW samples ranged from 10 mg/L to 24 mg/L; the average oil and grease content was 17 mg/L. The oil and grease content of sample S10 was minimum (10 mg/L), whereas that of S13 was maximum (24 mg/L).

23. Nitrate (NO_3^-) - Nitrate is a polyatomic ion and a common constituent of explosives and chemical fertilizers. Inorganic nitrates are generally soluble in water. Nitrate salts occur abundantly in arid environments as large deposits such as nitratine or Chile saltpeter (NaNO_3), a prominent source of sodium nitrate (NaNO_3). Nitrates are also produced by a species of nitrifying bacteria in a biotic environment from ammonia (NH_3) or urea (NH_2CONH_2). Moreover, natural lightning (electrical discharges) produces NO_x in an oxygen-rich atmosphere, which ultimately

forms nitrite (NO_2^-) and nitrate (NO_3^-). The totality of nitrate nitrogen ($\text{NO}_3\text{-N}$) and nitrite nitrogen ($\text{NO}_2\text{-N}$) is called total oxidized nitrogen (TON). Nitrate exists in trace amounts in surface water but it may be substantially present in groundwater due to geogenic phenomena caused by nitrate-containing rocks present in the earth's crust as well as due to contaminant transport of nitrates by groundwater plumes from agricultural fields. The accepted limit for NO_3^- in potable water as per BIS is 45 mg/L (BIS 10500: 2012). If TON is present in excess of the accepted limit fixed by the Bureau of Indian Standards (BIS) in drinking water it may cause methemoglobinemia in infants. In RMWW, nitrate is encountered due to the contaminated groundwater used for soaking paddy during the parboiling process as well as due to the use of urea in soaking aimed at imparting glazing to the rice grains for enhanced marketability of the processed parboiled rice. In the laboratory, the nitrate content of the water/wastewater sample is determined by a UV spectrophotometer at a wavelength of 275 nm. In our study, nitrate contents of RMWW samples ranged from 14.5 mg/L to 29.0 mg/L and the average nitrate content of the samples was 21.0 mg/L. The nitrate content of the sample S10 was minimum (14.5 mg/L) whereas that of S13 was maximum (29.0 mg/L).

24. Orthophosphate (PO_4^{3-}) – Phosphorus usually exists as orthophosphate (PO_4^{3-}) in fresh water and wastewaters. It is categorized as orthophosphate, condensed phosphate (meta-, pyro-, and other polyphosphates), and organic phosphates. It exists in particulates or debris or underwater creatures like fish. These forms of phosphorus originate from various sources. A small amount of condensed phosphate or orthophosphate is blended with water in some water treatment plants. A large amount of the same is added to waterbodies during cleaning and laundering since phosphates are the chief ingredients of all cleaning commodities including soaps and detergents. Orthophosphate is applied in agricultural fields as fertilizers, a part of which is ultimately transported to the surface waterbodies like ponds, streams, and rivers along with the runoff water. Polyphosphates are broadly used in boiler waters to minimize scaling. Organically bound phosphates are formed mainly by biological processes. The wastewater emerging from rice mills comprises orthophosphates considerably, part of which comes from the groundwater used for soaking. Moreover, part of the orthophosphates is contributed to the RMWW by the parboiling process of the paddy. The rice grains comprise phosphorus protein, which is synthesized by the paddy crops in the agricultural field during the cropping season. The paddy plants uptake macronutrients N, P & K from the soil (Vinod & Heuer 2012). A part of the phosphorus protein is eroded from rice grains at a high soaking temperature of 70-80°C and mixed with the soaking water during the parboiling process. Orthophosphates in water/wastewater are determined in the laboratory by Colorimetric Method (Ascorbic Acid Method) with the help of a UV spectrophotometer for use at the wavelength of 880 nm. In our study, the orthophosphate contents of the RMWW samples ranged from 72 mg/L to 91 mg/L and the average orthophosphate content of the samples was 80.7 mg/L. The orthophosphate content of the sample S10 was minimum (72 mg/L) whereas that of S13 was maximum (91 mg/L).

25. Sodium (Na) – Sodium is an alkali metal, which comes in Group 1A of Mendeleev's Periodic Table. It is broadly occurring on the planet and prevails in a number of minerals such as halite (NaCl), sodalite, and feldspar ($\text{AlNaO}_8\text{Si}_3$). The mean availability of sodium on the earth is 2.5%, in streams it is 6.3 mg/L, in the soil it is 0.02 to 0.62%, and in aquifers, it is generally more than 5 mg/L. Sodium atom has 11 electrons one more than the stable configuration of an inert gas

neon (Ne). Inorganic sodium salts are water-soluble, as a result of which surface and ground waters contain more Na-concentration as compared to sodium content in soils and the Earth's crust. The monovalent sodium ions (Na^+) are present in the sea and marine water in equilibrium with sodium bicarbonate (NaHCO_3) up to a concentration of 15,000 mg/L. The permissible concentration of sodium in potable water should be 20 mg/L as per the Safe Drinking Water Act (SDWA) 1974 of USEPA. In RMWW, sodium is encountered from sodium chloride (NaCl) added to the soaking water in the parboiling process to impede the boiling point of water. In the laboratory, sodium concentration in the RMWW is determined by atomic absorption spectrophotometer (AAS) for use at the wavelength of 766.5 nm. In our experimental outcomes, the sodium contents of the RMWW ranged from 60 mg/L to 82 mg/L and the mean sodium content of the samples was 69 mg/L. The sodium content of the sample S10 was minimum (60 mg/L) whereas that of S13 was maximum (82 mg/L).

26. Potassium (K) – Potassium is a silvery white and quite soft metal that can be cut with a knife. It is an alkali metal like sodium (Na) and comes in Group 1A of the Periodic Table. In a few seconds of atmospheric exposure, it reacts rapidly with oxygen to form flaky white potassium peroxide (K_2O_2). That is why it is always kept in paraffin oil to maintain the integrity of the metal. The potassium atom has 19 electrons, one more than the stable configuration of the noble gas argon (Ar). Potassium is associated with tectosilicate minerals such as orthoclase feldspar (KAlSi_3O_8), which is a common ingredient of granite and other igneous rocks. The mean availability of potassium on the planet is 1.84%, in soils it is 0.1 to 2.6%, in lotic surface waters it is 2.3 mg/L and in aquifers, it is 0.5 to 10 mg/L. Potassium compounds are extensively used in soft drinks, baking powder, glass, fertilizers, pigments, electroplating materials, and explosives. Potassium is a key ingredient in both human and plant nourishment and exists in surface and subsurface water due to various reasons viz., runoff water from agricultural fields enriched with plant macronutrients potassium, sodium, and phosphorus, mineral dissolution from Earth's crust, biodegradation of plant materials and contaminant transport from soil capillary via groundwater plume.

In RMWW, potassium is encountered because of two reasons. The first reason is the use of groundwater having potassium contamination, for soaking paddy in the parboiling process. The other reason is the presence of low potassium in rice grains like other cereal food-grains wheat, maize, and millet, as a result of which potassium oozes from the rice kernels during the parboiling process and assimilates with the hot soaking water. Potassium concentration in water/wastewater is determined in the laboratory by atomic absorption spectrophotometer (AAS) for use at a wavelength of 766.5 nm. In our study, the potassium contents of the RMWW samples varied from 410 mg/L to 675 mg/L; the average potassium content was 495 mg/L. The potassium content of sample S10 was minimum (410 mg/L) whereas that of S13 was maximum (675 mg/L).

27. Volatile Fatty Acids (VFAs) – VFAs are short-chain aliphatic monocarboxylic acids with 2 to 6 carbon atoms in the molecule. They are extremely malodorous and can cause odor nuisance for people residing in adjoining areas. They are mainly acetic, propionic, butyric, and isobutyric acids. They are called volatile acids since they can be distilled at ambient pressure. Acetic acid is the most common volatile organic acid produced as an intermediate product in the anaerobic

treatment of organic materials. The end product in this biochemical process is methane gas (CH_4). VFAs determination and pH measurement are beneficial in maintaining the able conditions during the initiation of an anaerobic reactor. Methane-forming bacteria work properly at pH values between 6.5 to 8.5. At $\text{pH} < 6.5$, methanogenic bacteria are severely inhibited but many fermentative and acidogenic bacteria are not unless $\text{pH} < 5$. VFA concentration increases to levels of 2000 mg/L to 6000 mg/L or more under such unbalanced conditions. Bicarbonate buffering by NaHCO_3 or $\text{Ca}(\text{HCO}_3)_2$ is done in the anaerobic digester to tide over this situation. VFAs determination in RMWW samples was done by Distillation Method as discussed in the Standard Methods for the Examination of Water and Wastewater 23rd edition by APHA, AWWA & WEF 2017. In our study, the VFAs contents of the RMWW samples ranged from 273 mg/L to 348 mg/L and the mean VFAs content of the samples was 307 mg/L. The VFAs content of sample S10 was minimum (273 mg/L) whereas that of S13 was maximum (348 mg/L).

The physicochemical characteristics of the rice mill wastewater comprising 27 salient parameters of 15 RMWW samples are given in three tables- Table 1, Table 2, and Table 3. Moreover, comparative analyses of various physicochemical parameters of the samples have also been performed. The comparative analyses of the TA & TH of the samples are shown in Figure 2, which reveals that the TH of samples from S1 to S15 is greater than their TA. It means that samples S1 to S15 contain both carbonate and non-carbonate hardness. The comparative analyses of TH, Ca-H & Mg-H of the samples are given in Figure 3. Comparative analyses of TS, TIS & TOS are given in Figure 4, which shows that TOS is significantly more than TIS in RMWW, and hence biological treatment of RMWW is feasible and cost-effective. Comparative analyses of TDS & TSS are given in Figure 5, which infers that TDS is substantially more in RMWW. Comparative analyses of BOD & COD are given in Figure 6, which manifests that COD of wastewater is always greater than BOD because COD includes non-biodegradable organics also. Comparative analyses of SO_4 , NO_3 & PO_4 are given in Figure 7, from which it is evident that PO_4 and SO_4 are remarkably high in RMWW compared to NO_3 . Comparative analyses of Na & K are shown in Figure 8, which infers that potassium content in rice mill wastewater is outstandingly more than its sodium content. Eventually, the comparative analyses of the lignin and phenol contents of the RMWW are shown in Figure 9, which reveals that the lignin content of RMWW is notably greater than its phenol content.

Table 1. Physicochemical characteristics of RMWW Samples

Sl. No.	Parameters	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
1	pH	5.57	5.43	5.19	5.63	6.05	5.17	5.11	5.09	4.35	4.28
2	Color	Faint Yellow	Faint Yellow	Faint Yellow	Faint Brown	Faint Brown	Faint Brown	Faint Brown	Faint Brown	Faint Brown	Faint Brown
3	EC (in $\mu\text{S}/\text{cm}$)	7.28	7.26	7.16	7.32	7.42	7.03	5.25	5.21	5.15	4.65
4	Turbidity (in NTU)	39.7	39.5	38.5	42.1	43.0	38.3	37.3	36.7	35.2	32.4
5	Total Alkalinity (mg/L as CaCO_3)	2,367	2,348	2,253	2,434	2,460	2,160	1,967	1,934	1,867	1,833
6	Total Hardness (mg/L as CaCO_3)	2,467	2,400	2,335	2,500	2,534	2,333	2,034	2,000	1,934	1,900
7	Ca-Hardness (mg/L as CaCO_3)	2,100	2,000	2,000	2,067	2,034	2,020	1,707	1,733	1,667	1,633
8	Mg-Hardness (mg/L as CaCO_3)	367	400	335	433	500	313	327	267	267	267
9	COD (mg/L)	6,080	5,967	5,653	6,187	6,400	5,547	5,227	5,120	4,800	3,947
10	BOD (mg/L)	3,736	3,650	3,387	3,740	3,837	3,575	3,387	3,285	3,167	2,890
11	TKN (mg/L)	53	51	42	55	56	40	35	34	29	28
12	Total Solids (mg/L)	4,157	4,150	4,011	4,157	4,200	3,967	3,807	3,710	3,510	3,437
13	Total Inorganic Solids (mg/L)	987	983	874	943	1,003	957	890	863	740	690
14	Total Organic Solids (mg/L)	3,170	3,187	3,137	3,214	3,197	3,010	2,917	2,847	2,770	2,747
15	Total Dissolved Solids (mg/L)	3,224	3,237	3,166	3,169	3,103	3,020	2,843	2,587	2,700	2,423
16	Total Suspended Solids (mg/L)	933	913	845	988	1,097	947	964	1,123	893	1,014
17	DO (mg/L)	1.1	1.2	1.4	1.0	0.9	1.5	1.8	1.9	2.1	2.2
18	Chloride (mg/L)	835	833	750	900	933	734	650	635	600	583
19	Sulfate (mg/L)	78	77	75	82	84	73	65	64	55	51
20	Oil & Grease (mg/L)	21	20	18	22	23	17	14	14	12	10
21	Nitrate (mg/L)	24.0	23.6	22.7	24.1	24.2	22.0	19.0	17.0	14.7	14.5
22	Orthophosphate (mg/L)	86	85	82	87	88	80	77	75	73	72
23	Lignin (mg/L)	158	155	149	163	164	147	142	137	133	122
24	Phenol (mg/L)	15.1	15.0	14.8	15.2	15.3	14.7	14.4	14.3	14.1	14.0
25	Sodium (mg/L)	74	73	69	75	76	68	64	63	61	60
26	Potassium (mg/L)	585	550	462	596	632	450	430	425	416	410
27	VFA (mg/L)	336	330	306	342	344	318	281	279	275	273

Table 2. Physicochemical characteristics of RMWW Samples

Sl. No.	Parameters	S11	S12	S13	S14	S15
1	pH	5.27	5.14	6.08	5.16	5.07
2	Color	Faint Yellow	Faint Yellow	Faint Yellow	Faint Yellow	Faint Yellow
3	EC (in $\mu\text{S}/\text{cm}$)	7.24	5.34	7.50	5.41	5.18
4	Turbidity (in NTU)	38.9	38.1	43.8	38.2	36.2
5	Total Alkalinity (mg/L as CaCO_3)	2,300	2,000	2,467	2,048	1,900
6	Total Hardness (mg/L as CaCO_3)	2,367	2,100	2,567	2,167	1,967
7	Ca-Hardness (mg/L as CaCO_3)	2,080	1,800	2,233	1,860	1,654
8	Mg-Hardness (mg/L as CaCO_3)	287	300	334	307	313
9	COD (mg/L)	5,760	5,333	6,507	5,440	5,013
10	BOD (mg/L)	3,617	3,476	4,223	3,527	3,275
11	TKN (mg/L)	46	36	58	38	30
12	Total Solids (mg/L)	4,113	3,927	4,200	3,963	3,617
13	Total Inorganic Solids (mg/L)	1,027	963	1,080	970	850
14	Total Organic Solids (mg/L)	3,086	2,964	3,120	2,993	2,767
15	Total Dissolved Solids (mg/L)	3,190	3,010	3,260	2,950	2,740
16	Total Suspended Solids (mg/L)	923	917	940	1,013	877
17	DO (mg/L)	1.3	1.7	0.8	1.6	2.0
18	Chloride (mg/L)	817	683	950	700	617
19	Sulfate (mg/L)	76	68	88	72	60
20	Oil & Grease (mg/L)	19	15	24	16	13
21	Nitrate (mg/L)	23.0	20.0	29.0	20.1	15.0
22	Orthophosphate (mg/L)	84	78	91	79	74
23	Lignin (mg/L)	153	145	171	146	135
24	Phenol (mg/L)	14.9	14.5	15.4	14.6	14.2
25	Sodium (mg/L)	71	65	82	67	62
26	Potassium (mg/L)	492	440	675	443	419
27	VFA (mg/L)	321	285	348	292	276

Table 3. Physicochemical characteristics of RMWW Samples

Sl. No.	Parameters	Unit	Range of Values	Mean value
2	Color	-	4.28 - 6.08	5.24
		-	Faint yellow to Faint Brown	-
3	Electrical Conductivity (EC)	$\mu\text{S/cm}$	4.65 - 7.50	5.84
4	Turbidity	NTU	32.4 - 43.8	38.5
5	Total Alkalinity (TA)	mg/L as CaCO_3	1,833 - 2,467	2,156
6	Total Hardness (TH)	mg/L as CaCO_3	1,900 - 2,567	2,240
7	Calcium Hardness (Ca- H)	mg/L as CaCO_3	1,633 - 2,233	1,906
8	Mg- Hardness (Mg-H)	mg/L as CaCO_3	267 - 500	334
9	Chemical Oxygen Demand (COD)	mg/L	3,947 - 6,507	5,265
10	Biochemical Oxygen Demand (BOD)	mg/L	2,890 - 4,223	3,518
11	Total Kjeldahl Nitrogen (TKN)	mg/L	28 - 58	42
12	Total Solids (TS)	mg/L	3,437 - 4,200	3,928
13	Total Inorganic Solids (TIS)	mg/L	690 - 1,080	921
14	Total Organic Solids (TOS)	mg/L	2,747 - 3,214	3,008
15	Total Dissolved Solids (TDS)	mg/L	2,423 - 3,260	2,975
16	Total Suspended Solids (TSS)	mg/L	845 - 1,123	953
17	Dissolved Oxygen (DO)	mg/L	0.9 - 2.2	1.5
18	Chloride (Cl^-)	mg/L	583 - 950	748
19	Sulfate (SO_4^{2-})	mg/L	51 - 88	71.2
20	Oil & Grease	mg/L	10 - 24	17
21	Nitrate (NO_3^-)	mg/L	14.5 - 29.0	21
22	Orthophosphate (PO_4^{3-})	mg/L	72 - 91	80.7
23	Lignin	mg/L	122 - 171	148
24	Phenol ($\text{C}_6\text{H}_5\text{OH}$)	mg/L	14.0 - 15.4	14.7
25	Sodium (Na)	mg/L	60 - 82	69
26	Potassium (K)	mg/L	410 - 675	495
27	Volatile Fatty Acids (VFA)	mg/L	273 - 348	307

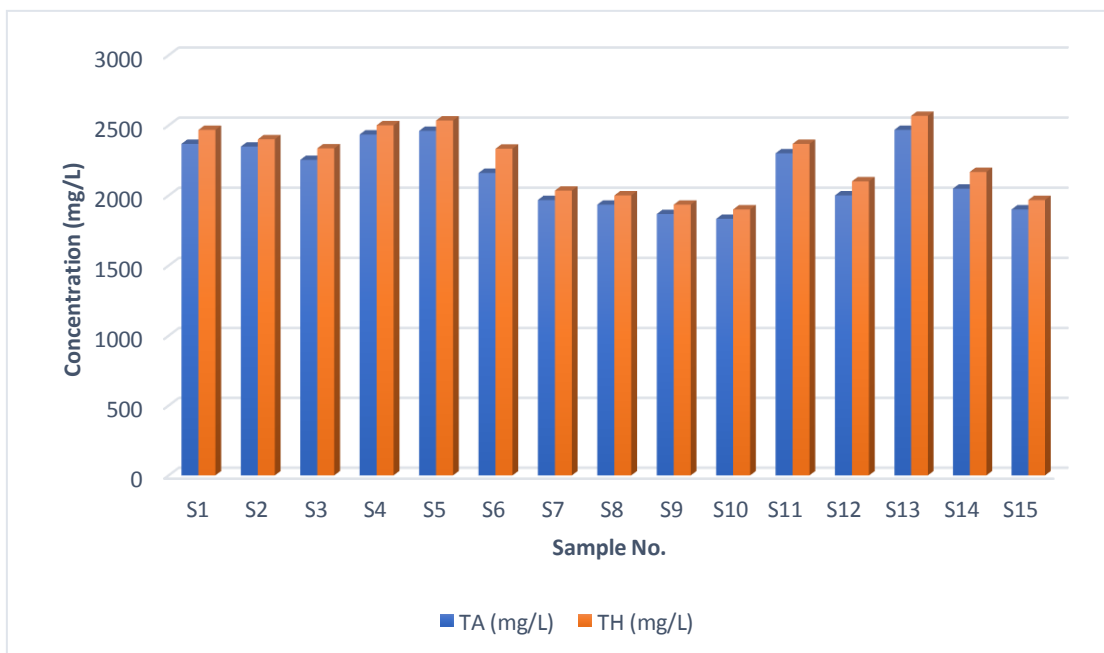


Figure 2. Comparative Analyses of Total Alkalinity & Total Hardness of RMWW Samples

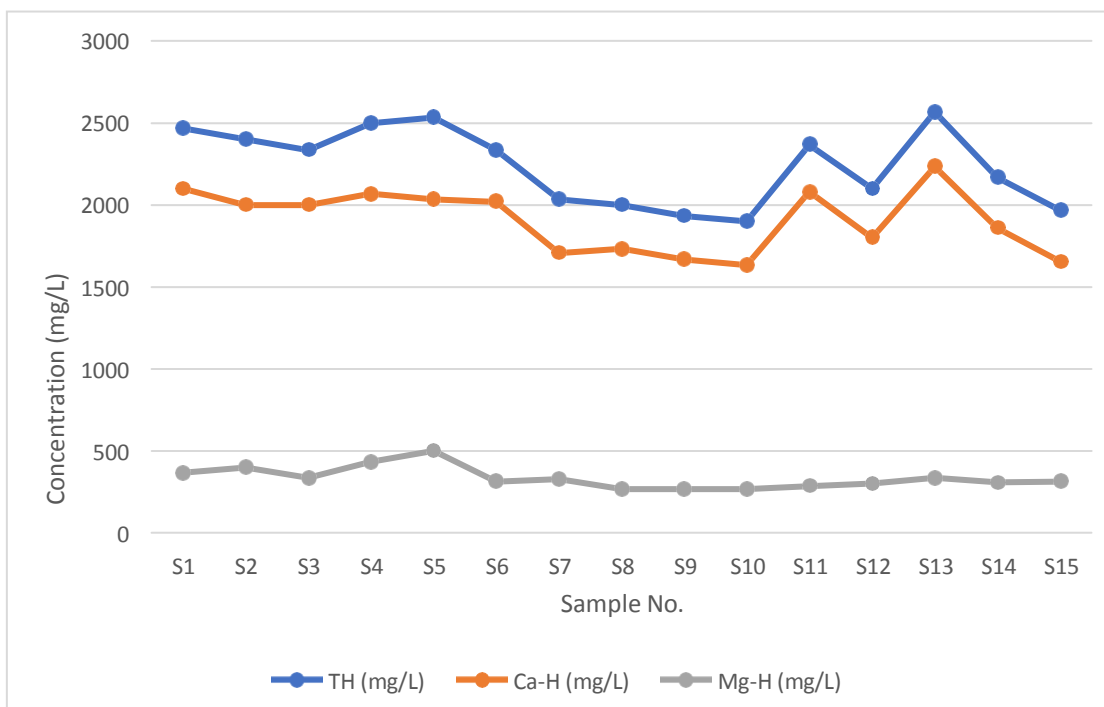


Figure 3. Comparative analyses of total hardness, Ca-hardness & Mg-hardness of RMWW samples

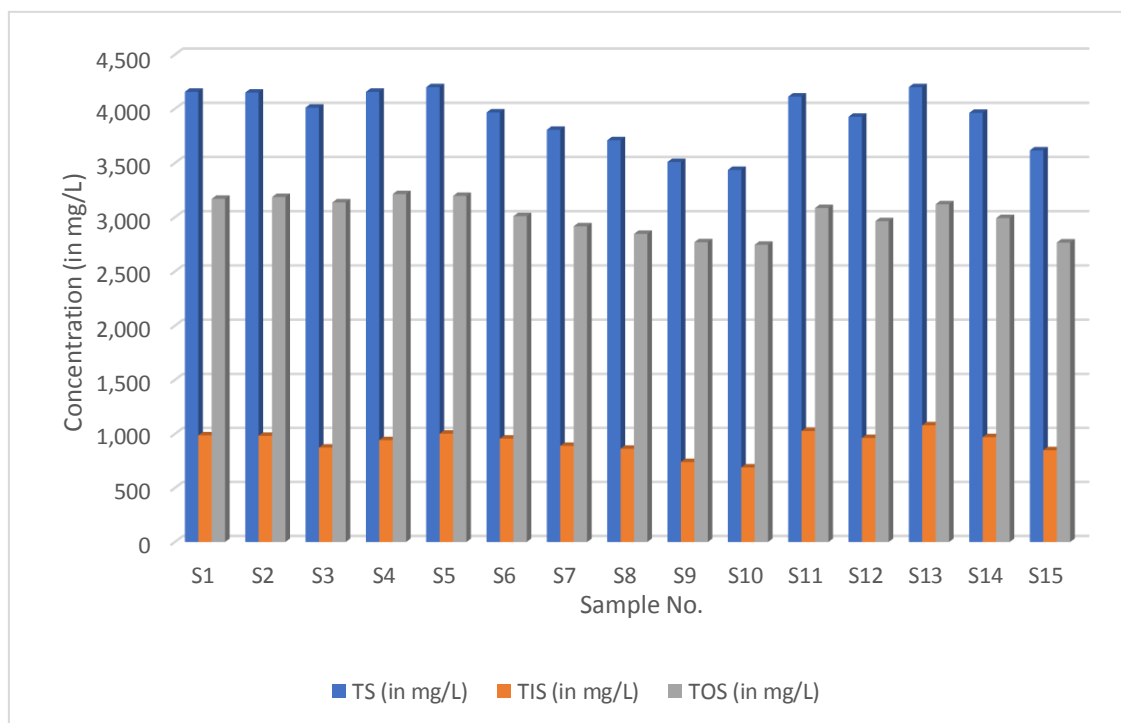


Figure 4. Comparative analyses of TS, TIS, and TOS contents of RMWW Samples

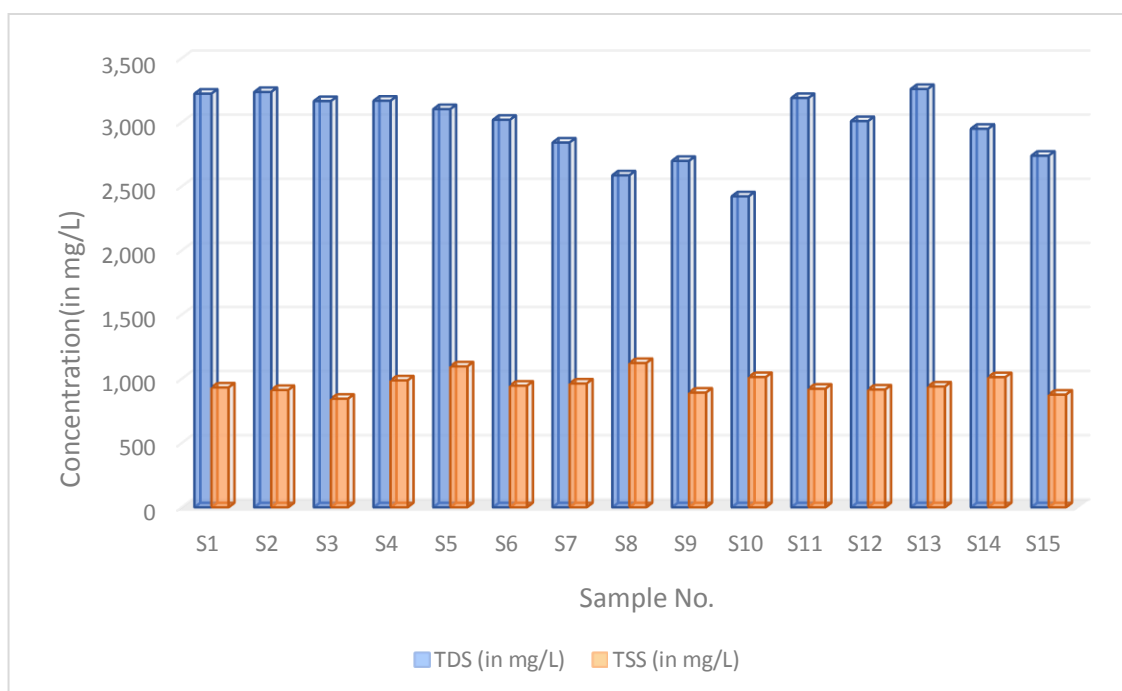


Figure 5. Comparative analyses of TDS & TSS contents of RMWW Samples

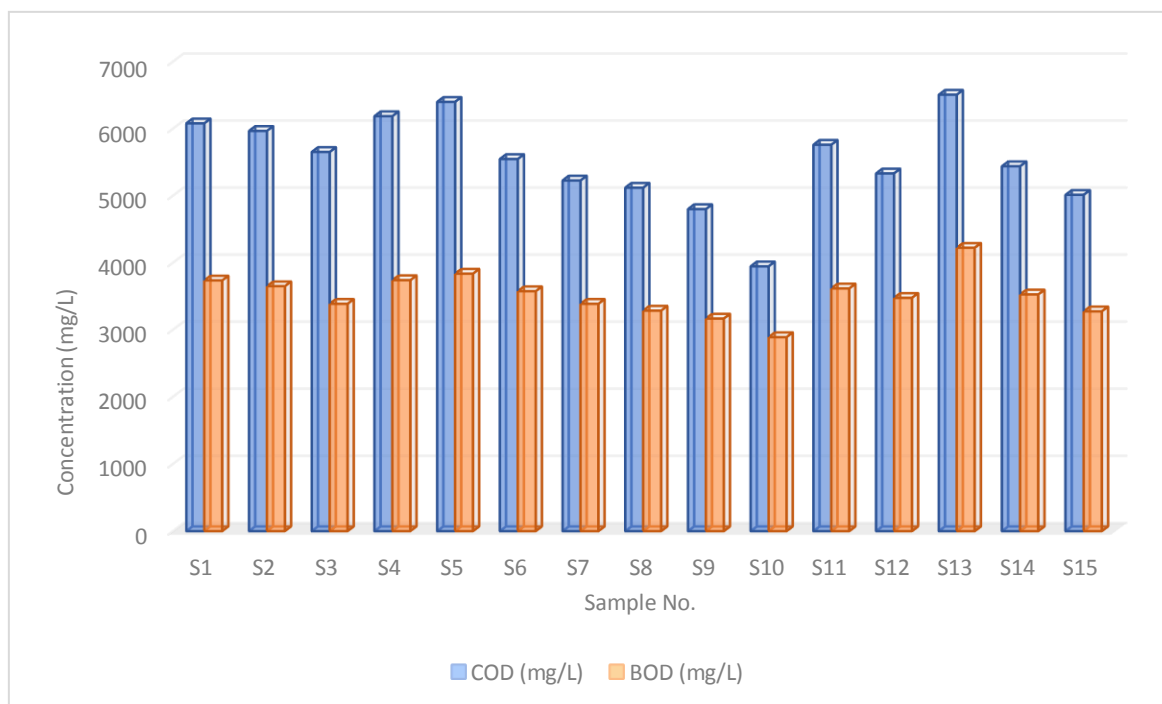


Figure 6. Comparative analyses of BOD5 and COD of RMWW samples

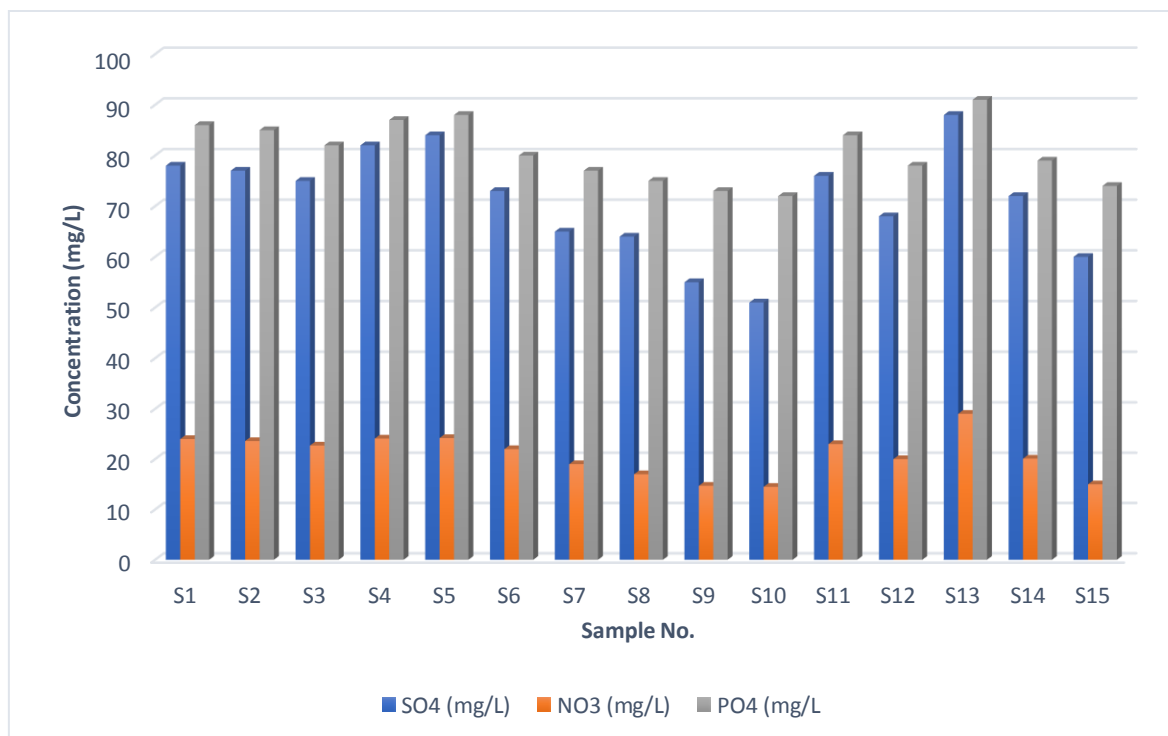


Figure 7. Comparative analyses of SO_4^{2-} , NO_3^- , and PO_4^{3-} contents of RMWW Samples

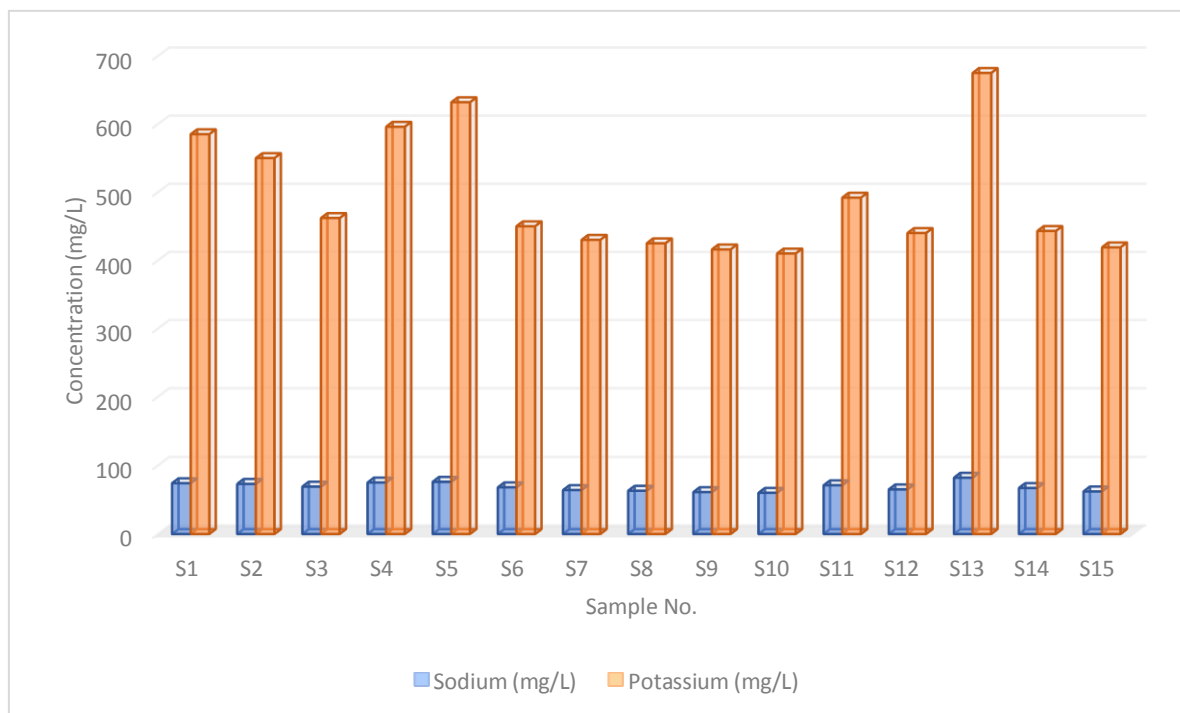


Figure 8. Comparative analyses of Sodium and Potassium contents of RMWW Samples

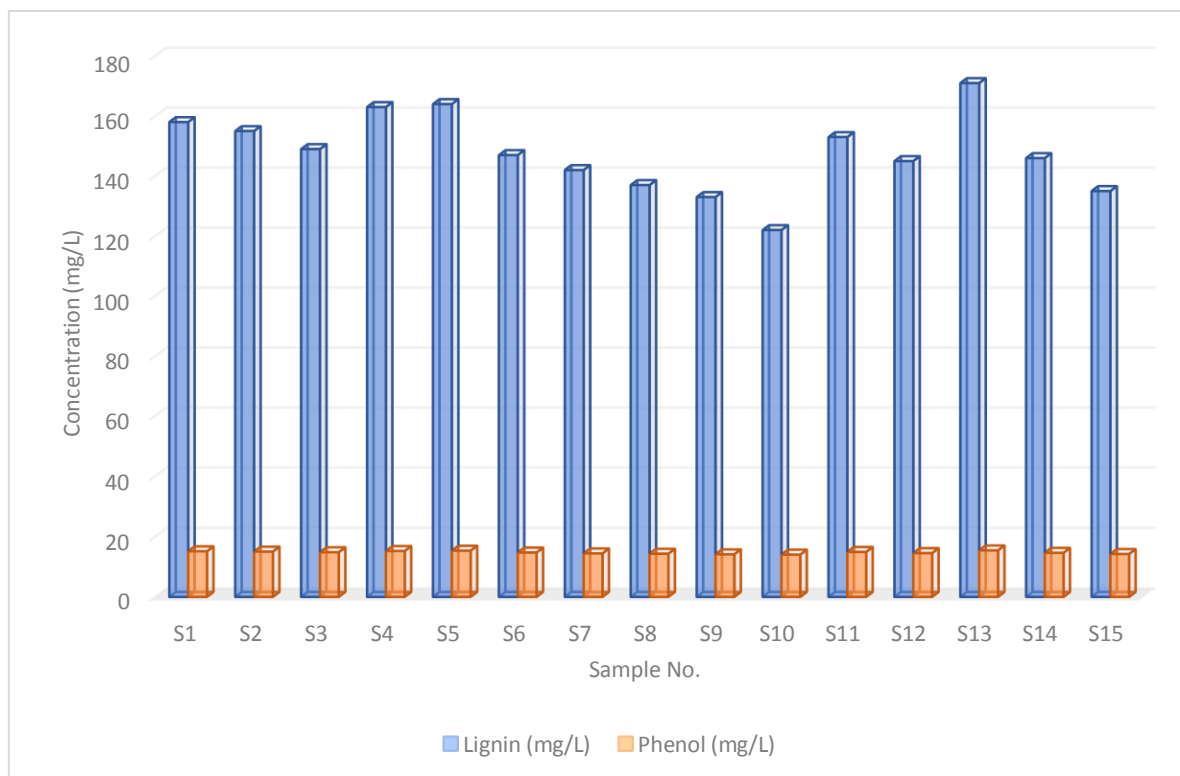


Figure 9. Comparative analyses of Lignin and Phenol contents of RMWW Samples

Table 4. reveals the physicochemical characteristics of wastewater emanating from some Indian Industries of utmost importance. According to the table, the salient characteristics of the wastewater produced from these industries vary widely from each other depending on the nature of raw materials, type of industry, and quality of intake water used, as well as the processing technologies involved. The wastewaters emanating from textile industries, pulp and paper industries, as well as food and chemical industries are alkaline in nature with high total solids (TS), total dissolved solids (TDS), chemical oxygen demand (COD), and biochemical oxygen demand (BOD₅), which indicate the presence of a vast quantity of organic materials in these wastewaters. The industries like tanneries and distilleries generate acidic wastewater with high COD, BOD, and TS contents. The total solids (TS) contents of distilleries and tanneries are 67,000 mg/L and 21,848 mg/L respectively, whereas the BOD₅ contents of distilleries and tanneries are 40,000 mg/L and 8,739 mg/L respectively. This indicates the existence of a tremendous amount of organic materials in wastewater emerging from distilleries and tanneries. The BOD₅ and COD contents of the wastewater emerging from distilleries are 40,000 mg/L and 80,000 mg/L respectively. On the other hand, the BOD₅ and COD contents of tanneries wastewater are 8,739 mg/L and 21,965 mg/L respectively. Therefore, the ratio of BOD₅ to COD (i.e., BOD₅/COD) of wastewaters emanating from distilleries and tanneries are 0.5 and 0.4 respectively, which infers that the level of biodegradability of distilleries effluent is superior to that of tanneries wastewater. Similarly, the chloride (Cl⁻) contents of wastewater originating from distilleries, food and chemicals, and textile industries are 3520 mg/L, 1321 mg/L, and 750 mg/L respectively, which manifests that the chloride content of distilleries wastewater is very high due to the raw materials used and the processing technology involved, in which 88% of the raw materials are converted into wastes giving rise to high pollution strength of the wastewater (Kharayat 2012). At the same time, the chloride (Cl⁻) contents of effluents emanating from food and chemicals as well as textile industries are moderately high and high respectively. According to Table 4, the ammonia nitrogen (NH₃-N) contents of wastewaters originating from paper and pulp mills as well as the textile industry are 3,217 mg/L and 346 mg/L respectively, which are very high and high respectively and can substantially contribute to Total Kjeldahl nitrogen (TKN) contents of these wastewaters. The lignin and phenol contents of paper and pulp mill wastewater (PPMWW) are 95 mg/L and 759 mg/L respectively, which shows that PPMWW comprises a very high amount of phenol content as compared to the phenol content of RMWW (14.7 mg/L) and a significant presence of lignocellulosic materials lignin in PPMWW resembling that in RMWW. Similarly, the total hardness (TH) content of tanneries wastewater is 3,262 mg/L as compared to 2,240 mg/L in the rice mill wastewater, which signifies that the TH content of tanneries wastewater is appreciably high like that of the rice mill wastewater (RMWW). This designates the remarkable presence of CO₃²⁻, HCO₃⁻, SO₄²⁻, and chloride (Cl⁻) of calcium (Ca) and magnesium (Mg) in both wastewaters. The sodium and potassium contents in PPMWW are 560 mg/L and 32 mg/L respectively, whereas Na and K contents in RMWW are 69 mg/L and 495 mg/L respectively. Thus, we see that Na and K contents in PPMWW and RMWW are remarkably different. The larger content of Na in PPMWW is caused by the application of NaOH in the delignification of the lignocellulosic materials viz., bagasse, bamboo, reeds, esparto grass, sisal, flax, jute, and recycled papers, etc. from which, pulp and paper are manufactured. Similarly, a higher concentration of K

in RMWW is due to the presence of potassium in each rice grain, a minor fraction of which is accumulated to become large and is assimilated with RMWW during the parboiling process.

Table 4. Physicochemical characteristics of wastewater emerging from some paramount industries in India

S. No.	Parameters	Units	Wastewater emanating from different industries						
			Distilleries	Food & Chemical	Olive mill	Paper & Pulp mill	Tanneries	Textile mill	Rice mill
1	pH	-	4.40	8.80	5.20	10.50	5.60	9.40	5.24
2	EC	$\mu\text{S}/\text{cm}$	-	2.00	5.50	1.90	5.48	2.40	5.84
3	DO	mg/L	-	-	-	-	-	-	1.20
4	TS	mg/L	67,000	-	-	-	21,848	-	3,928
5	TDS	mg/L	-	2,938	-	3,750	19,364	214	2,975
6	TSS	mg/L	-	294	-	1,918	2,489	-	953
7	TIS	mg/L	-	-	-	-	-	-	920
8	TOS	mg/L	-	-	-	-	-	-	3,008
9	TH	mg/L as CaCO_3	-	-	-	-	3,262	-	2,240
10	Ca-H	mg/L as CaCO_3	-	-	-	-	-	-	1,906
11	Mg-H	mg/L as CaCO_3	-	-	-	-	-	-	334
12	NO_3^-	mg/L	-	-	-	-	-	-	21
13	PO_4^{3-}	mg/L	38.80	5.08	-	Nil	-	1.00	76
14	SO_4^{2-}	mg/L	69.50	178	-	70	-	642	71
15	Cl^-	mg/L	3,520	1,321	-	146	1.44	750	748
16	Na	mg/L	-	73	0.15	560	-	19	69
17	K	mg/L	-	47.60	5.24	32	-	100	495
18	BOD_5	mg/L	40,000	1,671	-	2,104	8,739	2,032	3,532
19	COD	mg/L	80,000	6,000	-	3,000	21,965	6,000	5,568
20	$\text{NH}_3\text{-N}$	mg/L	51	80	0.88	3,217	-	346	-
21	Lignin	mg/L	-	-	-	95	-	-	148
22	Phenol	mg/L	-	-	-	759	-	-	14

References: Rani & Janardhan 1980, Somashekhar et. al. 1984, Srivastava & Sahai 1987, Madhappan 1993, Agrawal & Pandey 1995, Pillai et. al. 1996, Siddaramaiah et. al. 1998, Kharayat 2012, Neves et. al. 2020, Sharma et. al. 2022.

Conclusion

In the present investigation, it was discovered that the wastewater is generated in rice mills during the parboiling process, which is completed in three steps: soaking, steaming, and drying. More specifically, it may be said that the soaking of raw paddy is the major source of wastewater in a rice mill. The generated wastewater is discharged either untreated or partially treated with chemicals like lime. The stakeholders generally discharge the wastewater by open drainage system or by the conduit drainage system to the surface waterbodies- lakes, ponds, rivers, streams, watercourses, or roadside land. This haphazard and impromptu disposal of the rice mill wastewater generates a lot of problems like the obnoxious smell, the spread of diseases, the build-up of toxic chemicals, breeding sites of mosquitoes, unaesthetic and unagreeable scenarios, normal life disruption, contamination of water sources, road deterioration, environmental pollution, and ecological damage as well as degrades the water quality and soil fertility and ultimately is deleterious to human and animal health. The safe discharge of wastewater is inevitable for public health, ecological sustainability, and environmental conservation.

In this study, rice mill wastewater is found to be moderately acidic. The turbidity concentration varied from 32.4 to 43.8 NTU, the average being 38.5 NTU. The COD contents of the samples varied from 3,947 to 6,507 mg/L, whereas their BOD contents varied from 2,890 to 4,223 mg/L. It illustrates that rice mill wastewater comprises a high quantity of biodegradable organics. The average lignin concentration is 148 mg/L, which means that rice husk comprises a significant amount of lignin. Thus, we see that the rice mill effluent is absolutely not fit for disposal either into inland surface waters or onto land for irrigating crops as per the norms of CPCB. Therefore, proper treatment of the wastewater must be made mandatory to the stakeholders by the competent authority to run a rice mill, and it should be regularly monitored with a view to saving the ecosystem and public health.

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Authors' contributions

Raj Kishore Singh: Conduction of entire experiments, data analyses, and writing the manuscript.

Dr. Samir Bajpai: Data validation, and proofreading of the manuscript.

Declarations

Conflict of Interest

The authors proclaim that there is not any conflict of interest concerning the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, delinquency, counterfeiting, double submission, and prolixity have been appropriately visualized by the authors.

Data Availability

The datasets generated during the current study are available from the corresponding author upon reasonable request.

Compliance with ethical standards

Ethical approval and consent to participate: Not applicable.

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