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ASSESSMENT OF HEAVY METALS DISCHARGING IN HAIR BURNING LIMING OPERATION FROMTANNERIES, BANGLADESH

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Abstract- *In tannery at beamhouse, liming is the first and indispensible chemical operation where conventionally hide/skin is treated with the sodium sulfide (Na_2S) and lime (CaO) to dissolve keratins (hair/wool, epidermis), non-structural proteins and to preparethe peltfor the next operations. Due to having sulfhydryl (-SH) group in hair/wool; it acts as a good accumulator of heavy metals. In hair dissolving liming, heavy metals release into the wastewater. In this study, discharging of heavy metals was evaluated from the hair (cow and goat) and wool (sheep). The collected samples (hair and wool) were acid digested and the aliquots were analyzed by the atomic absorption spectroscopy (AAS). The heavy metals were found in cow hair arsenic 34.3 µg/kg, lead 6520 µg/kg and in sheep wool arsenic 53.2 µg/kg, lead 6386.4 µg/kg, and in goat hair arsenic 12.4 µg/kg, lead 2107 µg/kg and cadmium 123.9 µg/kg. The heavy metals containing wastewater is discharged from the tanneries at Hazaribagh, Dhaka through drain to low lying area and finally fall to the river, Buriganga. A fraction of heavy metals are adsorbed by the soil/sedimentand it could be eluted into groundwater that could be a great threat for human health in the near future.To prevent the heavy metals release from the tanneries, authorities should follow the alternative liming process e.g. enzymatic process.*

Keywords: Hair burning liming, Heavy metals, Arsenic, Cadmium andLead

1. INTRODUCTION

Environmental pollution due to toxic heavy metals has gained attention because of its various detrimental effects on human and other animals [1]. Due to increasing industrialization, disposing of industrial waste, mine tailings, metallurgical slags and municipal sewage sludge are also increased. Hereafter, soil is contaminated from where possibility of leaching toxic heavy metals into groundwater or surface water or enter the human food chain through various chemical and biological reactions. The common sources of arsenic (As), lead (Pb), cadmium (Cd) are diverse in nature including natural and anthropogenic process [2-5].

Hair (keratin) is a good bio indicator of heavy metal levels [6]. Mammalian hair is composed of keratin protein (cysteine) with containing sulfhydryl (-SH) groups which has the binding affinity for various metals [7]. The hair shaft is connected with the blood stream of the hair root which may incorporate metals circulating in the blood during growth [8]. Of course, many factors e.g. breed, sex, age, season, physiological and health state may modify the chemical composition of animal hair [9]. In any case of break down or dissolve the keratin protein is the pathway to enter metals to the environment. Heavy metals pose a threat to the environment due to their toxicity [10].

In tannery, tanning converts hide/skin into leather. Tanning is a complex procedure where a series of chemical and mechanical operations are employed. In tannery at beamhouse, unhairing and liming (generally known as liming) is the first and indispensible chemical treatment where keratinous substances (hair, wool, epidermis, etc.) and interfibrillary proteins (albumins, globulins etc.) are removed by dissolving. Generally there are two types of liming namely hair burning (hair dissolving) and hair saving (painting, enzymatic unhairing). Liming with hair burning is the most polluting part of the entire process of leather manufacture [11]. In the conventional liming operation, sodium sulphide (Na_2S) and lime (CaO) are used which lead to dissolving hair/wool [12]. No doubt heavy metals content in hair/wool release into wastewater by the hair dissolving liming process.

Worldwide contamination of soil with heavy metals due to the waste from tannery is a big problem [13]. The accumulation of heavy metals in soil adversely affects its physiochemical properties leading to infertility and low yield of crops [14]. Besides, the presence of heavy metals in the soil can enter into food chain by passing from soil to plants via herbivorous animals into meat or milk [15]. In addition, groundwater could also be contaminated due to the continuous leaching of heavy metals. Contamination of groundwater by heavy metals may

pose a more serious and continuing health risk to humans as well as to the environment [16].

The present study was a comparative assessment of the heavy metals *e.g.* arsenic (As), cadmium (Cd) and lead (Pb) content in the animal hair/wool especially cow, goat and sheep. The study could aid to quantify information on the environmental impact of the heavy metals, which could suggest various techniques to prevent discharging of hair dissolving wastewater containing heavy metals to the environment. The data generated would be served as baseline data for future studies.

2. MATERIAL AND METHODS

2.1 Sample collection

Hair/wool samples were collected from the hide/skin by using stainless steel knife at slaughterhouse, Fulbarigate, Khulna, Bangladesh. The samples were washed with distilled water to remove dirt/dust; sun dried and cut into0.5–1.0 cm size. The sizing samples were washed with ethanol and dried at 103±2°C in oven for 4 hrs. Then it was kept at desiccator for cooling. In Figure 1shows the hair and wool samples.

Cow Hair Goat Hair Sheep Wool

Fig.1: Hair and wool samples of cow, goat and sheep

2.2 Acid Digestion

The dried samples were weighted about 2 g each and acid digested with nitric acid (HNO_3 65%, Merck KGaA, Germany). The acid mixed samples were heated and refluxed on hot plate for several hours and occasionally nitric acid was added until no brown fumes was given off. Then the mixture was cooled and hydrogen peroxide (30%H_2O_2, Merck, India) was added. The mixtures were heated and refluxed on hot plate and occasionally hydrogen peroxide was added until the effervescence was minimal or the mixtures appearance was unchanged. The mixtures were heated continuing until the volume had become5 mL. Then 50 mL distilled water was added and again heated for another one hour. The mixtures were then cooled and filtrated through the filter paper (Whatman No.1) and solution was made up100 mL with distilled water. The samples were preserved in high density polyethylene (HDPE) bottles at 4°C until to complete the analysis.

2.3 Analysis the aliquot with AAS

Acid digested aliquot was analyzed by the atomic absorption spectroscopy (AAS)(SpectrAA-220, VARIAN, Australia) for the quantitative measurement of the arsenic (As), lead (Pb) and cadmium (Cd). Arsenic was measured hydride vapor generation method using sodium borohydride as reducing agent, carrier gas argon (Ar)at the wavelength of 193.7nm. Lead and cadmium were measured direct flame (air-acetylene) at the wavelength 217.0 nm and 228.8 nm, respectively.

3. RESULTS AND DISCUSSION

3.1 Concentration of heavy metals in hair/wool

Concentrations of three heavy metals were examined of the hair/wool samples. The obtained results of the various concentrations of arsenic (As), lead (Pb) and cadmium (Cd) in hair and wool are shown in the Table 1. The heavy metals were found in cow hair arsenic (As) 34.3 µg/kg, lead (Pb) 6520 µg/kg and in sheep wool arsenic (As) 53.2 µg/kg, lead (Pb) 6386 µg/kg, and in goat hair arsenic (As) 12.4 µg/kg, lead (Pb) 2107 µg/kg and cadmium (Cd) 123.9 µg/kg. Among the various concentrations of heavy metals, lead (Pb) was in higher level. The presence of heavy metals follows the series: Pb> As > Cd.

Table 1: Heavy metals content in hair or wool

Sample	As (µg/kg)	Pb (µg/kg)	Cd (µg/kg)
Cow	34.32±0.015	6520.25±0.002	BDL*
Goat	12.39±0.006	2106.88±0.010	123.93±0.020
Sheep	53.22±0.009	6386.38±0.005	BDL

*BDL → Below detection limit

In Bangladesh, annually about 300 million square feet hides/skins are supplied out of which cowhides 192 million square feet, goatskins 95.5 million square feet, sheep skins 6.8 million and buffalo hides 3.3 million square feet [17].There are 220 tanneries in Bangladesh and 85% of them are located at Hazaribagh [18]; occupying an area 25 ha, three sides are surrounded by the residential areas and the western side is by the flood embankment. Most of the supplied hides/skinsare processed at Hazaribagh tannery area. It seems that the hair burning liming process of the huge amount of hide/skin discharges the large of amounts wastewater.

Generally, the heavy metals containing wastewater is discharged from the tanneries at Hazaribagh, Dhaka through drain to the low-lying area and finally to the river, Buriganga. A fraction of heavy metals are adsorbed by the soil/sediment.It is suspected that heavy metals will be eluted to the groundwater in the tannery area that could be a great threat for human health in the near future. Accumulation of heavy metals in the soil adversely affects its physiochemical properties leading to infertility and low yield crops. The presence of heavy metals in soil can enter into food chain by chemical or biological reactions.

The heavy metals, such as lead, cadmium, arsenic are extremely toxic even in very small amounts. If any of these elements is present in the environment at high concentrations, living organisms are subjected to strong natural selection for tolerance [19].

3.2 Arsenic toxicity and environmental impact

Groundwater arsenic contamination is big issues in Bangladesh. Although arsenic concentration was in the hair/wool sample low but every day huge amount of

hide/skin are being processed at Hazaribagh, Dhaka, Bangladesh where arsenic is continuously discharged as wastewater. Arsenic is a carcinogen both for human and animals [20]. Drinking water is the most important source of intake arsenic by animals and human [21]. Arsenic toxicity symptoms depend on the chemical form ingested [22]. It has broad toxicity [23] which impairs the function of many proteins, forms complexes with coenzymes and inhibits the production of adenosine triphosphate during respiration [24]. Chronic ingestion of inorganic arsenic causes cancer of the skin, bladder, and lungs, as well as neurological and cardiovascular problems [25]. The presence of arsenic in water and its toxic effect on humans through drinking and agricultural practices is a serious environmental problem.

3.3 Cadmium toxicity and environmental impact

Cadmium was found with the lowest concentration in the hair/wool samples. All concentrations except that of goat are lower than the detection limit. Therefore, it can be deduced that cadmium poses little or no treat to this most of this environment.

Cadmium is toxic at extremely low level; it is also associated with the bone defects like osteomalacia, increased blood pressure and myocardia dysfunctions [26].Cadmium is hazardous both by the inhalation and ingestion [27]. The high concentration of cadmium in body is the primary effect of kidney damage and lung emphysema. Cadmium content in soil/sediment and water can be taken up by certain crops, aquatic organisms and accumulate in the foodchain [28].

3.4 Lead toxicity and environmental impact

Lead is the most significant of the toxic heavy metals and the inorganic forms are absorbed through ingestion of food and water as well as inhalation [29].Like arsenic and cadmium, lead is also a toxic heavy metal even at very low levels of exposure in human. Lead targets manifold organs in the body due to its systemic toxicity. It effects on human body that can be both acute and chronic depending on dose and exposure scenarios [30].Apart from the teratogenicity effects of lead, it is poisoning and causes the inhibition of synthesis of hemoglobin, dysfunctions in the kidneys, joints and reproductive systems, acute and chronic damage to the central nervous system, etc. [26].

Children are very vulnerable between the 0-5 years of Pbexposure, which lead the developmental impacts, and subsequently lowering of IQ [30].

4. CONCLUSION

It is obvious that heavy metals were found in the hair/wool samples of cow, goat and sheep. Lead (Pb) was significant amount in hair/wool of cow, goat and sheep. Arsenic concentration was between the range 12.39 µg/kg to 53.22 µg/kg. The goat hair cadmium (Cd) concentration was 123.93 µg/kg but in cow and sheep samples the level was below detection limit. However, hair burring liming process enhances the heavy metals discharge from the tannery through drain to the low-lying area at Hazaribagh, Dhaka and finally to river Buriganga. A fraction of heavy metals are accumulated in the soil that could be adversely affecting on the physiochemical properties of the soil. The presence of heavy metals in soil can enter into food chain. The adsorbed heavy metals by soil/sediment could be eluted to the groundwater that could be a great threat for human health in near future. To prevent the heavy metals pollution from the tanneries in leather processing especially hair burning liming operation should follow an alternative way like enzymatic liming process.

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