INVESTIGATION OF HEAVY METALS IN WASTE LIQUIDS DISCHARGED BY THE FACTORIES AT KALURGHAT INDUSTRIAL AREA, CHITTAGONG, BANGLADESH

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ABSTRACT
The waste products in liquid form discharged by the different types of industries like garments, dying, food, paint, paste, paper at Kalurghat Industrial Area, Chattogram, Bangladesh were analyzed for metallic elements Fe, Cu, Mn, Pd and Cd. The concentrations of these heavy metals were obtained by atomic absorption spectrophotometer (AAS) analysis with flame atomizer. The investigation showed that the waste liquids of all types of selected industries contained all the investigated elements where the highest concentration of Fe (17.84 ppm) was found in the waste liquids of Garments industries and the highest concentrations of other investigated elements Cu, Mn, Pb and Cd (Cu-1.93; Mn-1.98; Pb-1.94 & Cd-1.04 ppm) were found in the waste liquids of Dyeing factories. The overall investigation showed that the waste liquids might be considered for cultivated area but not for drinking water. However, the discharge of this wastewater in the open field or in the river may play a role to increase the heavy metals in the environment and in changing the ecosystem of the cultivated and river area.

Keywords: Atomic Absorption Spectrophotometer; Heavy Metals; Waste Liquids.

INTRODUCTION
Human are interfering nature since the dawn of civilization. The rapid increase in population and the increased demand for industrial establishment in order to meet human requirements have created problems on environment such as over exploitation of available resources and pollution of the land, air and water. Industrial pollution is one of the problems presently facing Bangladesh. Chittagong is the fastest rising industrial city in Bangladesh located on the banks of the Karnaphuli River in the south-eastern region of the country. Most of the industries discharge their untreated waste on the environment directly, which disturbs the ecological balance slowly & continuously. According to the WHO, about 80% of the diseases in human beings are caused by water. It is therefore becomes imperative to regularly monitor the quality of effluent from different industries in order to protect the Karnaphuli river as well as the agricultural fields that use the water of this river. In this study, we have chosen the Kalurghat BSCIC industrial area, which is nearer to Karnaphuli River.

Heavy metals are the main group of inorganic contaminants. Irrespective of the origin of the metals in the soil, excessive levels of many metals can result in soil/water quality degradation, crop yield reduction, and poor quality of agricultural products, posing significant hazards to human, animal, and ecosystem health. Therefore, it becomes essential to remove the accumulated metals. For assessing the effluent, an important parameter is to find out the heavy metals of raw wastewater in various industrial discharges and to investigate the toxicity level of the studied metals. It is calculated from the point of view of the ecotoxicology of the environment in regard to surface water pollution.

Some research works have found in literature about the pollution of Karnaphuli River. Ali et al. (Ali et al., 2016) assessed the heavy metals of As, Cr, Cd and Pb in water of this river. the study showed that the
concentrations of As, Cr, Cd and Pb were higher than the safe values which indicated that the river Karnaphuli is polluted by studied heavy metals and might create an adverse effect on this riverine ecosystem. Wang et al. (Wang et al., 2016) analyzed the surface and core sediments collected from Karnaphuli River estuary in Chittagong, Bangladesh for grain-size, total organic carbon (TOC) and heavy metals. The study found the heavy metal concentrations in surface sediments of Karnaphuli River estuary as: Metal contents (dry weight)- Al: 4.67–5.92%, Cr: 77.70–99.08 mg/kg, Cu: 20.34–33.06 mg/kg, Ni: 34.10–41.27 mg/kg, Pb: 23.66–25.05 mg/kg, Zn: 59.69–74.32 mg/kg. Their mean concentrations were 5.45%, 87.42, 25.92, 38.26, 24.20 and 65.53 mg/kg, respectively. These studies also recommended that continuous monitoring of water; sediment and other aquatic biota of Karnaphuli River should be directed to assess the risk of ecology in the vicinity of this river. In this study, therefore the focus will be not only on the elemental quality of effluent discharged in the Karnaphuli River but also on the ecological effect of the investigated heavy metals.

METHODOLOGY
Kalurghat is located several miles north of the port city of Chittagong, Bangladesh, and is mostly famous for several heavy industries located there. A bridge near Kalurghat on the Karnaphuli River connects Chittagong city with the southern parts of the district (Kalurghat, 2017). The BSCIC established an industrial area on a 12-acre stretch of land in 1980 at Kalurghat, Chittagong (Chowdhury, 2011). Fig. 1 shows the location map of the Kalurghat BSCIC industrial area in Chittagong, Bangladesh (Google Maps, 2017).

![Map of the study area](image_url)

To investigate the heavy metals as well as toxic elements in the waste liquids (effluent) discharged by selected industries situated at Kalurghat industrial area, Chittagong, the apparatus named Z-2000 polarized Zeeman Atomic Absorption Spectrophotometer (AAS) at Atomic Energy Center, Chittagong has been used. A number (29) of industries were chosen for sampling. The investigated elements were Fe, Cu, Mn, Pb and Zn.

The following steps had been involved in the proposed studies:
- Following some precautions, the waste liquids samples had been collected from the selected industries in the Kalurghat industrial area.
- Description of each sample had been noted.
- The geographical location of sampling points had been recorded by using Global Positioning System (GPS).
• All waste liquids samples had been mixed up by HNO₃ of analytical grade purity 65% (Merck, Darmstadt, Germany). The dissolved solution had been filtered with mixing DI water and x% HNO₃ and finally diluted by a certain times. Each investigated sample had same dilution factor and then had been stored to analyze.
• To measure the concentration of heavy metals as well as toxic elements in the investigated samples and standard samples, the procedure of the Z-2000 polarized Zeeman atomic absorption spectrophotometer (AAS) (AAS Manual, 2000) had been followed.
• For AAS analysis the measurement mode, level and atomizer were- flame (air- C₂H₂), ppm and standard respectively. The oxygen pressure and measurement time were 160 kPa and 5s × 3 times respectively.
• The concentration of each element found from the analyzer (AAS) had been multiplied by the obtained dilution factor to get the actual concentration of the element in the investigated sample.

Sample preparation and measurement of elemental concentration had been done at Atomic Energy Centre (AEC), Bangladesh Atomic Energy Commission (BAEC), Nasirabad Industrial Area, and Chittagong, Bangladesh and at Environmental Lab, Department of Civil Engineering, Southern University Bangladesh, Chattogram.

Reliability of measurements
Before analyzing the investigated samples, we had done the reliability test of the AAS analyzer by the certified reference materials (CRM) of investigated elements (Fe, Cu, Mn, Pb and Zn) that were produced and certified in accordance with ISO/IEC 17025 and ISO Guide 34. The linear curve of the following Fig. 3 shows the reliability of the measurements.

![Absorbance vs. concentration curve for quantitative determination of Fe measurement](image)

[Fig. 2] Images for Sample and Data collection

[Fig. 3] Absorbance vs. concentration curve for quantitative determination of Fe measurement
RESULTS AND DISCUSSIONS

The Figs. 4–8 present the concentration of heavy metals found in the investigated waste liquid samples and the permissible limit for plant, water and soil to compare with the metal concentrations of the investigated waste liquids for showing the acceptance of these liquids for plant and drinking water. (Permissible Limits for Metals. 2019, WHO permissible limits for heavy metals, 2019).

Fig. 4 shows the average Fe concentration in the investigated waste liquids. Fe was found in all the waste liquid samples except the samples collected from Anwar Fashion (sl.no. 6) and Regent Textile (sl.no. 18) where the element Fe was found below detection limit (Zero or negative values are considered as below detection limit). The maximum concentration of Fe was found in Shyms Fashion Ltd (sl. no. 12) amounted to 17.84 ppm. The minimum concentration of Fe above the detection limit was found in Regent Sping Mill (sl. no. 23) amounted to 0.08 ppm. Therefore, above the detection limit the range of concentration of Fe was found 0.08 – 17.84 ppm. The permissible limit of the Fe concentration for plant is 20 ppm (Shah et al., 2013), which is higher than the maximum concentration of Fe found in the investigated samples (17.84 ppm). The permissible limit of Fe in soil is 550000 ppm which is much higher than the Fe concentration found in the investigated waste liquid samples. However, the waste liquids in this research may be considered for plant with respect to Iron (Fe).

For drinking purpose of human being, the permissible limit of Fe in water is 1 ppm (Gautam and Irfan, 2011). A total number of 18 samples out of 29 investigated samples have Fe concentration above 1 ppm. Therefore maximum of these samples are not acceptable for drinking as regards Fe.

Fig. 5 shows the average concentration of Cu in the investigated waste liquids. Cu was found in all the waste liquid samples except the samples collected from T.K Paper Mill Ltd (sl.no. 1) where the element Cu was found below detection limit. The maximum concentration of Cu was found in Regent Fabrics Ltd (sl. no. 25) amounted to 1.93 ppm. The minimum concentration of Cu above the detection limit was found in several industries amounted to 0.01 ppm. Therefore, above the detection limit the range of concentration of Cu was found 0.01 – 1.93 ppm. The permissible limit of the Cu concentration for plant is 10 ppm (Hassan et al., 2012), which is higher than the maximum concentration of Cu found in the investigated samples (1.93 ppm). The permissible limit of Cu in soil is 36 ppm, which is much higher than the Cu concentration found in the investigated waste liquid samples. However, the waste liquids in this research may be considered for plant with respect to Cu.

For drinking purpose of human being, the permissible limit of Cu in water is 5 ppm (IOM. 2001). None of the samples out of 29 investigated samples has Cu concentration above 5 ppm. Therefore these samples are acceptable for drinking as regards Cu.

Fig. 6 shows the average concentration of Mn in the investigated waste liquids. Mn was not found in seven investigated liquid samples (sl.no. 1, 6, 17, 19, 22, 26 and 29) where the element Mn was found below detection limit. The maximum concentration of Mn was found in Regent Fabrics Ltd (sl. no. 24) amounted to 1.98 ppm. The minimum concentration of Mn above the detection limit was found in the industry Regent Textile (sl. no. 18) amounted to 0.01 ppm. Therefore, above the detection limit the range of concentration of Mn was found 0.01 – 1.98 ppm. The permissible limit of the Mn concentration for plant is 6.64 ppm (WHO Guidelines, 2011), which is higher than the maximum concentration of Mn found in the investigated samples (1.98 ppm). The permissible limit of Mn in soil is 3000 ppm, which is much higher than the Mn concentration found in the investigated waste liquid samples. However, the waste liquids in this research may be considered for plant with respect to Mn.

For drinking purpose of human being, the permissible limit of Mn in water is 0.01 ppm (WHO Guidelines, 2011). A total of 21 samples out of 29 investigated samples have Mn concentration above 0.01 ppm. Therefore, maximum numbers of these samples are not acceptable for drinking as regards Mn.

Fig. 7 shows the average concentration of Pb in the investigated waste liquids. All the investigated samples have Pb concentration above the minimum detection limit. The maximum concentration of Pb was found in Regent Fabrics Ltd (sl. no. 25) amounted to 1.94 ppm. The minimum concentration of Pb above the detection limit was found in the several industries amounted to 0.01 ppm. Therefore, above the detection limit the range of concentration of Pb was found 0.01 – 1.94 ppm. The permissible limit of the Pb concentration for plant is 2 ppm (Hassan et al., 2012), which is little bit higher than the maximum...
concentration of Pb found in the investigated samples (1.94 ppm). The permissible limit of Pb in soil is 85 ppm, which is much higher than the Pb concentration found in the investigated waste liquid samples. However, the waste liquids in this research may be considered for plant with respect to Pb.

For drinking purpose of human being, the permissible limit of Pb in water is 0.05 ppm (Hassan et al., 2012). A total of 27 samples out of 29 investigated samples have Pb concentration below 0.05 ppm. Therefore, maximum numbers of these samples are acceptable for drinking as regards Pb.

Fig. 8 shows the average concentration of Cd in the investigated waste liquids. All the investigated samples have Cd concentration above the minimum detection limit. The maximum concentration of Cd was found in Regent Fabrics Ltd (sl. no. 25) amounted to 1.04 ppm. The minimum concentration of Cd above the detection limit was found in the several industries amounted to 0.006 ppm. Therefore, above the detection limit the range of concentration of Cd was found 0.006 – 1.04 ppm. The permissible limit of the Cd concentration for plant is 0.02 ppm (Hassan et al., 2012), which is lower than the maximum concentration of Cd found in the investigated samples (1.04 ppm). The permissible limit of Cd in soil is 0.8 ppm, which is also lower than the maximum concentration of Cd found in the investigated waste liquid samples. But 27 samples out of the 29 samples have lower concentration of Cd than the above permissible limit of Cd for plant and soil. However, the waste liquids (except two samples sl. no. 16 & 25) in this research may be considered for plant with respect to Cd.

For drinking purpose of human being, the permissible limit of Cd in water is 0.01 ppm (Hassan et al., 2012). A total of 25 samples out of 29 investigated samples have Cd concentration above 0.01 ppm. Therefore, maximum numbers of these samples are not acceptable for drinking as regards Cd.

[Fig. 4] Average metal concentrations (Fe) in the waste liquids discharged by the selected factories at Kalurghat Industrial Area, Chittagong, Bangladesh.
[Fig. 5] Average metal concentrations (Cu) in the waste liquids discharged by the selected factories at Kalurghat Industrial Area, Chittagong, Bangladesh.

[Fig. 6] Average metal concentrations (Mn) in the waste liquids discharged by the selected factories at Kalurghat Industrial Area, Chittagong, Bangladesh.

[Fig. 7] Average metal concentrations (Pb) in the waste liquids discharged by the selected factories at Kalurghat Industrial Area, Chittagong, Bangladesh.
CONCLUSION
The elemental analysis of the waste liquids discharged by the dyeing, garments, paper, textile, salt, soup, paste, paint, fisheries and spinning mills at Kalurghat Industrial Area, Chittagong, Bangladesh has been completed. In this investigation, it has found that the waste liquids of all types (10 types) of industries contained all the investigated elements (Fe, Cu, Mn, Pd and Cd). The waste liquids samples in this research may be considered for using in plantation but maximum of these samples are not acceptable for drinking as regards Fe. The investigated samples may be considered for plant and for drinking as regards Cu. Mn concentrations of these investigated samples are not acceptable for drinking but for plant, these may be considerable. Regarding Pb the waste liquids samples in this research may be considered for plant and for drinking purpose, except two factories (dyeing and garments). Cd concentrations of the investigated samples collected from dyeing and garments factories are not acceptable for drinking and plantation but the Cd concentrations of all other samples are acceptable for drinking and plantation.

ACKNOWLEDGMENTS
We are deeply indebted to the authority of AEC, BAEC, Chattagong for their all administrative and laboratory support during this research work. Thanks are also extended to the authorities of the industries at Kalurghat Industrial Area, Chattogram, Bangladesh, for giving permission and cooperation to collect the samples.

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