Physicochemical Properties and Metal Ions in Water and Sediment of the Dhaleshwari River

Md. Mazharul Islam, Md. Hossan Sohid Shoraoardy Bhuiyan, Rakibul Islam, Mohammad Shoeb*, Md. Iqbal Rouf Mamun and Md Hafizur Rahman

Department of Chemistry, University of Dhaka, Dhaka-1000, Bangladesh

Abstract

This study was aimed to measure sediment and water quality parameter such as moisture and ash content, pH, TOC, TSS, BOD, TOC, DO, Electrical Conductivity (EC) and Na, K, Ca and Cr metal ions from Dhaleshwari River close to the Savar Tannery Estate (STE). The moisture and ash content of sediments were 23.45-31.42% and 2.09-5.80%, respectively. The pHs of sediment and water samples were 5.20-6.21 and 7.68-8.03, respectively. The average of Ca-hardness, DO and BOD in water were 885.9$\pm$88.8, 1.80$\pm$0.10 and 16.70$\pm$ 1.43 mg/L, respectively. The EC of the sediment and water were 24.60-374.00 µS/cm and 32.80-39.50 mS/cm, respectively. The amount of TOC in sediment and water samples were 1.29-3.25g/100g and 2.28-2.70 mg/kg which are very low indicating the fewer amounts of plant and animal residues and sediment biota. TSS in water was 776-936 mg/L which is higher than the permissible limit (600 mg/kg). The Cr content was determined by AAS which implies that the sediment has significantly higher Cr content (38.78-681.62 mg/kg) compared to water (< 0.005 mg/L). The amount of Na and Ca ions were 26.81-45.00 and 16.04-27.36 mg/L, respectively while K ion was very negligible in water.

Keywords: Tannery industries, Water quality, Sediment quality, Physicochemical parameters, Dhaleshwari River, Pollutants

I. Introduction

Raw hides are processed into leather in tanneries for manufacturing different products like shoe, belt, bags, suitcase, jacket, wallet which are high in quality and meet the demand of our own and foreign countries.[1] Tannery industry is entirely run by raw materials available locally like buffalo and cow hides, goat and sheep skins. However, tannery waste can cause serious environmental pollution. Industrialization in the bank of river is one of the major sources of river pollution.[2] It is now a global issue beyond Bangladesh. Tannery industries are the largest producer of hazardous wastes through leather tanning to its finished products.[3] Both the persistent and non-persistent pollutants like as chlorides, sulphate, sulphides, lime, chrome salts, tannins including some organic pollutants as well as dyes, finishing agents, newer synthetic chemicals for processing, etc associated with the threat of human health and environment are discharged from the tanneries.[4-7] Because of the discharge of these wastes into the nearby land, these can be leached and spread into the water bodies and contaminate environment.[8,9] High salinity, High organic and inorganic chemicals, and Cr levels are the index of tannery waste and those degrade the quality of environment.[10, 11] Recently, tannery estate has been relocation from Hazaribagh to Savar area close to the Dhaleshwari river in order to avoid the pollution of the Buriganga River.

But the Dhaleshwari River is now started to suffering from pollution due to the lack of proper technologies for cleaning tannery effluents and proper recycling. At the same time it pushes the tannery workers to the serious health jeopardy.[12] It was reported in the daily newspaper that before relocation tannery killed the Buriganga and after relocation it is killing the Dhaleshwari and its ecosystem (Figure 1).[13-16] The same scenario is repeating, causing the river death and public health in danger and pulverize the fishing system in the

river. Since both the sediment and water are very important part of our environment, the main purposes of our present study are to quantitative determination of different physicochemical parameters such as moisture content, ash contents, pH, DO (Dissolved Oxygen), BOD (Biological Oxygen Demand), TOC (Total Organic Carbon), EC (Electrial Conductivity) for both the sediment and water quality of Dhaleshwari River.

Fig. 1. Tannery waste polluting Dhaleshwari River (a[13], b[14], c[15] and d[16])

II. Experimental

20 water and 20 sediment samples were collected (August, 2019) from the Dhaleshwari River at Jhauchor near Savar in Dhaka. The locations were selected as it covers a range of few meters to several kilometers. Water samples were collected using plastic sampling bottles and sediment samples in polythene bags with proper leveling (Table 1 and 2) stored at -4 ^{0}C. The instruments used were pH meter (Model: JENWAY 3510), EC meter (Model: JENWAY 4510), TOC analyzer (Model: TOC-VCPH, Shimadzu,

*Author for correspondence. e-mail: *shoeb71@yahoo.com*

Japan), Basic titration glass apparatus, Incubator and multi parameter instrument (Model: session 156, Hach), AAS (Model: 6800, Shimadzu), Vortex machine (Model: KEBO Lab REAX-2000).

Physicochemical Parameters

The pH of the water samples were measured with a pH meter at 25-30ºC (Table 1). Intense fluctuation of pH threatens the aquatic life whether it can be acidic, basic or neutral.[17] Sediment sample was mixed with distilled water at 1:10 into a 50 mL Teflon tube and vortexed for 5 min. Then it was centrifuged and filtered for pH. The EC of water is an index of salt content and it is the ability of water to conduct electricity which was measured with a conductivity meter.[18] To determine EC of sediment, it was mixed with distilled water at 1:10 into a 50 mL Teflon tube and vortex for 5 min. Then it was centrifuged and filtered for EC. TOC in water was measured in Centre for Advanced Research in Sciences (CARS), Dhaka University by TOC analyzer. TOC in a sediment sample was determined by Walkley and Black's Wet oxidation method. The oxidation was done by weighing 2g air dried sample passing through a 75-mesh sieve into a 500 mL conical flask. 10 mL of standard 0.5 M $K_2Cr_2O_7$ and 20 mL conc. H_2SO_4 was added and mix thoroughly about 30 min. for completing the reaction. Then 200 mL distilled water was added for dilution. 10 mL of orthophosphoric acid or 0.2gof NaF powder and 2mL of diphenylamine indicator were added. A deep violet color was appeared. Then titration was done with standard $FeSO_4$ solution till the color changes from violet to blue and finally bright green or bottle green and recording the volume of ferrous sulphate needed. A blank titration was carried out (without sediment) in same way. Calculation was done as, Organic carbon% in sediment=(X-Y) ml× 0.003 × 100 ÷ 2×W=Z

Organic carbon% in sediment= Z×1.3= R, Where, X= blank titration reading, Y= sample reading, W= Weight of sediment used. Assume that organic matter contains 58% carbon, thus the organic matter content of the sediment will be calculated as Organic matter in sediment (%) = R × 1.724

The hardness of water was measured by titrimetric method. DO and BOD of water samples were measured using a BOD incubator and a multi parameter analyzer (Model: Session 156, Hach).   BOD implies the presence of biologically active living systems in the water body that use DO and reduce the amount of it in water.[19] TSS test is performed by Whatman 934-AH glass microfiber filter (or equivalent) which has pore size of 1.5 mm and a pre-determined volume usually 0.1 L is passed through it. The filter is weighed before the sample is filtered, and after the filter is dried to a constant weight at 103-105°C. Certain amount of sediment sample was taken into pre-cleaned, weighed and dried crucible and placed them into the furnace. To determine moister content sample was heated for 4 hours at 105 °C, then cooled and weighed and from that we got moisture content. Finally, these samples were

heated for another 6 hours at 700 °C to determine ash content in sediment samples.

Metal ions were measured by flame AAS. Samples were aspirated through nebulizer and absorbance was measured with a blank as reference. At first standard solution of different concentration was prepared for individual elements. 10 water samples were analyzed for Cr at the laboratory of Bangladesh Council of Scientific and Industrial Research (BCSIR), Dhaka, Bangladesh. For analysis of Cr in sediment, samples were dried and then microwave digestion was carried out. The digestion was done by weighing about 0.5 g of sample into each vessel then 10 mL of conc. HNO_3 was added followed by 1 mL of H_2O_2 and stand about 15 min.[20] When the initial reaction between the acids and the samples subsided, all vessels were tightly sealed with screw caps and placed in the microwave. For this program, no cooling step was used and microwave digestion was carried out for 30 min. at 180 °C. After digestion, the content in the vessels were poured into clean 50 mL plastic tubes and diluted with MilliQ-water up to 50 mL. In this study, a statistical calculation, called Pearson Correlation matrix, is done to correlate the physicochemical parameters analyzed in sediment and water.

III. Results and Discussion

20 water and 20 sediment samples of Dhaleshwri River were analyzed (Table 1-3). pH of waters were 7.68-8.03 indicating slightly alkaline in nature while pH of sediment samples were 5.20-6.21 accounting for moderately acidic to slightly acidic in nature. The presence of hydrogen carbonate, carbonates, borates, silicates, phosphates and free hydroxyl ions are responsible for the basic nature of the tannery waste and natural water.[21, 22] The standard limit of pH for water is 6.5-8.5 which indicates the level of pH of the samples are in recommended level.[23,24] Alkalinity of water depends on different salts or anions (chloride, bromide etc.), metal ions or alkaline earth metal elements that form OH^- when dissolved in water. The acceptable sediment pH for most plants is 6.00-7.50, as nutrients are available in this range[25] whereas according to USDA (1998), a pH of 6.60-7.30 is favorable for microbial activities that contribute to the availability of N, S, and P in sediments.[26] Thus, the pH data are within the close vicinity of reported values.[26] The EC implies the overall ionic species in the water[17] and this study reports as 32.80-39.50 mScm-[1] with the average value of 36.15 mScm-[1](Table 1). The higher EC indicate the higher amount of ions in the water. The moderate EC indicate the good numbers of ions present in water. The EC values of water are above the standard level (3 mScm-[1]) (Table 1)[27, 28] due the ionic chemicals or high amount of acid, base and salt in the river water from tannery waste[21, 29] that causes incompatibility of availability free metal ions for living organism in the water body.[21,30]   The EC of sediment is an indication of the presence of water-soluble ions. Most importantly to fertility, EC is an indication of the availability of nutrients in the sediment. The EC of the sediment samples was

24.60-374.00 μScm^{-1}(Table 2) that indicates tannery discharge the soluble salt waste into the land. All the values are below the standard level 2210 μS/cm.[10] Too low EC levels indicate low available nutrients, and too high EC levels indicate an excess of nutrients. The range of TOC was 2.28-2.70 mg/L with mean value 2.48±0.11 mg/L for water samples indicating low TOC in water implies water might contain fewer amounts of plant and animal residues, root exudates, living and dead microorganisms, and sediment biota, organochlorine pesticide, Persistent Organic Pollutants (POPs) etc. Direct release of ternary and other industrial waste into environment can also dramatically increase the value of TOC.

The TOC of sediment was determined by simple Walkley and Black's Wet oxidation method.[31] TOC of sediment was 1.29-3.25% (Table 2).The lower amount of organic matter in other sediment samples might be due to lower amount of organic pesticides was deposited. The Hardness of water was 740-1048 mg/L which is higher as normal surface river water. An acceptable range for free calcium in culture waters is 25-100 mg/L.[32] The high hardness values indicate the abundance of lime stone and other alkaline materials discharged from the tannery industries. For water samples, the DO was 1.61-1.99 mg/L. The permissible standard limit of DO is above 4.5-8 mg/L according to Bangladesh Atomic Energy Commission and 4.5 mg/L.[33] Low DO level of all water samples indicates that these systems are not well oxygenated. BOD of water was 14.20-19.50 mg/L (Table 1). The higher values of BOD are an indicator of polluted quality water due to the waste disposal from tanneries and dairy industries, while a low BOD indicates unpolluted water.[34, 35] The permissible limit of BOD is 30 mg/L.[33]All data are below this standard limit, so there are insignificant amount of organic substance present in the river water which is still in suitable condition for fisheries.[36] But the result in depletion of aquatic DO, and fish and

aquatic insects may die when oxygen is depleted by microbial metabolism which increases the BOD over the standard value. The TSS were 776-936 mg/L with an average of 872±37.44 mg/L (Table 1) which is much more higher than the surface river water. TSS causes turbidity in water disrupting photosynthetic action in aquatic flora.[37] The standard limit of TSS for waste water is 600 mg/L and all the studied data transcend this limit.[33] High-level dumping of carbonates, bicarbonates and chlorides salt of Ca, Mg and Na from industries causes opaqueness.[38]

Both moisture and ash contents of sediment were determined by simple gravimetric method to get an idea about physical and chemical behavior of sediment and these varies place to place and in some place ash content is relatively higher than others. The moisture content was 23.45-31.42% and the ash content was 2.09-5.80%. Cr found in all sediment samples as 38.78-681.62 mg/kg. M.N. Mondol reported the moisture content of sediment as 18-28 and 22-36% in dry season and wet season, respectively, at various sampling points of Hazaribagh area.[39] Our results are also close to these values in Savar tannery zone. The concentration of Cr in sediment was 38.78-681.62 mg/L. Approximately, all the leather production globally follows the chrom-tanning, than vegetable tanning, where salts of chromium like chromium sulphate are widely used.[40,41] Md. Abdul Mottalib reported that Cr in tannery wastewater contaminated sediment of leather industrial areas of Dhaka as 994-1120 mg/L in dry sediment.[42] This concentration is higher enough than Cr in water because dumping of tannery wastes in land is now a general habit of the industries. The world standard limit for Cr in sediment is 70 mg/L.[43] From Table 2, it is clear that more than fifty percent of the samples are below this limit. This may be due to the fact as the water flows downstream, the dilution effect increases; as a result Cr concentration gradually decreases away from main ditch.

Table 1. Water quality parameters of the water samples collected from River side area

Water Samples	Sampling Area	pH	Conductance(mS/cm)	TOC (mg/L)	Ca-Hardness (mg/L)	DO (mg/L)	BOD (mg/L)	TSS (mg/L)
W-01		7.90	38.40	2.51	840	1.75	17.6	854
W-02		7.97	37.80	2.51	780	1.82	16.2	905
W-03	Rim Jhim Point-1	7.75	37.00	2.65	925	1.79	16.8	870
W-04		8.03	39.40	2.45	790	1.68	19.5	826
W-05		7.89	38.00	2.58	865	1.77	16.8	776
W-06		7.69	35.50	2.55	795	1.83	17.5	858
W-07		7.81	34.20	2.44	740	1.61	17.6	874
W-08	Rim Jhim point-2	7.78	36.00	2.53	820	1.65	17.5	840
W-09		7.68	33.80	2.56	790	1.73	14.5	845
W-10		7.77	34.60	2.48	810	1.75	14.8	856
W-11		7.89	39.50	2.28	970	1.85	15.5	936
W-12		7.83	36.80	2.53	1048	1.99	16.8	918
W-13	Jauchor point-1	7.80	37.20	2.46	930	1.73	16.7	846
W-14		7.75	38.40	2.33	980	1.79	14.3	872
W-15		7.90	36.80	2.39	870	1.93	14.2	884
W-16		7.95	33.50	2.50	885	1.96	14.5	908
W-17		7.79	34.80	2.47	970	1.87	14.8	922
W-18	Jauchor point-2	7.83	34.40	2.30	950	1.88	15.2	846
W-19		7.89	32.80	2.70	940	1.78	16.9	860
W-20		7.80	33.40	2.42	1020	1.80	16.3	886

Table 2. Sediment quality parameters and Cr content of the sediment samples collected from River side area

Sediment Samples	Sampling Area	pH	Conductance(μS/cm)	TOC (g/100g)	Moisture Content (%)	Ash Content (%)	Cr content (mg/kg)
S-01		5.39	365.00	1.29	25.71	4.35	44.66
S-02		5.29	374.00	1.52	27.42	5.31	47.89
S-03	Rim Jhim Point-1	5.70	27.20	2.11	28.86	3.98	50.43
S-04		5.68	34.70	2.33	26.14	3.85	49.96
S-05		6.01	24.60	3.10	25.45	4.50	39.64
S-06		5.70	28.60	1.88	29.10	5.20	41.49
S-07		5.98	36.70	2.06	31.42	3.42	41.82
S-08	Rim Jhim point-2	6.15	52.70	2.19	24.53	2.09	38.78
S-09		5.20	60.80	2.67	27.22	3.69	44.63
S-10		5.85	65.90	2.28	24.90	5.10	45.12
S-11		6.10	60.90	1.95	25.60	4.70	68.56
S-12		6.06	65.40	3.25	28.17	4.32	44.63
S-13	Jauchor point-1	5.97	53.20	2.15	27.49	4.07	63.28
S-14		5.48	77.40	2.41	29.13	5.40	100.58
S-15		5.65	106.90	2.56	28.60	5.25	681.62
S-16		5.52	105.20	2.16	26.10	4.20	345.56
S-17		5.62	108.50	2.91	23.65	5.62	105.67
S-18	Jauchor point-2	6.21	90.30	1.85	24.68	4.95	140.50
S-19		6.02	80.60	3.04	23.90	5.80	127.78
S-20		6.12	103.40	3.21	23.45	5.39	234.68

Table 3. Metal ions content in water samples (mg/kg)

Water Samples	Sampling Area	Cr	Ca	Na	K
W-01		<0.005	23.58	35.90	BDL
W-02		<0.005	16.04	26.81	BDL
W-03	Rim jhim point-1	<0.005	27.36	45.00	BDL
W-04		<0.005	19.81	26.81	BDL
W-05		<0.005	23.58	31.36	BDL
W-06		<0.005	19.81	40.45	BDL
W-07		<0.005	16.04	31.36	BDL
W-08	Rim jhim point-2	<0.005	23.58	35.90	BDL
W-09		<0.005	19.81	31.36	BDL
W-10		<0.005	19.81	26.81	BDL
W-11			23.58	40.45	BDL
W-12			27.36	35.90	BDL
W-13	Jauchor point-1	Not observed	23.58	40.45	BDL
W-14			23.58	40.45	BDL
W-15			19.81	35.90	BDL
W-16			27.35	40.45	BDL
W-17			27.36	40.45	BDL
W-18	Jauchor point-2		23.58	40.45	BDL
W-19			27.36	31.36	BDL
W-20			27.36	35.90	BDL

Ten water samples from different sources were analyzed for Cr and were found below 0.005 mg/L. The standard limit of Cr in water is 0.05 mg/L.[44,45] Ahsan *et al.* reported that the concentration of Cr is <0.005 mg/L in Dhaleshwari river which is closest to this study. The very low concentration of Cr is may be due to the stream of river water.[17] Amount of Na, Ca and K ions were analyzed by flame photometer and found in the order of Na (26.81-45.00 mg/L)>Ca(16.04-27.36 mg/L)>K (BDL) ions(Table 3).The permissible level of Na and K ions are 175 and 10 mg/L, respectively (EC)[46] which indicates that all the values are in below permissible limit.

Pearson Correlation (r-value) matrix Table 4 and table 5 elucidate the interconnected relationships among the different physiochemical parameters of water and sediment samples, respectively. In in table 4, the DO of the water sample inhibits a positive significant correlation with Ca Hardness ($r= 0.580$ and $p= 0.007$) as well as with TSS ($r= 0.563$ and $p= 0.010$). Whether, BOD is shows a negative significant correlation with DO ($r= -0.519$ and $p= 0.019$) which indicate that BOD is inversely proportional to DO.

Additionally, in other parameters show some positive and negative interconnection among them but which are not significant statistically. This result suggested that several unused chemicals and tannery waste discharged from the tannery industries are reducing DO in the river water through increasing TSS which causes turbidity in water by disrupting different photosynthetic actions. As a result turbidity stimulate to rise up the conductance. Furthermore, BOD is rapidly increasing through reduction of DO in river water.

Table 4. Pearson Correlation (r) matrix of physiochemical parameters of the water samples

	pH	Conductance	TOC	Ca Hardness	DO	BOD	TSS
pH	1						
Conductance	0.357	1					
TOC	-0.104	-0.274	1				
Ca Hardness	-0.081	-0.010	-0.220	1			
DO	0.152	-0.059	-0.156	0.580**	1		
BOD	0.259	0.288	0.347	-0.300	-0.519*	1	
TSS	0.064	-0.073	-0.297	0.408	0.563**	-0.384	1

** Correlation is significant at the 0.01 level (2-tailed), * Correlation is significant at the 0.05 level (2-tailed).

Table 5. Pearson Correlation (r) matrix of physiochemical parameters and Cr of the sediment samples

	pH	Conductance	TOC	Moisture	Ash Content	Cr content
pH	1					
Conductance	-0.500*	1				
TOC	0.311	-0.496*	1			
Moisture Content	-0.287	-0.119	-0.265	1		
Ash Content	-0.119	0.237	0.199	-0.200	1	
Cr content	-0.072	0.029	0.171	0.018	0.284	1

*. Correlation is significant at the 0.05 level (2-tailed).

However, in case of sediment sample, conductance shows negative significant correlation with pH (r= -0.500 and p= 0.025) and TOC is significantly negative correlated with conductance (r= -0.496 and p= 0.026) (Table 5). That means conductance is inversely proportional to pH and TOC is inversely proportional to conductance. It may be occurred directly release of ternary and other industrial waste into environment which can increase the TOC level usually. Statistically any remarkable correlation is not observed in Cr content including other parameters although some alterations are noticed among them. This finding indicates that due to the reduction of conductance through enhancement of TOC level gradually the pH level is diverging in the sediment of river side. Therefore, it may concluded that due to the discharging of unused chemical and directly releasing of ternary and other industrials waste gradually increase the TOC, pH and BOD through the decreasing of DO level in the river water and river side sediment.

IV. Conclusions

According to this study it was found that water quality parameters varied with different locations of the collected samples. The average pH values of sediment below the neutral condition and that for water was higher than neutral condition. The average EC of the collected water was much higher than surface water. The DO levels were lower than the permissible limit that indicates the water samples were not well oxygenated. The BOD levels were found higher that is an indicator of polluted water. The low TOC values of water indicate that water might contain fewer amounts of plant and animal residues, root exudates and organochlorine pesticides etc. The concentrations of Cr in water samples was very insignificant level and below the detection limit but significantly high in sediments samples. Savar industrial area has established in recent years but our study indicates that it may affect the ecosystem of river in near future unless the respective authority takes measures.

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