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Characterization of Tannery Effluent of Savar Tannery Estate in Bangladesh

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Abstract: Tannery industrial effluents comprise a huge volume of chemical composites, including toxic chemicals. The study aimed to analyze various physicochemical parameters of the composite tannery industrial effluents of Savar Tannery Industrial Zone. All the physicochemical parameters of the effluents were measured using the standard methods of analysis. The mean concentration of total suspended solids (TSS), total dissolved solids (TDS), and pH of the effluents were 1756, 6817, and 8.2 mg/L, respectively. The average value of dissolved oxygen (DO), biological oxygen demand (BOD), and chemical oxygen demand (COD) were 0.6, 553 mg/L, and 1646 mg/L, respectively. The average electrical conductivity (EC) was 10996 µS/cm, and the concentration of anions, including NO_3^-, SO_4^{2-}, HCO_3^-, PO_4^{3-}, and Cl^- were 60.18, 1560,1200, 28.3, and 2417 mg/L, respectively. The concentration of the cations of the tannery effluents was in the following order: Na>Ca>Cr>Cu>Zn. The BOD and COD ratio revealed that the tannery effluents were less biodegradable. The study observed that the tannery industrial effluents should be treated before discharging into surface water bodies.

Keywords: *BOD_5; COD; Composite; CETP; Effluents; Tannery.*

1. Introduction

The tannery industry is one of the most pollution-generating sectors in Bangladesh. During leather processing, in almost all steps substantial amounts of chemicals are used [1]. About 90 percent of tannery companies in Bangladesh adopt the chrome tanning method since it is simple to use and gives the leather great characteristics. The tanning process is entirely a wet process that uses a lot of water and wastes it unevenly 90% of it was discharged as effluent [2]. Tannery effluents contain huge amounts of organic and inorganic pollutants including glossily colored chemicals, sodium chloride, sulfate, chromium salts, toxic metallic compounds, physiologically oxidizable tanning constituents, and vast amounts of rotten suspended debris [3,4]. The soaking step of the tanning process, which is the most polluting, accounts for 50–55 percent of the tanning industry's overall pollution burden. Protein, hair, skin, and emulsified fats are taken from the hides during the liming stage and then discharged into the effluent, enhancing the total solids content. Sulfides, ammonium salts, and calcium salts were present in the effluents from the tanning, de-liming, and bating operations and the effluent is somewhat alkaline. Sulfates, sodium bicarbonate, chlorides, sulphuric acid, and chrome are found in chrome and pickling tanning effluents. Numerous studies showed that the effluents from beam house procedures have a huge amount of whole solids content [5,6].

There is 20 percent of the chemicals used in the tanning procedure are fascinated by leather, with the rest being discharged as effluent [7,8]. Chrome salts, dyestuff residues, fat liquoring agents, systems, and other organic debris are the principal contaminants of the post-tanning process [9]. Vapors from degreasing and

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finishing solvents are a cause of exposure [10]. Each year, it is estimated that 300–400 million tons of heavy metals, solvents, toxic sludge, and other pollutants are thrown into water bodies by tanneries across the world [11,12].

The foremost pollutants of the post-tanning process are chrome salts, dyestuff residues, fat liquoring agents, systems, and other organic matter [9]. Vapors from degreasing and finishing solvents are a cause of exposure [10]. Toxic dangers raised by the uncaring and unsafe use of insecticides, tanning chemicals, and treated hides and skins can also harm workers' health. The final composite tannery effluents (wastewater) include high organic matter, dissolved and suspended particles, organic nitrogen, and ammonia content, as well as a high pH [13,14]. The pollution problem is deteriorating due to a lack of effective monitoring, rules and regulations, insufficient processing practices, and the use of unpolished traditional leather processing techniques. Unfortunately, an emerging country like Bangladesh is suffering from a lack of technological facilities and information regarding the amount and types of hazardous waste generated by industries including tannery, textile dyeing, sugar, and paper industries [15-17]. The study area is located at the Central effluent treatment plant (CETP) of Savar, alongside the Dhaleshwari River. But unfortunately, the performance of the plant is not satisfactory, and hence, the discharge effluent of the CETP threatens aquatic life and the environment. Several reports on the characterization of tannery effluents of different industries have been published, but no detailed work has been done so far on the discharge effluent of the Savar tannery industrial zone. The status of harmful contaminants in effluents is given special attention in this context. Even while tanneries generate currency and employment, pollution from their effluent is a big problem. Because of the improper discharge of untreated effluents on land and water, all contaminants, including heavy metals, pose substantial health risks. The study aimed to characterize the discharged tannery effluents and identify the pollutants in the composite tannery effluents. For this reason, composite effluents were collected from the drain just before entering the CETP at Savar Tannery Industrial Estate in Bangladesh and analyzed for various physicochemical parameters.

2. Materials and Methods

2.1 Study area

The study area is located in the recently shifted tannery industrial zone in Savar Upazila, situated in the northwest part of Dhaka city, Bangladesh. It is located at 23°51′30″N 90°16′00″E / 23.8583°N 90.2667°E / 23.8583; 90.2667. Fig. 1 shows the sampling location of the study area.

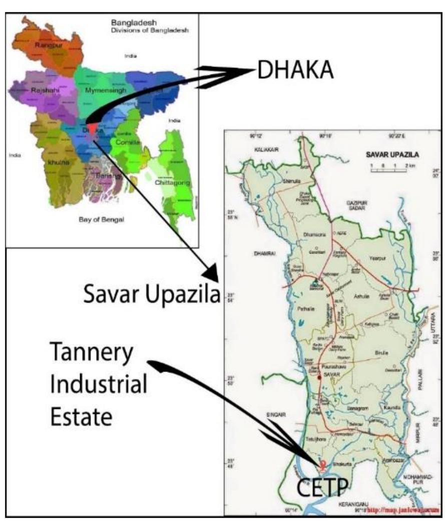

Fig. 1: Location map of the study area

2.2 Sample collection

About 155 tannery industries have been transferred from Hazaribagh, Dhaka to the Savar Tannery Estate at Hemayetpur to save the Buriganga river from further pollution, and 132 industries are active in the production of leather goods [18]. The industries discharge the effluents through a pipeline and they enter the CETP for treatment (Fig. 2). These industries generated a large number of tannery effluents that must need proper treatment. The study was conducted from September 2021 to March 2022, and the samples were collected three times during this period. A composite mixture of the tannery industry's effluents was collected before entering into the CETP. Sterile plastic containers (500 ml) and polyethylene bags were used to collect the effluents. The samples were kept in ice boxes and taken to the laboratory for analyses of several physicochemical parameters. One ml of concentrated HNO_3 (65%) was poured into each sample bottle and mixed well to keep the pH below 2 and minimize the precipitation and adsorption on the wall of the container to determine the cationic concentrations. But the samples were collected in a separate bottle without adding the HNO_3 for the analysis of the anions.

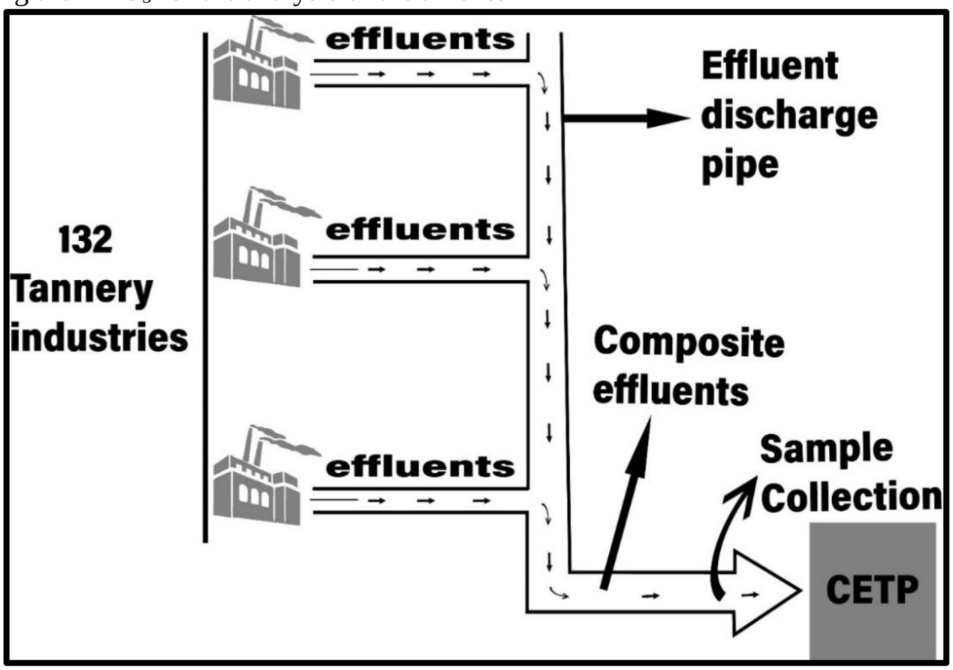

Fig. 2: Sample collection area at Savar tannery estate

2.3 Characteristics of Tannery Effluent

The collected effluent samples were analyzed for various physicochemical parameters like pH, electrical conductivity (EC), total suspended solids (TSS), total dissolved solids (TDS), biological oxygen demand (BOD_5), and chemical oxygen demand (COD). pH and EC values were measured on the spot using a portable digital pH meter (Model KRK, KP-5z, Japan) and a digital multi-range conductivity meter (Model Hanna HI 9033, Singapore). TSS and TDS were measured gravimetrically following standard methods [19]. The DO, BOD_5, COD, Cl^-, bicarbonate (HCO_3-), hardness, sulfate (SO_4^{2-}) and phosphate (PO_4^{3-}) were determined by standard methods [20] of analysis. Fig. 3 illustrates the different steps of the leather production process. These steps were involved in the generation of various pollutants (Fig. 3)

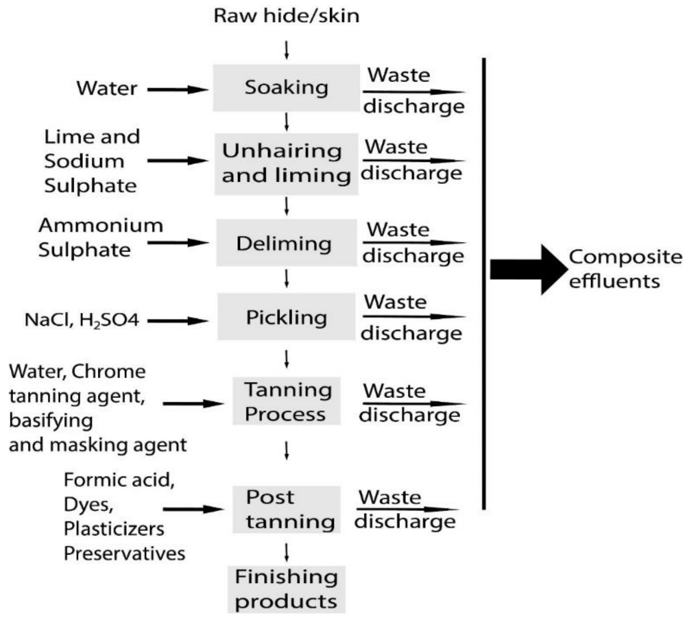

Fig. 3: Flow diagram of leather production from row hide

The concentrations of Na, Ca, Zn, Cu, and Cr ions in the effluents were estimated by the AAS method following digestion of the samples with concentrated HNO_3 and HCl mixer in the ratio of 1:2 [19]. All the instruments were calibrated with the standard solution before being used and the chemicals used were of analytical grade. Experiments were performed at least three times to minimize analytical error. The results were compared with effluent limit values of the Department of Environment, Bangladesh (DoE, BD), National Environmental Quality Standards [21], and Inland Surface Water-Bangladesh Standards [22].

3. Results and Discussion

3.1 Physico-chemical characterization of effluent samples

The tannery industrial effluents of the Savar tannery estate were analyzed to determine the concentration of some major physicochemical parameters. The analyzed parameters included pH, TDS, TSS, EC, hardness, DO, BOD_5, COD, Na, Ca, Cr, Cu, Zn, HCO_3^-, Cl^-, NO_3^-, SO_4^{2-}, and PO_4^{3-} etc. These physicochemical parameters represented the pollution status of the tannery effluent. The analysis results of the physicochemical parameters of the effluents are stated below.

3.1.1 pH and DO

The pH values in untreated composite tannery effluents ranged from 6.9 to 8.9 with a mean of 8.2 (Table 1). The mean value of pH was within the standard value of the discharge limit of the Department of Environment, Bangladesh (DoE, BD), NQES, and ISW-BDS permissible limit for inland water. The alkaline nature of these composite tannery effluents was owing to the use of lime, Na_2CO_3, Na_2S, and NaOH during the hide and skin processing. The highest and lowest values of Dissolved Oxygen (DO) of the analyzed effluent samples were 0.6 and 0.8 mg/L, respectively, with the mean concentration of 0.6 mg/L, which is far below the standard prescribed limits set by the NEQS and ISW-BDS-ECR [21,22].

The low DO values of the effluent samples indicate a higher level of organic pollutants present in the composite effluents, and also, the higher values of BOD_5 in the effluents indicate the presence of organisms in the effluents [23]. The DO value (<1 mg/L) indicated that the discharged composite effluents were heavily polluted and potentially harmful to aquatic life if the effluents were discharged without proper treatment.

Table 1. Physicochemical parameters of Tannery industrial effluents

Parameters	Effluents (Sep 2021)	Effluents (Dec 2021)	Effluents (March 2022)	Mean	DoE	ISW-BDS-ECR	NEQS-2000
					Standard		
pH	6.9	8.9	8.9	8.2	6.9	6-9	6-9
DO (mg/L)	0.6	0.8	0.6	0.6	4-6	4.8-9	4-6
EC (µs/cm)	11900	10820	10270	10996	1200	1200	288
TDS (mg/L)	7378	6708	6367	6817	2100	2100	3500
TSS (mg/L)	1866	1918	1486	1756	150	-	150
BOD_5(mg/L)	508	590	560	553	50	-	50
COD (mg/L)	1540	1647	1750	1646	200	-	200
Hard-ness(mg/L)	635	730	672	676	-	-	-

3.1.2 EC, TDS, and TSS

The study results showed that the concentration of TDS ranged from 6367 to 7378 mg/L**.** The samples exceeded the standard permissible limits (2100 mg/L, DoE, BD), indicating the presence of large amounts of dissolved solids. The mean TDS concentration was 6817 mg/L, which is almost double compared to the standard permissible limit, set by the [22]. Rouf et al. (2013) stated that the TDS concentration of the tannery effluents was 3455 mg/L in the sample's sources from various points of the Hazaribagh tannery industrial zone, which was lower than the TDS concentration of the present study [24]. The TSS contents of the analyzed composite tannery effluents were 1486 to 1918 mg/L with a mean value of 1756 mg/L (Table 1). These values exceeded the prescribed permissible limit set by the DoE, BD (150 mg/L), indicating huge amounts of suspended solids present in the discharge effluents. The higher values of TDS and TSS in the tannery estate were due to the presence of various organic and inorganic substances. The high levels of TDS and TSS in the effluents indicated that the effluents must be treated before discharging into the surface water bodies. The electrical conductivity values of the composite effluent samples ranged from 11900, 10820, and 10270 µs/cm respectively in the study period and almost showed higher EC as compared to the prescribed standard limit (1200 µS/cm, DoE, BD; NEQS, 2000; 288 mg/L). Kabir et al. (2007) reported that the EC values of the tested tannery effluents in the Hazaribagh area ranged from 587 to19000 µs/cm [25], which showed some similarity with the results of the present research. The higher EC content in the tannery effluent samples shows the existence of an adequate amount of organic and inorganic compounds and salts, mostly sodium and chromium salts used in the pickling and tanning procedures, which may have boosted the electrical conductivity of the effluent samples [26]. The average EC of all composite samples was far above the permissible limits, signifying a very poisonous environment for the aquatic biota.

3.1.3 Biological and chemical oxygen demand (BOD_5 and COD)

The values of BOD_5 in the effluent samples were in the range of 508- 590 mg/L (Table 1). A maximum of 590 mg/L of BOD_5 was found in the effluents of the Savar tannery industrial area. All the BOD_5 values of the tannery effluents obtained were higher than the discharge standard of tannery effluents (50 mg/L, DoE, BD). The high value of BOD_5 indicates the presence of a huge quantity of organic substances in the tannery effluent. The larger content of organic ingredients consumed a huge quantity of O_2 and increases the level of BOD_5. A study conducted by Gosh and Hossain (2019) illustrated that the BOD_5 of the tannery effluents obtained was 160 mg/L, which was much lower than the present study findings, indicating that the pollution level is increasing day by day [27].

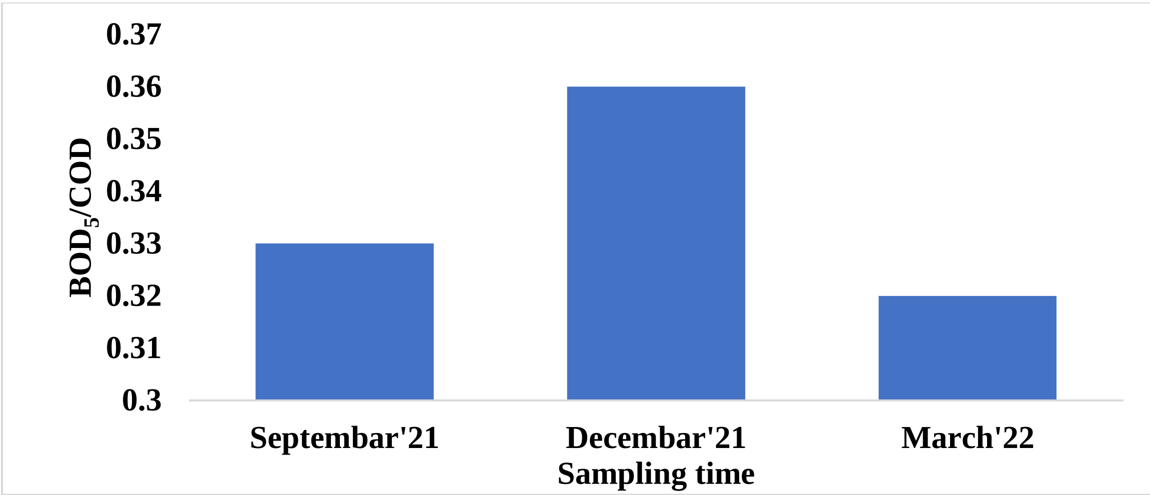

Fig. 4: BOD_5 to COD ratio of the Savar tannery effluents

In the present study, COD values in the tannery effluents at Savar were 1540, 1647, and175 mg/L respectively (Table 1). An average value of COD observed was 1646 mg/L in the composite mixture of the effluent discharged by the tannery industries, which is eight times higher than DoE, and BD discharge standard limits. Jahan et al (2014) stated that the COD value of Hazaribagh tannery industrial effluents was 12840 mg/L, which is about seven times the present study results [28]. The results also indicated that the COD level at all monitoring tannery industries did not meet the standard discharge limit into inland surface water (permissible limit:200 mg/L, DoE BD). The COD level commonly indicates the concentration of organic and inorganic matter in wastewater that is not decomposed by microorganisms [29]. Fig. 4 shows that the BOD_5 and COD ratio of the tannery effluents was found to be between 0.32 and 0.36, indicating low biodegradability. Due to the decrease in water volume in the month of December, the concentration of BOD_5 was getting higher compared to the COD, and thus a higher ratio was obtained. [30]. The reduction of oxygen produces stress on many aquatic organisms, including fish. Effluents released into aquatic ecosystems change pH and increase the BOD_5 and COD. So, the tannery effluents should be treated before being discharged into adjacent water bodies.

3.1.4 Total Hardness

The total hardness of the study ranged from 635, 730, and 672 mg/L in the composite tannery effluents during the study period (Table 1). The highest total hardness observed was 730 mg/L in the discharge effluents. Gosh and Hossain (2019) illustrated that the total hardness of the tannery effluents for the same industrial estate was 490 mg/L, which was lower than in the present study [27]. The higher content of total hardness of the effluents depends on their high carbonate and bicarbonate content and specifies the existence of higher levels of liquified salts in the effluents at CTEP of Savar [31].

3.1.5 Anionic parameters

The chloride (Cl^-) concentration in the effluents of the Savar tannery industrial estate was found to be 2350, 2500, and 2400 mg/L during the study period. The incidence of a higher amount of chloride content in tannery effluents was the consequence of adding the surplus quantity of NaCl for the preservation and pickling procedures of the skins and hides. Thus, it remained a load on the surrounding environment [32]. Hence, a higher value of chlorides in the composite effluents increased the chloride contamination of the adjacent water bodies.

Table 2. Anionic parameters of Tannery Industrial effluents

Parameters	Composite Effluent (Sep 2021)	Composite Effluent (Dec 2021)	Composite Effluent (March 2022)	Mean	DoE	ISW-BDS-ECR	NEQS-2000
HCO_3^- (mg/L)	1250	1050	1300	1200		-	-
PO_4^{3-} (mg/L)	26.6	28.70	29.6	28.3	10	-	-
SO_4^{2-} (mg/L)	1560	1500	1500	1520	400	-	5
Cl^- (mg/L)	2350	2500	2400	2417	600	-	600
$N\text{-}NO_3^-$(mg/L)	56.2	60.1	64.25	60.18	10	-	50

The results of the present research showed that the concentration of phosphate, nitrate, sulfate and bicarbonate ions in the tannery effluent samples of the Savar tannery industrial area ranged from 26.6 to 29.6 mg/L, 56-64, 1500- 1560, and 1050 -1300 mg/L respectively (Table 2). Whitehead et al. (2021) illustrated that the mean concentration of phosphate, nitrate, sulfate, and chloride of the tannery effluents in Bangladesh were 17.6, 61.7, 2783.6, and 6631.7 mg/L, respectively, which have some similarities with the present study results [33]. The values of phosphate, bicarbonate, nitrate, and sulfate of all effluent samples of the tannery industrial estate exceeded the discharge limits set by the NEQS and DoE. The higher content of sulfate in the composite tannery effluent samples may also be the result of many auxiliary chemicals used in the industry. Soaking, pickling, and chrome tanning effluents (stages 1, 4, and 5) confined the level of chloride, to what is shown in Fig. 3.

3.1.6 Cationic parameters

Table 3 shows the concentration of metallic ions in the composite tannery effluents collected from the input of CETP at the Savar tannery industrial area. The results show that the concentrations of metal ions ranged from Ca 185 to 238 mg/L, Cr 75.6 to 85.8 mg/L, Na 1691 to 2000 mg/L, Zn 1.5 to 1.6 mg/L, and Cu 1.7 to 1.8 mg/L during the research period.

The higher content of Na ions in the effluent might be owing to the NaCl salts used in skin and hide preservation and pickling procedures. The presence of Cr in the effluents might be due to chrome-rich tannery wastewater samples. Several researchers reported similar results for metal ions in the tannery effluents [3,35]. The content of metallic ions in the composite tannery effluents was in the following order: Na>Ca>Cr>Cu>Zn based on the mean values. Various health and aquatic hazards are caused by metals released from the leather industry.

Table 3. Cationic parameters of Tannery industrial effluents

Parameters (mg/L)	Effluents (Sep 2021)	Effluents (Dec 2021)	Effluents (March 2022)	Mean	ISI-2000	DoE
Ca	185	232	238	218		-
Cr	75.6	85.8	80.9	80.84	0.1	0.5
Na	1691	1960	2000	1884	-	-
Cu	1.7	1.7	1.8	1.7	2	0.5
Zn	1.5	1.4	1.6	1.5	5	5

Copper is a common environmental metal and is essential in cellular metabolism but at high concentrations, it can be highly toxic to fish [35]. It is an essential substance for human life, however, in high concentrations, it can cause anemia, liver and kidney damage, and stomach and intestinal irritation [36]. It is generally re-mobilized with an acid-base ion exchange or oxidation mechanism [37]. Long-term exposure to copper may lead to liver and kidney damage [38]. Zinc is also an important nutrient in the human diet. A lack of Zn in the diet may be more harmful to human health than an excess of it [39]. However, Zn is highly toxic to some aquatic organisms in aquatic ecosystems. Although the above-mentioned Zn is not carcinogenic to humans, large doses can be fatal [39]. Zinc is an essential micronutrient for all organisms and serves as the active site for a variety of metalloenzymes [40]. Excessive Zn consumption can cause vomiting, dehydration, abdominal pain, nausea, lethargy, and dizziness [39].

4. Conclusion

The pollution due to the discharge of untreated or poorly treated tannery effluents in Bangladesh is the foremost environmental and public alarm. The study results showed high values of EC, TSS, TDS, TA, BOD_5, COD, NO_3-, $SO_4^{2-,}$ HCO_3-, PO_4^{3}-, $Cl^{-,}$ and metals (Na, Ca, Cr, Cu, and Zn) in the composite tannery effluents collected from the tannery estate at Savar. The values of the physicochemical parameters were above the standard permissible limits of effluent discharge prescribed by the ISW-BDS-ECR (1997), DoE, BD, and NEQS (2000). The mean content of TDS, TSS, COD, and BOD_5 were 6817, 1756, 1646, and 553 mg/L, respectively. The nitrate, bicarbonate, sulfate, phosphate, and chloride ions of the discharged tannery effluents at Savar exceeded the standard permissible limit. The values of metal ions in the composite tannery effluents were in the following order: Na>Ca>Cr>Cu>Zn. The BOD_5 and COD ratio revealed that the tannery effluent was low biodegradable. The untreated tannery effluent is not suitable for discharging into nearby surface water bodies. Such performances pose intimidation to humans, aquatic life, and the environment. The study observed that the discharge effluents should be treated before discharge into surrounding water bodies, and the performance of the CETP should be monitored regularly in order to achieve a sustainable environment. Further, the biological treatment process combined with the conventional treatment process could be adopted, and more research should be considered for developing an efficient treatment plant for sustainable industrial wastewater management.

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