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Heavy Metal Speciation and Toxicity Characteristics of Tannery Sludge

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Abstract. Heavy metals present in tannery sludge can get mobilized in the environment in various forms and can be a cause for concern for the natural ecosystem and human health. The speciation of metals in sludge provides valuable information regarding their toxicity in the environment and determines their suitability for land application or disposal in landfills. Concentrations of seven heavy metals (Cr, Pb, Cd, Ni, Zn, As and Cu) in tannery sludge were determined to evaluate their toxicity levels. Metal contents ranged over the following intervals: As: 1.52-2.07 mg/kg; Pb: 57.5-67 mg/kg; Cr: 15339-26501 mg/kg; Cu: 261.3- 579.5 mg/kg; Zn: 210.2-329.1 mg/kg and Ni: 137.5-141.3 mg/kg (dry weight basis).The concentrations of all heavy metals in the sludge samples were lower compared to EPA guidelines except chromium which was found to be several orders of magnitude higher than the guideline value. Toxicity Characteristics Leaching Procedure (TCLP) test indicated that the leaching potential of chromium was higher compared to the other heavy metals and exceeded the EPA land disposal restriction limits. To quantitatively assess the environmental burden of the chromium associated with tannery sludge, the IMPACT 2002+ methodology was adopted under the SimaPro software environment. Considering the USEPA limit for chromium as the baseline scenario, it was found that chromium in the tannery sludge had 6.41 times higher impact than the baseline in the categories of aquatic ecotoxicity, terrestrial ecotoxicity and non-carcinogens. Chromium has the highest contribution to toxicity in the category of aquatic ecotoxicity while copper is the major contributor to the category of terrestrial ecotoxicity in the tannery sludge.

INTRODUCTION

Leather industry plays a significance role in the economy of Bangladesh. Bangladesh earned $1.29 billion from exports of leather, leather goods and footwear in the 2013-14 fiscal which accounts for 4.2 percent of the country's total exports [1]. There are reportedly around 220 tanneries in Bangladesh but, in fact 113 tanneries are in effective operation which are mostly situated at Hazaribagh area [2]. Although the tanning industry is environmentally important as a principal user of meat industry waste, the industry is perceived as a consumer of resources and a producer of pollutants. Annually about 85000 tons of raw material are processed in Bangladesh [2]. Processing one metric ton of raw hide generates 200 kg of final leather product, 250 kg of non-tanned solid waste, 200 kg of tanned waste, and 45-50 m3 of wastewater containing 2500-12500 mg/l suspended solid [3]. In wastewater treatment process, different chemicals are added and most of the chemicals get settled out during the process. Finally they end up in the sludge. Tannery sludge is an unwanted residual solid generated in the tannery wastewater treatment plant and its management is a critical environmental issue. In Bangladesh, there is no set method for tannery sludge disposal, and the sludge are disposed in landfill sites haphazardly or openly, leading to soil, surface water and

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groundwater contamination, and can pose a threat to natural resources, the environment and residents living within the immediate vicinity of the sludge disposal locations [4]. Very common heavy metals like As, Cr, Co, Ni, Cu, Zn, Fe, Cd may be prevalent in the tannery sludge due to use of basic chromium salt, different syntans, dyes, pigments, retanning agents etc. in the tanning process. These heavy metals are very harmful because of their non-biodegradable nature, long biological half-lives and their potential to accumulate in different body parts [5][6][7]. Metal-containing sludge application in agricultural land is risky, because these metals may be taken up by the crop roots and incorporated into the plant tissue. Ultimately, these toxic metals can get entrance into the human body and lead to bio-accumulation and bio-magnification. So excessive accumulation of heavy metals in agricultural soils through wastewater irrigation and sludge disposal may not only result in soil contamination, but also affect food quality and safety [8]. Health effects of these metals include kidney malfunction, the possibility of DNA damage or cancer development, damage to the central nervous system, reproductive failure and possibly even infertility. [5][9][10][11]. Heavy metal concentration in tannery sludge and their mobilization potential are therefore of great interest. Here we determine the various heavy metal contents in sludge generated from the Effluent Treatment Plant of a leather manufacturing industry in Bangladesh. The heavy metal leaching potential from the sludge and its toxicity effect on the environment are also assessed.

MATERIALS AND METHOD

Sludge samples were collected from Apex Tannery Ltd, unit-2, Gazipur, Bangladesh in January, 2015. One month, 6 month and 12 month aged sludge were collected from the sludge drying beds and dump sites to assess the temporal variation of sludge constituents. The samples were stored and conveyed using polythene bags. After collection, some portion of sludge samples were dried in a vacuum oven at 105°C until constant weight, lightly ground for homogenization and prepared for the analysis of selected heavy metals, moisture content and organic content. For heavy metal analysis, 5 gm. of dried sample was digested with acid (HNO3: HCl =1:3 volume ratio) to prepare a 500 ml solution. Finally, concentration of seven heavy metals (As, Pb, Cd, Cr, Ni, Cu, and Zn) was determined in the environmental engineering laboratory, BUET by using Atomic Absorption Spectrophotometer (AAS) (Shimadzu AA 6800). Toxicity characteristics leaching procedure (TCLP) test for sludge samples were performed according to USEPA 1311 method to determine the immediate toxicity level of heavy metals [12]. The environmental impact assessment was conducted based on impact 2002+ methodology using SimaPro, a commonly used Life Cycle Analysis (LCA) software. This software is integrated with various databases and impact assessment methods [13].

RESULT AND DISCUSSION

Physical characteristics of sludge

The pH of sludge samples ranged between 7.4-7.8 and therefore, the sludge can be regarded as neutral. The moisture content of the sludge samples ranged between 60% - 76%. The organic contents of one month, six month and twelve month aged sludge were 33.53%, 27.11% and 24.75% respectively. This indicated that with the increasing the age of sludge the organic content reduced gradually due to degradation of organic substances.

Heavy metal content in sludge

The selected heavy metal concentrations for each sample found in the sludge in this study are shown in Table 1 where sample 1, sample 2 and sample 3 represent one-month, six-month and twelve-month aged sludge respectively. Metal contents ranged over the following intervals: As: 1.52-2.07 mg/kg; Pb: 57.5-67 mg/kg; Cd: < 0.01 mg/kg; Cr: 15339-26501 mg/kg; Cu: 261.3- 579.5 mg/kg; Zn: 210.2-329.1 mg/kg and Ni: 137.5-141.3 mg/kg (dry weight basis). Mean concentration of the metals were: As: 1.769 mg/kg; Pb: 63.77 mg/kg; Cd: BDL; Cr: 19229 mg/kg; Cu: 385.73 mg/kg; Zn: 250.6 mg/kg; Ni: 139.5mg/kg, allowing to arrange the metals from higher to lower mean content in this sludge as: Cr > Cu > Zn> Ni > Pb > As > Cd.

The total heavy metals content found in the sludge were compared to several international regulatory limits of heavy metal content for sludge utilization. The present study found that the average concentration of arsenic, cadmium, lead, nickel and zinc except chromium and copper were well below the India, China and USA Land

Disposal Restriction Limits. When compared with recommended limits, Cr showed more than 75 times higher than SEPAC (State Environmental Protection Administration of China) limit and about 7 times higher than USEPA limit (Table 1) [14]. Usually tannery sludge contains high levels of chromium as most of hides and skins are tanned with basic chromium salt and more than 60% of the chromium is wasted and ultimately transferred to sludge through wastewater treatment processes [15]. Due to high chromium content the sludge will not be suitable for soil amendment applications in agricultural land or home vegetation. The average concentration of copper in the sample was 385.73 mg/kg which exceeded the India (270 mg/kg) and China (100 mg/kg) land disposal restriction limit but was below the USEPA (4300 mg/kg) limit.

TABLE 1. Concentration of heavy metals in tannery sludge and different legislations for sludge utilization

Parameter	Heavy metals in the sample (mg/kg)						
	As	**Cr**	**Pb**	**Cd**	**Ni**	**Cu**	**Zn**
Sample 1	1.7	15339	57.3	BDL	139.7	579.5	210.2
Sample 2	2.1	26501	67.0	BDL	137.5	261.3	212.5
Sample 3	1.5	15847	67.0	BDL	141.3	316.4	329.1
Average	1.8	19229	63.8	-	139.5	385.7	250.6
Standard Deviation	0.3	6303	5.6	-	1.91	170.1	68.0
Permissible limit in India [16}	-	-	250-500	3-6	-	135-270	300-600
SEPAC limit in China [17]	-	250	350	0.6	26600	100	300
USEPA limit (18)	75	3000	840	85	420	4300	7500

NA: Not Available, BDL: Below Detection Limit. (Detection limit for Cd is 0.001 mg/l)

Toxicity Characteristics Leaching Procedure (TCLP) Test

The Toxicity Characteristics Leaching Procedure (TCLP) test is designed to identify wastes that are likely to leach hazardous concentrations of particular toxic constituents into the groundwater. During the TCLP test, constituents are extracted from the waste to simulate leaching actions that occur in landfills.

TABLE 2. Results of concentrations of As, Cr, Pb, Ni, Cu and Zn in Standard TCLP leaching test of leachates from raw sludge

Parameter	Leached as mg/l					
	As	**Cr**	**Pb**	**Ni**	**Cu**	**Zn**
Sample 1	0.013	2.75	0.082	0.32	0.055	0.044
Sample 2	0.015	0.453	0.033	0.088	BDL	0.01
Sample 3	0.019	0.407	0.018	0.147	BDL	0.002
Average	0.016	1.203	0.044	0.185	0.055	0.019
Standard Deviation	0.003	1.340	0.033	0.121	-	0.022

Note: BDL: Below Detection Limit (Detection limit for Cu is 0.001 mg/l)

The result of mean concentrations of As, Cr, Pb, Ni, Cu and Zn in TCLP test is given in Table 2. When the TCLP result is compared with the EPA Land Disposal Restrictions Limits (LDR) [19] (Figure 1), the mean concentration of As, Pb, Ni, Cu and Zn were found to be under the prescribed limit but the mean concentration of chromium exceeded the EPA standard. This indicates that there is a potential risk of ground water contamination by chromium.

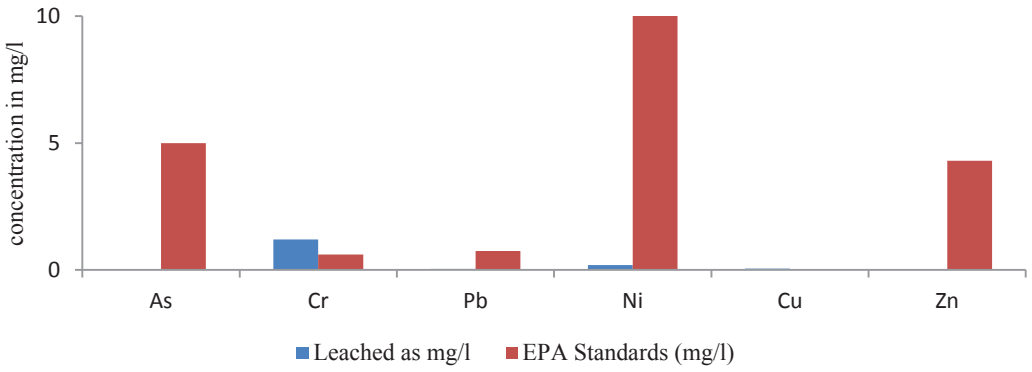

FIGURE 1. Results of average concentrations of As, Cr, Pb, Ni, Cu and Zn in Standard TCLP leaching test of leachates from raw sludge and their EPA Standards

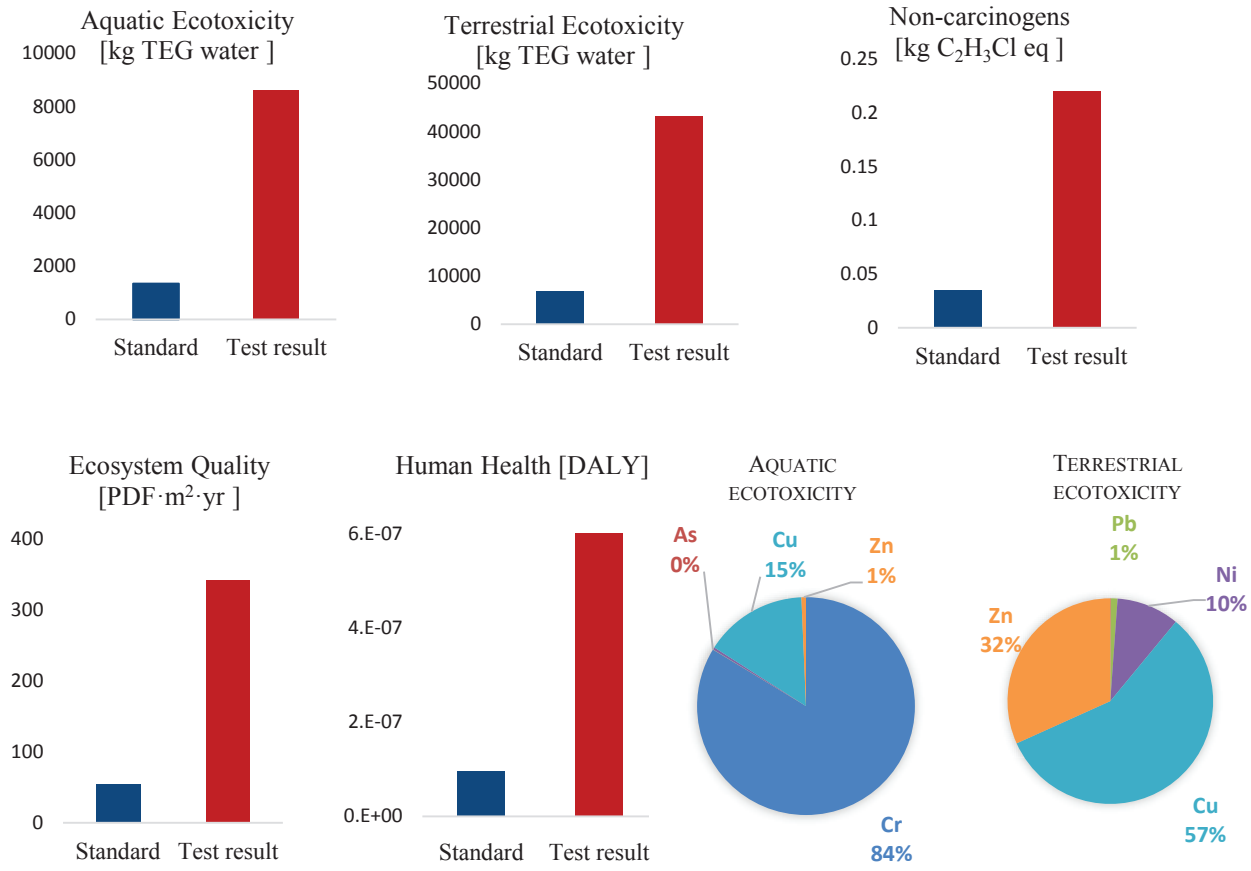

FIGURE 2. The environmental impact (aquatic ecotoxicity and terrestrial ecotoxicity) and damage assessment (ecosystem quality and human health) of chromium obtained from total extraction. Pie charts indicate the relative contribution of heavy metals over impact categories aquatic ecotoxicity and terrestrial ecotoxicity.

Impact assessment

Impact assessment is a technical quantitative, and/or qualitative process to characterize and assess the effects of the environmental burdens. The impact assessment of tannery sludge containing chromium was conducted based on impact 2002+ methodology [20]. This method links all types of results via several midpoint categories like carcinogens, non-carcinogens, aquatic ecotoxicity, terrestrial ecotoxicity, aquatic acidification, aquatic eutrophication, terrestrial acidification/nitrification, land occupation, global warming, non-renewable energy consumption and mineral extraction to four damage categories (human health, ecosystem quality, climate change and resources). Linking to midpoint is associated with certain conversion factors for each pollutant and conversion to damage categories is also associated with damage factors. SimaPro was used to analyze the impact of heavy metal measured from total extraction. It has been found that only chromium goes beyond the USEPA standard limit (Table 1) which has impact in terms of aquatic and terrestrial ecotoxicity (contributing to the damage category of ecosystem quality) and non-carcinogens (contributing to the damage category of human health). The extent of impact with respect to the USEPA standard for all impacts and damage categories is shown in Figure 2. Assessment has been done based on the leachate of heavy metals per kg of tannery sludge released into the agricultural area. It can be seen that the impact of heavy metals in the sludge is estimated to be about 6-7 times higher than that corresponding to the permissible standards stated in USEPA over all the damage categories. This is mainly due to the toxic effect of heavy metals on the ecosystem (both aquatic and terrestrial) and human health. In Figure 2, Kg equivalent of a reference substance expresses the amount of a reference substance that equals the impact of the considered pollutant (e.g. TEG-Triethylene glycol) in the midpoint categories. PDF·m^2·y (Potentially Disappeared Fraction of species disappeared on 1 m^2 of earth surface during one year) is the unit to measure the impacts on ecosystems. DALY (Disability-Adjusted Life Years) characterizes the disease severity, accounting for both mortality (years of life lost due to premature death) and morbidity (the time of life with lower quality due to an illness, e.g., at hospital)[21].
The relative contribution of heavy metals over these damage categories has also been assessed. It has been estimated that chromium has higher order of toxicity (84%) in the aquatic ecotoxicity category followed by copper (15%) for tannery sludge. On the other hand copper contributes the maximum (57%) to terrestrial ecotoxicity followed by Zinc (32%) and Nickel (10%). This assessment has only been done based on the total heavy metal content of the sludge samples.

CONCLUSION

Tannery sludge management in Bangladesh is a challenging task for the industries, which are producing wastewater treatment residues. The traditional means of disposal of sludge has been either by open dumping (sometimes near the rivers) or by land filling which are all uncontrolled processes. This may lead to serious soil and ground water pollution through leaching of heavy metals. Results presented in this study show that Chromium is the principal heavy metal contaminant in tannery sludge that has potential to be released in the environment leading to soil and groundwater pollution. High chromium concentrations in the sludge from tanneries may also render the sludge unsafe for agricultural and home vegetation applications. The impact assessment using SimaPro showed that the release of toxic sludge in the environment has high potential for environmental degradation. In order to reduce the environmental burden of tannery sludge or promote its beneficial uses as compost or soil conditioner, chromium recovery is essential in the effluent treatment process.

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