

Quantitative Estimation of Cr and Pd in *Heteropneustes Fossilis* Fish due to Absorption from Tannery Waste Water

A. C. Bhowmick^{1*}, R. R. Bhowmick², M. I. Moim¹

¹Department of Chemistry, Mawlana Bhashani Science and Technology University, Santosh, Tangail-1902

²Department of Chemistry, Chhagalnaia Govt. College, Chhagalnaia, Feni-3910

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Abstract

The objective of this research is to reveal the pollution level and its impact on fresh water fish and finally, to estimate the concentration (ppm) of toxic metals chromium (Cr) (53.9 ppm) and lead (Pb) (13.2 ppm) in raw waste water (100%) and in fish (*heteropneustes fossilis*) (Cr 3.4 ppm, and Pb 2.0 ppm) by Atomic Absorption Spectrometry (AAS). Fresh tannery effluent is collected from Hazaribag-Dhaka and as early as possible some physico-chemical parameters of that effluent such as Electrical Conductivity (EC) (535 ms/cm) and pH (6.1), Total Dissolved Solids (TDS) (30336 ppm), Dissolved Oxygen (DO) (2.0 ppm), Chemical Oxygen Demand (COD) (9480 ppm) are determined. Pisci-culture is done by constructing some pilot base fresh water systems in the laboratory and it has been found that in raw waste water (100%), the fish survival rate is only a few hours (5h), where in rest of others such as 75%, 50%, 25% and 5% waste water systems, the survival rate of fishes is longer than a week after increasing the amount of DO artificially. So, if fishes are eaten from nearby fresh water bodies of Hazaribag-Dhaka, ultimately it may harm the normal physiology of human.

Keywords: Waste water; Chemical oxygen demand; Dissolved oxygen; Dissolved solids.

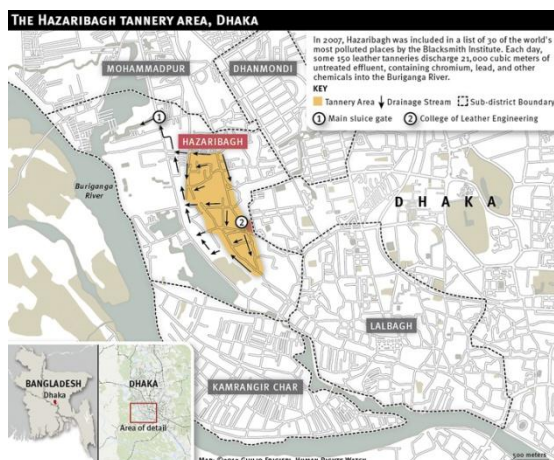
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1. Introduction

Water pollution is one of the major problems of the world and it is increasing day by day due to rapid urbanization and industrialization so, research is going on to estimate the extent of pollution in all aquatic environment and also on marine lives. The major culprit of water pollution is toxic metals and in many forms, it is easily intruding into water. It has been established by research that toxic metals from antifouling paint particles [1], microcystin-LR (MCLR) and copper (Cu) [2], dietary or water borne cadmium (Cd) [3], silver (Ag) nanoparticles from antibacterial agents [4], nickel (Ni) and zinc (Zn) from coal

* Corresponding author: bhowmick_mbstu@yahoo.com

mining [5] are polluting aquatic environment and ultimately, it is harming the dependents of water such marine life even human beings. Recently, it has been investigated the Ni toxicity in marine and estuarine invertebrates and fish [6], mercury (Hg) concentration in sharks [7], toxicity of Cu and chromium (Cr) nanoparticles to *Daphnia magna* [8]. Similarly, due to large scale usage of chemicals in various human activities, industrialization, and also for population [9] growth, Bangladesh is going to a victim from water pollution. The released organic compounds and heavy metals are one of the key factors that exert negative influences on man and environment, those are causing toxicity to plants and marine life [10]. Hence, aquatic pollution [11,12] has become a global problem in recent years. Natural waters are contaminated by untreated wastes of industrial, technological and agricultural, these often contains various metallic compounds. Heavy metals due to the bio accumulative and non-biodegradable properties constitute a core group of aquatic pollutants. While water pollution is easier to study and manage, its control is highly complex and very costly. The effects of water pollution are not only devastating to people but also to animals, fish and birds. Polluted water is unsuitable for drinking, recreation, agriculture [13], industry and all other activities. It diminishes the aesthetic quality of lakes and rivers. Much severely contaminated water destroys aquatic life and reduces its reproductive ability. Tanneries are one of the most prominent sources of pollution of toxic metals (Cr, Pb) to the aquatic environment. If it is not adequately treated, waste water from tanneries contaminates surface water and put sediments to an unacceptable level, as shown by numerous studies from Poland [14,15], Ireland [16], Brazil [17], Mexico [18], Italy [19], Morocco [20], India [21] and many other countries. Various chromium salts as tanning agents introduce reactions lead to the cross-linking (coordination bonds) of collagen fibers, giving the leather its durable finish and stability. Chromium from tanneries is thus discharged principally as Cr (III) bound to organic and inorganic ligands. At neutral or slightly basic pH, Cr and Pb are relatively immobile in tannery sludge [22]. Sabur *et al.* could perceive that property and published their research work of removing these toxic metals from tannery effluent [23]. That's why research is going on to remove all type of toxic chemicals [24] not only from tannery waste, but from any other types of industrial waste water. In Bangladesh the river Buriganga is severely polluting due to direct discharge of waste water from 270 tannery units in Hazaribag-Dhaka (Fig. 1). The physical look and smell of the water body in that area is frightening and annoying. These cause immense harm to the fish and other species in water. Although a lot of research had done previously about pollution, but pollution is continuing and hence, previous studies will no longer valid. So, recent research is very essential to understand the present pollution extent in that area. So, our present study is to reveal the recent pollution level in Hazaribag-Dhaka, to determine some physico-chemical parameters and also, to estimate the amount of Cr and Pb in fresh water fish *Heteropneustes Fossilis*.



Source: Google.com (images for geographical map of Hazaribagh, Dhaka).

Fig. 1. Map of the area of Hazaribagh-Dhaka in Bangladesh.

2. Materials and Methods

2.1. Sample collection

In some plastic containers tannery effluents were collected from the Hazaribagh, which is situated in Dhaka (Fig. 1) and stored in laboratory for further analysis at room temperature in dark place (to avoid precipitation from light). To stop the deterioration of waste water, all experiments were done within one week. However, in one week Cr and Pb could not settle down too much at room temperature.

2.2. Determination of physico-chemical parameters

Some electronic instruments were used to determine the physico-chemical parameters such as temperature, pH (Adwa, model: AD1000, range: -2 to 16, Hungary), DO (Model: D-5509, Auto Cal. Taiwan), TDS (Model: HANNA HI-8734, Germany) and EC (HANNA, HI-8633, India) of the tannery waste water.

2.3. Determination of chemical oxygen demand (COD)

20 mL of sample (tannery waste water) was taken in the conical flask (Pyrex, Germany) (diluted when sample was highly concentrated,) and 10 mL of 0.25 M potassium dichromate solution was added. Later, 1 g of mercuric sulphate (HgSO_4) and 30 mL of sulphuric acid were added to the solution. A water condenser was attached to the mouth of flask and the flask was refluxed for 2 h. The flask was cooled and was diluted to 150 mL by adding distilled water. 2-3 drops of ferroion indicator solution were added and titration was carried out against 0.25 M ferrous ammonium sulphate (FAS) solution. At the end

point, blue-green color of contents was changed to reddish brown. In the same manner blank titration was done by using distilled water with equal volume like first titration instead of sample waste water and all reagents were added in same amount.

Calculation

$$\text{Chemical Oxygen Demand, COD (mg/L)} = \frac{(A - B) \times M \times 1000 \times 8}{V}$$

Where A is volume (mL) of FAS used for blank, B is volume (mL) of FAS used for sample, M is molarity of FAS, V is volume (mL) of sample, 8000 is milli-equivalent weight of $O_2 \times 1000$ mL/L

2.4. Pisi-culture

The fish *Heteropneustes Fossilis* (13 cm length) was collected from local market. Five pilot base aquatic systems were constructed in laboratory with Raw (100%), 75%, 50%, 25% and 5% waste water and distilled water was used for rest of water in these systems. To raise the dissolved oxygen in the water an electric device was used (collected from local market). Next, five fishes were introduced in each artificial pond and monitored their survival condition for one week. During the time of adaptation, the fishes were fed with dried prawn powder mixed with cooked rice and libitum.

2.5. Collection of fish muscle and analysis

After one week fishes were washed by distill water. Thin slices of muscle were taken. Then 1 gm muscle of fish was taken in a round bottom flask (100 mL) with 15 mL distilled water and 15 mL concentrated HNO_3 . Next, the flask was attached with a water condenser and refluxes the mixture for 1h. The resulting solution was cooled and filtered in a volumetric flask and diluted the digest sample into 100 mL. Finally, the resulting solution was used to determine the amount of Cr and Pb by Atomic Absorption Spectrophotometric (AAS) technique.

3. Results and Discussion

All physico-chemical parameters are listed in Table 1 and it is noted that tannery water is heavily polluted and the EC, TDS, COD are found 535 ms/cm, 30336 ppm and 9480 mg/L, respectively. It is also estimated the amount of chromium (Cr) (53.9137 ppm) and lead (Pb) (13.1701 ppm) in the raw tannery waste water (Table 2) by using direct waste water in AAS technique. The physico-chemical parameters of the rest of other artificial aquatic systems are shown in Table 1 and it is seen that their amounts are also in higher proportion, but less than the raw waste water. Various proportions of aquatic system was used, because when waste water from tannery enters into nearby lakes or rivers in Hazaribag-Dhaka, the concentration of toxic metals changes with mixing lake water. In this way, toxic metals concentration is vary from place to place. It was also noted that

fishes survived only for 5h (Table 1) in raw waste water (100%) and within this small amount of time Cr (3.3949 ppm) and Pb (1.9998 ppm) entered into fish muscle (Table 2) at a dangerous level.

Table 1. Physical and chemical estimation of tannery waste water.

Parameters	Raw waste water	75% waste water	50% waste water	25% waste water	5% waste water
Fish life time	5 h	1 week	1 week	1 week	1 week
Physical parameters					
Temperature	28.8°C	28.7°C	27.4°C	29.2°C	29.5°C
EC (ms/cm)	535	245	126	65	27
TDS (ppm)	30,336	20,513	12,502	7739	1535
Chemical parameters					
pH	6.14	6.79	6.89	7.01	7.06
DO (ppm)	2.0	-	-	-	-
COD (mg/L)	9480	7873	5816	1756	502

In all other pilot base aquatic systems fishes survived more than one week with increasing dissolve oxygen and it is also observed that Cr and Pb also entered into fish muscle with good amount. For, 75%, 50%, 25%, 5% waste water Cr amounts in fish muscle were 4.0295, 3.4930, 2.3256, 1.5046 ppm, respectively and also Pb amounts were 2.5972, 2.1374, 1.5539, 1.0009 ppm, respectively (Table 2). So, it is clearly indicating that no marine life could sustain in nearest lakes or rivers of Hazaribag-Dhaka due to pollution from tannery industries. Moreover, if some fresh water fishes could survive there, their body is accumulating huge amount of toxic metals. So, to eat those fishes are hazardous for human life and also for rest of other lives.

Table 2. Concentration of metals in tannery waste water and fish.

Parameters	Raw waste water	75% waste water	50% waste water	25% waste water	5% waste water
Cr in Waste water (ppm)	53.9137	42.9965	28.3312	16.4435	5.8662
Pb ²⁺ in Waste water (ppm)	13.1701	9.4893	7.2265	5.2643	2.0652
Cr in Fish (ppm)	4.3949	4.0295	3.4930	2.3256	1.5046
Pb ²⁺ in Fish (ppm)	1.9998	2.5972	2.1374	1.5539	1.0009

4. Conclusion

Our present study is clearly indicating that day by day the nearest rivers, lakes and ponds of Hazaribag-Dhaka are dangerously polluting by the tannery waste water, since those toxic tannery effluents without doing any treatment are disposed into those water bodies. Thus, toxic metals are directly entering into fish mainly through their gill surface and hence, some organs are facing toxic stress that is leading to structural alternations of fish which may pose a threat for human and dependent other creatures by eating them. So, the water from these rivers should not be used for any purposes even for irrigation. Hence, proper management policies, chemical and biological treatments are needed to ensure safe

disposal of the effluents and to save the natural resources from the severe contamination, otherwise the aquatic environment of the adjacent area will be polluted severely in near future.

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