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REGULAR ARTICLE

HEAVY METALS CONCENTRATION IN DIFFERENT PROCESSING OPERATIONAL WASTE WATER FROM TANNERY INDUSTRY

MD DIDARUL ISLAM*[1], ASHIQUR RAHAMAN[2]. ABONI AFROSE

[1]Department of Applied Chemistry and Chemical Engineering, University of Dhaka, Bangladesh

[2]Institute of Leather Engineering and Technology, University of Dhaka, Bangladesh

ABSTRACT

An investigation was conducted to assess the concentration of heavy metals from waste water of tannery industry located at Hazaribagh area, Dhaka, Bangladesh. The total contents of Cr, Ca, Na, Zn, Hg, Mn and Ni were determined using Atomic Adsorption Spectroscopy (AAS) method which were followed by a wet ashing Digestion process. Average concentration of those heavy metals obtained from different operational section of Samina tannery industry were found 416.89, 628.03, 235.78, 3.912, 0.054, 20.952 and 3.106 mg/l for Cr, Ca, Na, Zn, Hg, Mn and Ni respectively. As recommended by the World Health Organization, the level of those heavy metals in the tannery effluent from different sections have been found highly contaminated and not suitable for irrigation purpose and harmful for environment.

Keywords: Effluents, Digestion, Contamination, Toxic, Heavy metals

INTRODUCTION

Industrial waste are the main sources of all pollutants and is the major concern for reducing the pollution problem. The rapid industrialization has both direct and indirect adverse effects on the environment. The rate of effluent as well as contamination is increasing with increasing unbalanced industrialization [1]. Bangladesh has now more than 30000 industrial units of them 10% of industries and waste water flow from these units to the river without any treatment or with minimal treatment which contaminate agricultural fields, surface water and finally introduced into the food chain [2].

Among all industries tannery industry is ranked as having a highest pollutant producer in different operations and processing purpose. All of the tannery industries in Bangladesh are mainly concentrated in the Hazaribagh area of Dhaka city. More than 200 tannery industries are located in Hazaribagh area and near about 90% of them are engaged in chrome tanning operation [3]. The tannery industry produces wide varieties of toxic chemicals and heavy metals [4, 5]. In each of the steps of tannery processing operation like washing and soaking, liming, deliming and bating large amount of water is consumed. During those operations near around 90% of the water is discharged as organic loading, loading with neutral salts, ammonium and sulfates [6]. The main sources are chromium containing rocks and can be redistributed by volcanic eruptions, some of tannery industries. It is required in small amounts for normal body functions like digesting food, helps to move blood sugar from the bloodstream into the cells. It also used for type 2 diabetes treatment for some peoples, slows the loss of a which prevent bone loss in women during menopause. But its high concentration in drinking water may lead to stomach problems and low blood sugar, too much chromium may damage liver, kidney, nervous system and irregular heart rhythm. In tannery industry during chrome tanning and re-tanning operation, basic chromium sulfate is used as a tanning agent and make leather more soft and pliable [7]. Huge amount of water used during chrome and re-tanning process of them 90% is discharged as effluent which contain untreated unused chromium salts (40%) which causes a serious threat to the environment [8].

Calcium is one of the most abundant mineral which is required for normal development and maintenance of the skeleton and for functioning some neuromuscular and cardiac function [9, 10]. Daily Recommended Dietary Allowance (RDA) is ranging from 700 to 1300 mg for different age and gender. Calcium deficiency may results low bone density, kidney stones, abnormal heart rhythms, poor appetite, lethargy, convulsions and colon cancer [11, 12]. Tolerable Upper Intake Level of calcium depending on age and gender is ranging from 2000 to 3000 mg/day. Overdose of calcium in the human body may lead hyperparathyroidism due to hypercalcemia, increased the risk of kidney stones, prostate cancer, cardiovascular disease [11]. In tannery industry during liming operation, high content of lime is used to swell raw hides and skin. The main purpose of this swelling is to remove hair, flesh and splitting up the fiber bundle from each other [13].

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*Corresponding Author

Md Didarul Islam

Department of Applied Chemistry and Chemical Engineering, University of Dhaka, Bangladesh

Email: didarulislam1992dh@gmail.com

There is no such kind of maximum contamination level of calcium in surface water, but its high concentration in water increase hardness, TDS value and alkalinity of water.

Though sodium is an essential nutrient for human and animal life, there is no fixed minimum daily requirements of it. However, it has been observed that the daily needs of growing infants and young children is ranging from 120-400 mg and for adults 500 mg. Overdose of sodium may lead to kidney damage, cerebral and pulmonary edema, congestive heart failure, gastrointestinal infection [14]. In tanning industry NaCl is used during salting operation as a preservative before soaking operation. Sodium sulfide and sodium hydrosulfite are used to separate the hair from the hide and skin during liming operation. Sodium metabisulphite is used during de-liming operation to prevent toxic H_2S gas formation. Sodium formate used to increase penetration capacity of chrome salt into hides and skins during tanning process. Sodium bicarbonate is used to raise pH during neutralization process. After treatment unreacted components are disposed as effluents and disposed into the environment. All of them contribute to increase the concentration of sodium in surface water, which contaminate surface water of the local Hazaribagh area [7, 15].

The daily requirement of zinc for a healthy adult man is 15-20 mg/day. Though it is an essential element its level in drinking water should be controlled. More than 5 mg/l in water causes a metallic bitter taste and 25-40 mg/l may cause nausea and vomiting. According to WHO, USEPA and ISI permeable limit of zinc in drinking water is 5 mg/l [16]. In tannery industry, there are no use of zinc and zinc compound the contribution of it in de-liming, chrome-tanning, neutralization and re-tanning operation may be due to leaching from steel or from water used during those operations.

Mercury is highly toxic and can cause many types of diseases [17]. In tannery industry, there is no use of mercury so it was found that the level of mercury was very little or no mercury was found in a different processing section of tannery industry. Manganese is an essential in human body functioning both as an enzyme cofactor and as well as constituent of metalloenzymes. Though manganese present in all food its low concentration in water and food have no such kind of adverse effect. The Recommended Daily Intake of manganese from 3 to 7 mg for adults [18]. Overdose of manganese has some toxicity. The Department of Public Health (DPH) sets a permeable level for manganese of 0.5 mg/l to ensure protection against toxicity. Manganese is least toxic elements but its higher oral doses ranging from 1 to 150 mg/kg of body weight may damage central nervous system [19]. Long term exposure of it from 1 to 2 mg/kg may change appetite and reproduction of hemoglobin in rabbits, pigs and cattle were investigated [18]. Manganese dioxide is used in the tannery industry during chrome tanning operation due to the fixation of chromium into the surface of leather. After treatment huge amount of unused MnO_2 remain in the effluent which can contaminate environment if these are not treated before disposed.

Nickel and its compounds are mainly used in industrial purposes and due to the increase of industrialization nickel contamination in the environment also increased. Though it has some unknown metabolic function in the human body, but its high level of human health is highly toxic to living organism [20]. Long term inhalation of nickel may damage the respiratory tract and immune system and also responsible for allergic problem. According to WHO and USEPA permeable limit of nickel in drinking water is 0.025 mg/l [21]. There is no use of nickel in tannery industry and no or very low amounts of nickel will be found in each operational effluents, it may be due to the leachate of nickel from stainless steel as well as from the dye compound which contain some nickel and used during dyeing andfat liquoring operation. So that effluents from dyeing and fat liquoring operation contain some nickel, which can contaminate the surrounding environment.

Experimental

Sample collection

All samples were collected in polyethylene container that were kept overnight in nitric acid and rinsed well with distilled water to avoid contamination from different operational parts of Samina tannery industry located in Hazaribagh area in Dhaka in Bangladesh. After pouring in the bottles, samples were immediately placed in icebox. The samples were taken to the lab within an hour and frozen at-20 °C until analysis. The location of the sample collected area was 23.7361 °N and 90.3631 °E.

Sample preparation (digestion method) and determination of heavy metals

Samples were prepared and determination of heavy metals were done as explained previously [22].

Table 1: Concentration of metals and its maximum contamination level (mg/l) in different part of tannery effluent

Sample ID	Cr	Ca	Na	Zn	Hg	Mn	Ni
Soaking	0.01	0.1	523	1.01	0.01	0.01	0
Liming	0.01	5230	1020	2.01	0	0.5	0
De-liming	0.5	924	500	5.05	0	0	0
Bating	0.04	101	53	1.01	0.01	1	0
Pickling	0.8	5.02	5.5	2.01	0.5	0.01	0
Chrome tanning	2750	5.02	10.5	5.01	0	197	0
Neutralization	297	1.01	223	15.01	0.01	10.5	0
Re-tanning	1050	11.1	20.3	5.5	0	0.5	0
Dyeing	50.3	1.01	2.03	1.01	0.01	0	15.03
Fat liquoring	20.3	2.01	0.5	1.5	0	0	16.03
Average concentration	416.89	628.027	235.783	3.912	0.054	20.952	3.106
MAC*Value WHO guideline	0.05 [22]	-	-	5 [22]	0.002 [22]	0.4 [22]	0.025 [22]

MAC* Maximum Allowable Concentration

RESULTS AND DISCUSSION

In drinking water maximum contamination of chromium level is 0.05 mg/l so concentration should be low as possible. The concentration of chromium in different processing operational part of the tannery effluent ranging from 0.01 to 2750 mg/l. Maximum and minimum concentration are for chrome tanning and soaking and liming operation. Chrome tanning operational effluents possess maximum chromium concentration due to the use of basic chromium in chrome tanning operation for making leather smoother and more resistant to bacteria and high temperature. During tanning and re-tanning operation huge amount of unreacted chromium remains in water, which contaminate other processing water as well as total environment. The average chromium concentration is 416.89 mg/l which exceeds the contamination level. This effluents should be treated before disposed into the sewage system. During liming operation CaO is used to separate the two structural proteins keratin and collagen. From the data table 1 and fig. 2 it is found that calcium concentration is ranging from 0.1 to 5230 mg/l maximum and minimum concentration are liming concentration of Ca in different sections is 628.027 mg/l. There are no such kind of MCL value for Calcium content in water but it is responsible for hardening of water. The acceptable limit of total hardness is 300 mg/l. For that reason calcium level should be removed from effluents.

Table salt is used during soaking operations. Sodium sulfide and sodium hydrosulphide are used to destroy the hair from hides or skins during liming operation. Sodium metabisulphite is used during de-liming operation to prevent toxic H_2S gas formation. Sodium formate used to increase penetration capacity of chrome salt into hides and skins during tanning process. Sodium bicarbonate is used to raise pH during neutralization process. After treatment unreacted components are disposed as effluents and disposed into the environment. From the table 1 and fig. **3** it is found that during soaking, liming and de-liming process higher amount of sodium are disposed into the environment. The maximum and minimum concentration of sodium were recorded 1020 and 0.5 mg/l for liming and fat liquoring respectively. There is no such kind of permeable limit for sodium in drinking and industrial effluent but in those process operation soaking, liming, de-liming and neutralization producing effluent should be treated for removing high content of sodium in water to balance aquatic environment.

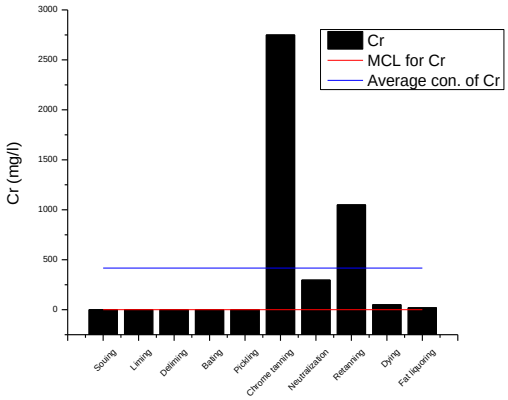

Fig. 1: Concentration of Cr in different parts of processing effluent and average and MCL value

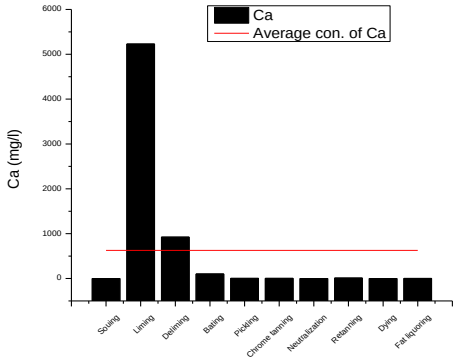

Fig. 2: Concentration of Ca in different parts of processing effluent and average value

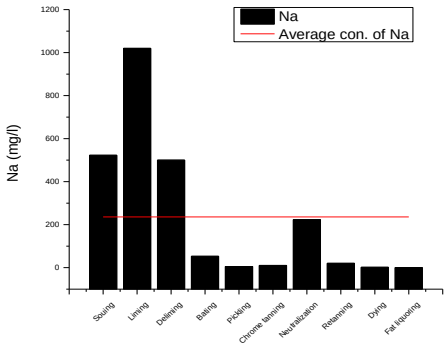

Fig. 3: Concentration of Na in different parts of processing effluent and average value

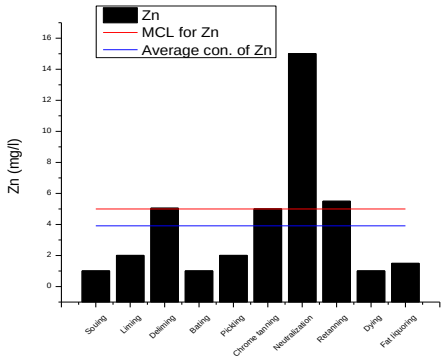

Fig. 4: Concentration of Zn in different parts of processing effluent, Average value and MCL value

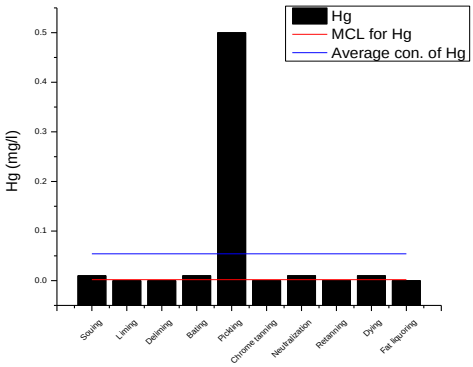

Fig. 5: Concentration of Hg in different parts of processing effluent, Average value and MCL value

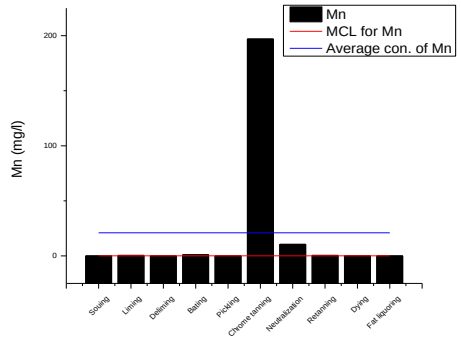

Fig. 6: Concentration of Mn in different parts of processing effluent, average value and MCL value

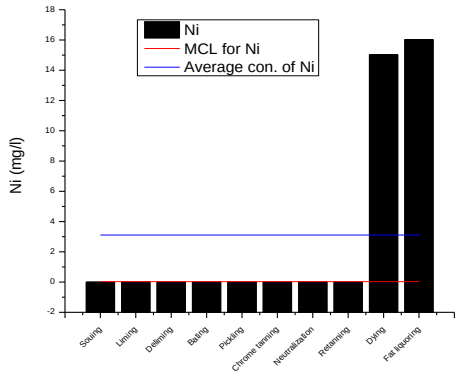

Fig. 7: Concentration of Ni in different parts of processing effluent, average value and MCL value

Zinc is one of the most essential nutrient for human health whose maximum permeable limit is 5 mg/l in drinking water. From table 1 and fig. 4 it was found that the concentration of zinc was ranging from 1.01 to 15.01 mg/l. Its average concentration was found 3.912 mg/l. Effluents from de-liming, chrome-tanning, neutralization and re-tanning operation exceed maximum permeable limit of zinc in drinking water. If all effluents same amounts are mixed and disposed into sewage system no toxicity will happened with zinc because average concentration were lower than the maximum contamination level of zinc in drinking water.

Mercury is one of the highly toxic heavy metals whose maximum contamination level in water is 0.002 mg/l. It was observed most of the effluents does not contain any mercury because in tannery processing operation there was no use of mercury. But effluent from pickling operation contain the maximum amount of mercury (0.5 mg/l). Effluents from soaking, bating, pickling neutralization and dyeing operation contain some mercury which exceed MCL value. The average value of mercury 0.054 mg/l also exceeds MCL of mercury in drinking water. So before disposing this effluent in the sewage system, it should perform a special ETP system to remove mercury from water.

Manganese another toxic heavy metal, the U. S. EPA secondary drinking water regulations recommend its concentration should be low as 0.05 mg/l. For industrial purposes its concentration should not exceed 0.01 to 0.02 mg/l. Concentration higher than 0.05 mg/l water becomes impairing color, order and test. According to EPA and WHO in water its concentration should not exceed 0.5 mg/l. From table 1 and fig. 6 it is found during chrome tanning operation (197 mg/l) large amount of manganese is released into the environment. The average concentration of it is 20.952 mg/l which means this water is highly contaminated by manganese. In this case, before releasing effluents chrome tanning operation, it should be treated to remove manganese.

Nickel and its compounds are highly toxic for human according to WHO and USEPA maximum permeable level of nickel in drinking water is 0.025 mg/l [21]. From the table 1 and fig. 7 it was found that soaking to re-tanning operation there is no presence of nickel in water, but during dying and fat liquoring operation huge amount of nickel is introduced into the system concentration are 15.03 and 16.03 mg/l respectively. The average concentration of Ni in all process effluents is 3.106 mg/l. From the above data, maximum and the average concentration of Ni exceed permeable limit of Ni in drinking water. To make the environment safe from nickel toxicity effluents from dying and fat liquoring should be treated to remove excess nickel.

CONCLUSION

From the study it was found that maximium sample exced the permeable limit of heavy metal in drinking water. Another information was found from the above experiment that if all the sample was mixed in equal amount this mixer also permeate maximum contamination level. So before dumping/mixing with domestic sewage system this effluent should be treated to remove or reduce those contaminants (specially chromium, mercury and nickel) from effluents. These can be done by membrane filtration, precipitation, adsorption and solvent extraction process seperately from after each of the process or after all of the operational effluents are mixed.

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