Full Length Research Paper

Pollution assessment and heavy metal determination by AAS in waste water collected from Kushtia industrial zone in Bangladesh

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This study was to investigate the contamination level of waste water in the Kushtia industrial region of Bangladesh. Some parameters of waste water were analyzed like pH, electrical conductance, total dissolved solids (TDS), hardness, biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), and for heavy metal (Pb, Cd, Cr, Cu, Mn) concentration. The pH was found to be of range from 8.485 to 4.187; whereas, the electrical conductance was 8.4×10^{-4} to 2.9×10^{-3} $ohm^{-1}cm^{-1}$. In addition, the lowest value of TDS was 567 and the highest was 956 ppm. Furthermore, the hardness was 848 to 485 mg/l as $CaCO_3$. Besides, at 20°C, the BOD values were evaluated from 57 to 88 ppm. The COD values retained were from 150 to 108 ppm. In contrast, heavy metals (Pb, Cd, Cr, Cu and Mn) were analyzed and compared with standards of drinking water. The results indicate that the concentration of Mn (0.68 to 0.72 ppm) exceeded the standards, although Pb and Cu were found within the standard limit at 0.0045 to 0.0085 and 1.33 to 1.58 ppm, respectively. Interestingly, contamination of Cd and Cr identified were below detective level. This study points out the health risk status of waste water for residents and aquatic living being, an ultimate concern for their survival in the region.

Key words: Waste water, pollution assessment, physico-chemical parameters, atomic absorption spectrophotometer (AAS), heavy metal contamination.

INTRODUCTION

Water is an inseparable part of life. Every living being needs water for their survival in this globe. Water is not only used for physical need, but also for various other purposes. In addition, the needs of water are increasing with increasing population. Besides, water is also a crucial raw material for most of the industries; however, it would be detrimental for living beings when polluted. In maximum cases, the effluents discrete from various

industries are not treated before disposal to waterway because of the treatment cost, unconsciousness and other various causes (Shaktibala and Bhagat, 2012; Valipour, 2015a, 2015b; Ladwani et al., 2012). As a result, it is being highly polluted with different kinds of harmful contaminants. As a riverine country, the excretion of industrial effluents of Bangladesh is generally run off into the rivers or the canals. Due to this, the water environment around us is getting polluted and it's getting beyond our control. Although our world contains almost 70% water, the gap between supply and demand is widening and reaching to an alarming level. Every conscience person is trying to find out a way to adjust the gap; but, the disposal of municipal and industrial wastes in the water sources is causing major problems regarding the environment and making it fragile (Paul et al., 2012). In consequence, attempts are been made all around the world to recycle and reuse it effectively and efficiently (Franco et al., 2000; Klavins et al., 2000; Rekha and Ambujam, 2012). In the developed countries, there are strict rules for the evacuation of industries pollutants, whereas in developing countries like Bangladesh, the rules are not followed properly. As a result, most of the rivers in the industrial areas are the final destination of the effluents from the industries. African and Asian countries are experiencing rapid industrial growth and thus this problem hinders the effort to keep the environment free of contamination (Patil et al., 2012; Animesh and Saxena, 2011).

Waste water is water affected in quality from various standard parameters set by anthropogenic influences. The liquid wastes discharged from domestic, industrial, agricultural and related sectors containing various kinds of diseases causing contaminants can be found in waste water. Industrial waste water contains a broad range of contaminants depending on the production of the industry (Gulp and Gulp, 1971). Various kinds of components may be present in wastewater. They can be rinsed waters, including residual acids, plating metals and toxic chemicals (Husain et al., 2014). If the effluents are contaminated with toxic metals, it can compromise human health with acute and chronic diseases (Alam et al., 2007; Rahman, et al., 2014). The waste water from agricultural fields is flowing through numerous water sources, as it may contain various organic matter and plant nutrients. Besides, this effluents may contain considerable amounts of potentially harmful substances and heavy metals like Fe, Cu, Zn, Mn, Cd, Cr, Pb etc (Ram et al., 2011). Plants can accumulate these metals in their tissues in concentration above the standard levels, which may be a threat to life in a complete cycle (Patil et al., 2012; Amin et al., 2010). The dependence of people on this part of the world is ground and surface water. Industrial and municipal wastes are considered as one of the leading causes to pollute water. The water available for drinking, household and irrigation purpose gets contaminated with heavy metals, metal ions and harmful microorganisms (Gupta et al., 2009; Gupta et al., 2012). For this reason, the water used for this purpose should be tested with a regular interval being conscious about various parameters of the water.

Therefore, the goals of this study were to evaluate the characteristics of waste water and heavy metal contaminations which affect the ecosystem. Further study is needed to evaluate the level of contamination of sediments, aquatic species, plants and animal kingdom to obtain a complete status of the environment in this study area so that proper steps to control the water adulteration by toxic chemicals would be taken.

MATERIALS AND METHODS

Study area

Kushtia is one of the fastest-growing industrial areas of Bangladesh. The topography of this area comprises irregular elevated land blocks on which people live in and surround; low-lying areas which are mostly cultivable lands and water bodies. There are two regions where the main industries are set up. These are BSIC industrial area and Gorai river flowing through Kumarkhali Upazilla. Our study area was Kumerkhali Textile and BSIC industrial areas belonging to Kushtia district. This area was selected because in the dry season, the effluents of BSIC deposit on the dry land, while in the rainy season the land is overflowed, and the toxic constituents of the effluents are carried away to nearby villages and other water bodies. The study areas are shown in Map 1.

Physical characteristics

Color

Color is a qualitative characteristic of waste water. With the help of its general condition, the waste water contamination can be assumed. If the color is dark grey or black, the waste water is typically septic, having undergone extensive bacterial decomposition under anaerobic conditions. The color of the sample was compared with the glass comparator and colorless distilled water.

Odor

The determination of odor has become increasingly important, as the odor may give a hint about the presence of various organic unwanted components in the waste water samples. The principal odorous compounds are hydrogen sulphide (the smell of rotten eggs). Other compounds, such as indol, skatol, cadaverin and mercaptan, formed under anaerobic conditions or present in the effluents of pulp and paper mills (hydrogen sulphide, mercaptan, dimethylsulphide etc.), may also cause a rather offensive odor. Odor is measured by successive dilutions of the sample with odor-free water until the odor is no longer detectable.

pH

pH Is considered to be the most important wastewater parameter. Wastewater pH were less than 6 meaning corrosiveness in nature
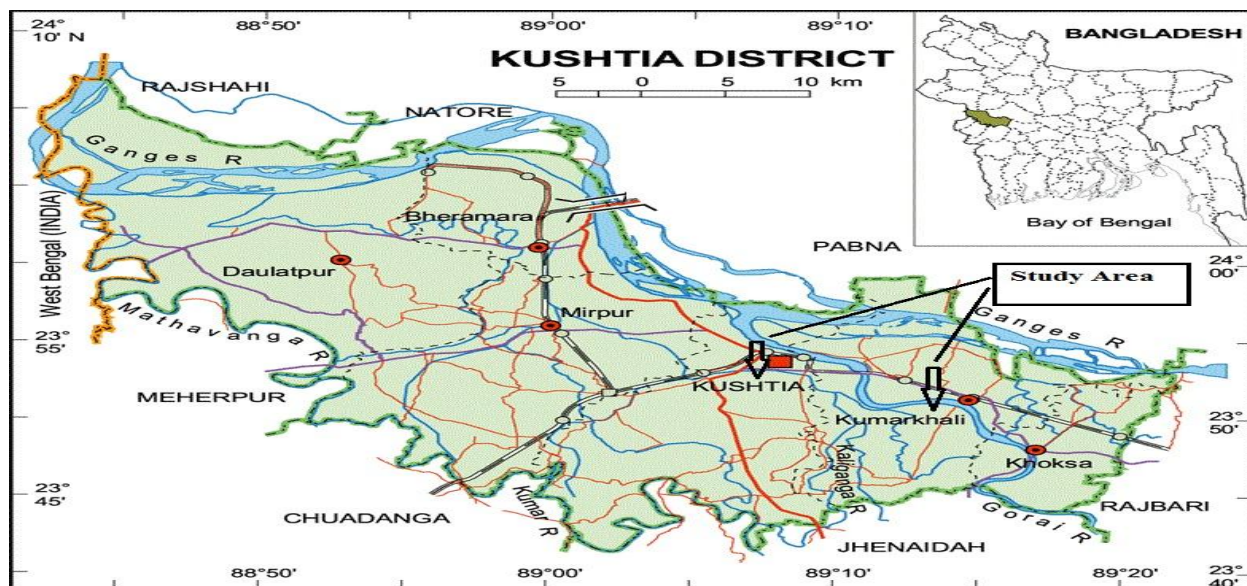
Map 1. Study area of Kushtia distict indicated by black arrow.

and those having pH more than 9 will cause some metal ions to precipitate as carbonates or hydroxides. In this study, pH was determined by digital pH meter (model BT-600) brought from BOECO, Germany.

Electrical conductivity

Electrical conductivity showed the significant correlation with various other parameters. The various drinking water qualities can be checked by controlling conductivity of water and this may also be applied to water quality management of other study area. The electrical conductivity was measured with the help of an electrical conductivity meter (CM-230 meter) which determine the resistance offered by the waste water between two platinized electrodes.

Total dissolved solids

The suspended and dissolved solids in waste water are considered as total solids. Solids that are able to settle can be removed by sedimentation. The unit of solids that are able to settle is milligrams per liter (ppm). Usually, about 60% of the suspended solids in an industrial wastewater have solids that are able to settle. This test was done by measuring the volume of solids in one litre of a sample that will settle on the bottom of a conical flask during the subsequent evaporation and drying in oven at specific temperature 103-105°C.

Chemical characteristics

Organic compounds are the main responsible character for the pollution of water. The organic compounds determine the measure of hardness, dissolved oxygen, BOD, COD, alkalinity etc. It is also caused by various microbial activities of microorganisms. The following parameters have been done to see the waste water contamination levels.

Hardness

Hardness is produced in waste water due to various reasons by multivalent metallic cations. The total hardness in water is defined as the summary concentration of calcium and magnesium cations expressed in milligram equivalents per kilogram or microgram equivalents per kilogram. Hardness is determined by the EDTA method by alkaline condition. When EDTA was added as a titrant, Calcium and Magnesium divalent ions formed complexes resulting in a sharp change from wine red to blue which indicates endpoint of the titration (Kaur and Malik, 2012; Islam et al., 2015).

Biological oxygen demand (BOD_5)

BOD_5 test is a valuable test in the analysis of sewage, industrial effluents and grossly polluted water. It is considered as the major characteristic used in stream pollution control. It is generally the amount of dissolved oxygen required for the biochemical decomposition of organic compounds and the oxidation of certain inorganic materials under controlled conditions of temperature and incubation period which was done for five days incubated at 27°C in BOD_5 incubator (APAO, 1995).

$$BOD_5 = \frac{(D_0 - D_5)}{P}$$

Where, D_o is the dissolved oxygen (DO) of the diluted solution after preparation (mg/l). D_5 is the DO of the diluted solution after 5 day incubation (mg/l); P is the decimal dilution factor.

Chemical oxygen demand (COD)

COD test is useful in studying performance evaluation of wastewater treatment plants and monitoring relatively polluted water bodies. It is used as a measure of oxygen requirement of a

Table 1. Physical properties (color and odor) of samples.

Sample	Colour	Odor
Sample 1	Deep yellow	Pungent odor
Sample 2	Blackish	No odor
Sample 3	Ash colour	Very pungent odor
Sample 4	Blackish yellow	Pungent odor
Sample 5	Light violet	Mild pungent odor
Sample 6	Light ash colour	Mild pungent odor
Sample 7	Light ash colour	No odor
Sample 8	Blackish	No odor

sample that is susceptible to oxidation by a strong chemical oxidant. COD was done with the closed reflux method in which results were obtained in 3-4 h. The test is useful in studying performance evaluation of wastewater treatment plants and monitoring relatively polluted water bodies. We took 15 ml COD digestion tubes (pre-washed with dilute H_2SO_4) and added the following in sequence as transferred 0.50 ml wastewater sample (Inlet) or 1.00 ml treated sample. Then 2.5 ml standard potassium dichromate digestion reagent was added slowly and mixed. Further, 3.5 ml sulfuric acid reagent was added through the side of the tubes and allowed to settle at the bottom. The contents was capped and mixed (wear gloves as the contents are very hot) and cooled. Again, transfer tubes in the pre-heated COD digested at 150°C in 2 h. 3 blanks was applied by substituting DW for sample and the process continued exactly as the sample. In a titration, the contents of the COD digestion tube in 100 ml beaker were transferred. Thereafter, distilled water was added to make the volume to 50 ml. Finally, 1-2 drops of Ferroin indicator was added and titrated against 0.05 M ferrous ammonium sulfate (FAS) solution (Rodríguez-Abalde et al., 2012).

$$COD \text{ as mg } O_2/L = \frac{(A-B) \times M \times 8000}{\text{Sample in ml}}$$

Where, A = ml FAS used for blank; B= ml FAS used for sample and M= molarity of FAS.

Determination of heavy metals by AAS

Heavy metals are important for all living organisms in varying amounts, such as iron, copper, zinc and cobalt, for proper growth. However, the excessive amount of these heavy metals can also produce toxic effects. Thus, the determination of the amounts of heavy metals is especially important where there is a risk of having anthropogenic influence on aquatic environment. Before analysis for heavy metals, the effluent and water samples were filtered through Whatman no. 541 filter paper (Whatman, Germany) into 100 ml of prewashed plastic bottles and the analytical grade HCl was used to adjust water pH to 3.5. After that the samples were kept in a room temperature until analysis. Cadmium (wavelength 228.8 nm), Chromium (wavelength 357.9 nm), Copper (wavelength 324.8 nm), Manganese (wavelength 279.5 nm) and Lead (wavelength 283.3 nm) specific hollow cathode lamps were used to analyze the samples. The instrument has a minimum detection limit of 0.01 mg/l for Cd, 0.10 mg/l for Cr, 0.03 mg/l for Cu, 0.02 mg/l for

Mn and 0.2 mg/l for Pb in the flame method. Samples were aspirated through nebulizer and the absorbance was measured with a blank as a reference. Calibration curve was obtained using standard samples (containing 0.5, 1.0, 1.5 and 2 mg/l for Cd, 0.5, 1.0, 2.0, and 3.0 mg/l for Cr, 0.2, 0.4, 0.8,1.0 and 2.0 mg/l for Cu, 0.1, 0.2, 0.4, 0.8 and 1.0 mg/l for Mn, 1.0, 2.0, 4.0, 8.0 and 10.0 mg/l for Pb). The correlation coefficient was found for Cd 0.998, for Cr 0.999, for Cu 0.999, for Mn 0.999 and for Pb 0.999. The sample had to be diluted many folds to keep the results in the analytical range. The heavy metals (Pb, Cd, Cr, Cu and Mn) concentrations in all samples were determined by atomic absorption spectrophotometer (AAS) (Model AA-6800, Shimadzu Corporation, Japan) using an air-acetylene flame with digital read-out system (Kenawy et al., 2000; Loska and Wiechuła, 2003; Tapia et al., 2012).

RESULTS AND DISCUSSION

Physical characteristics

There were two types of test through which the contamination of waste water samples can be measured. They were physical and chemical tests. The results of various physical tests are given below and discuss about them briefly.

The color and odor of the samples ensure us that the samples collected were contaminated. The color of the most of the samples was yellow, pale yellow or ash, which enhances the probability of presence of various inorganic and organic pollutants. In addition, the odor of the samples was also very pungent or low pungent which also informs the existence of the unwanted contaminants (Table 1).

The maximum pH of 8.485 was reported in sample, number 4 and the least pH of 4.187 were reported of sample number 8. Besides, the low pH of this place and high pH may be due to the various raw materials used and processing techniques adopted in the different industries existing in different areas. In the rest of the places, pH varied between these two extreme values of 4.187 and 8.485, respectively (Figure 1). Furthermore, the electrical conductivity was quite similar. The lowest level was found 8.4×10^{-4} ohm^{-1}cm^{-1} while the highest
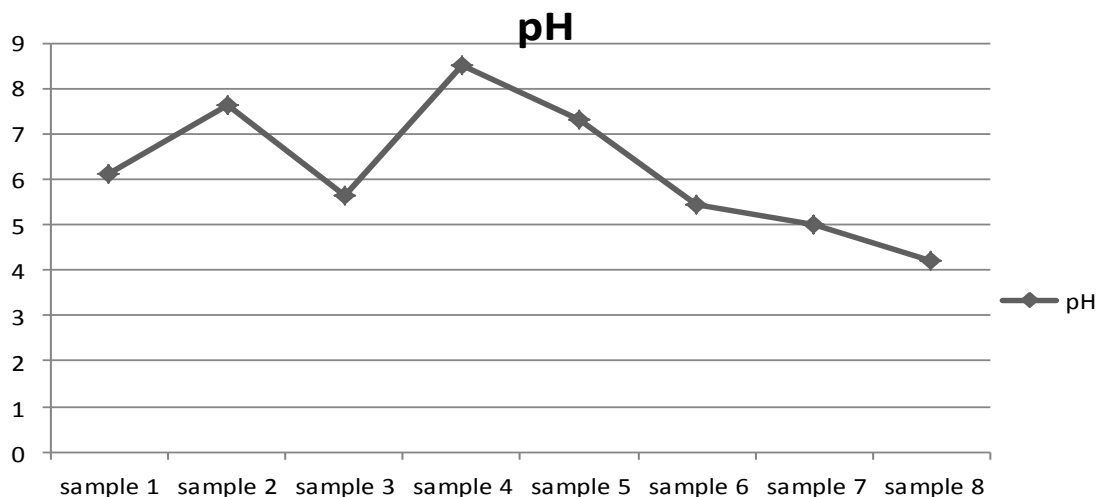
pH

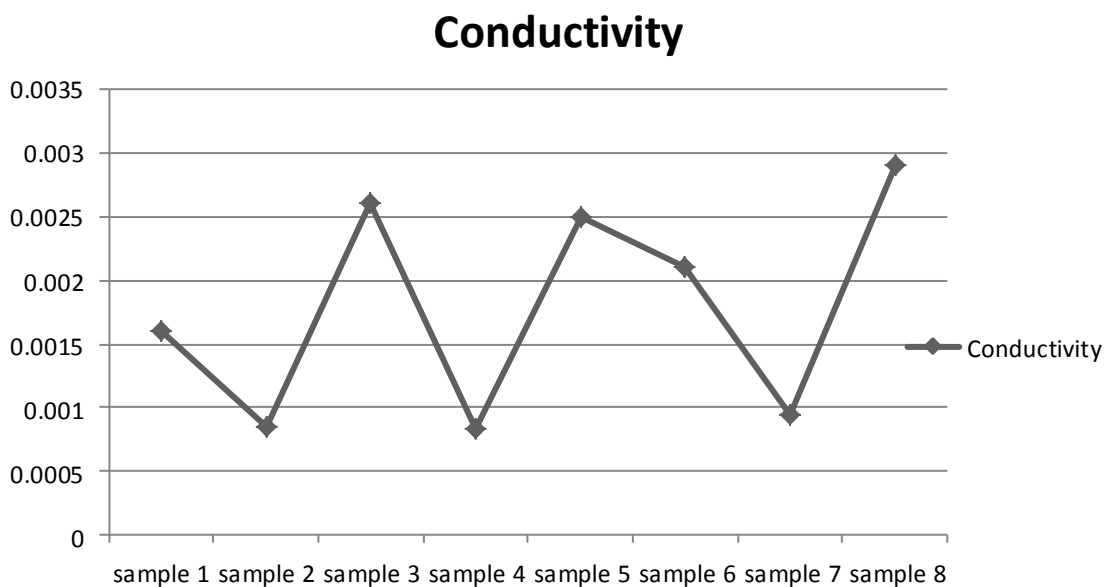**Figure 1.** Graphical representation of observed values of pH.

Conductivity

Figure 2. Graphical representation of observed values of electrical conductivity in ohm^{-1}cm^{-1}.

level was 2.9×10^{-3} ohm^{-1}cm^{-1}. Finally, the TDS of the wastewater samples contained 567 to 956 ppm (Figures 2 and 3).

Chemical characteristics

The highest total hardness level of 848 mg/l as $CaCO_3$ was reported from the waste water sample of BSIC industrial area. This may be due to high total hardness levels in the ground water of this area because most of the water used in residential buildings and industries in this area is taken from the ground water source. Again the lowest total hardness value was 485 mg/l as $CaCO_3$ (Figure 4), these are unacceptable values as compared to those of WHO, the maximum hardness should not exceed 500.

The least BOD_5 value of 57 mg/l at 20°C and the highest BOD_5 value of 88 mg/l were reported (Figure 5). This is because of the low level of micro-organisms present in the wastewater. The BOD_5 values at all other places were found to be within these extreme values
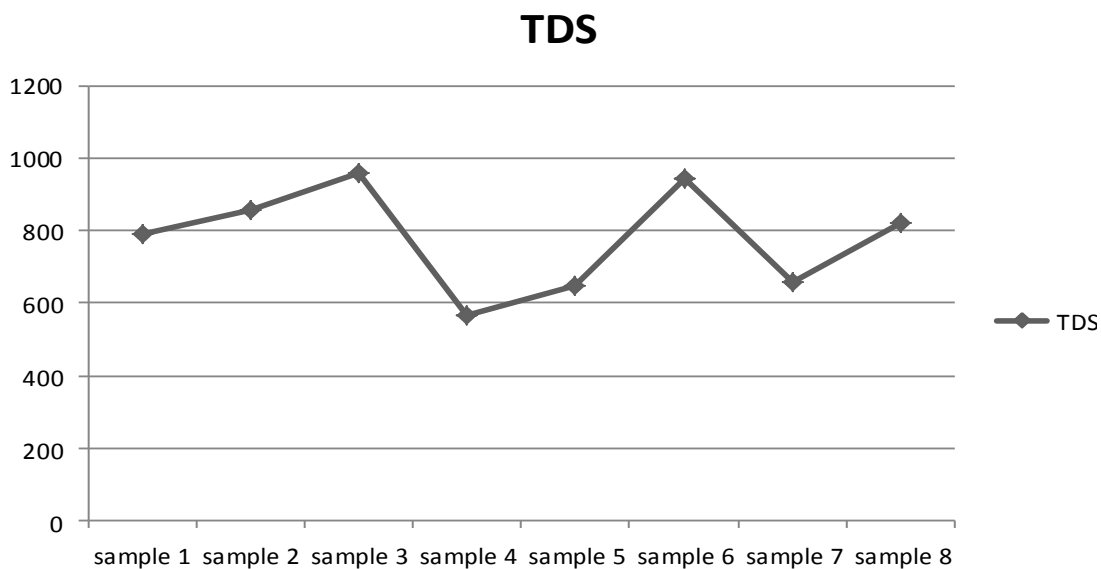
TDS

Figure 3. Graphical representation of observed values of TDS in ppm.
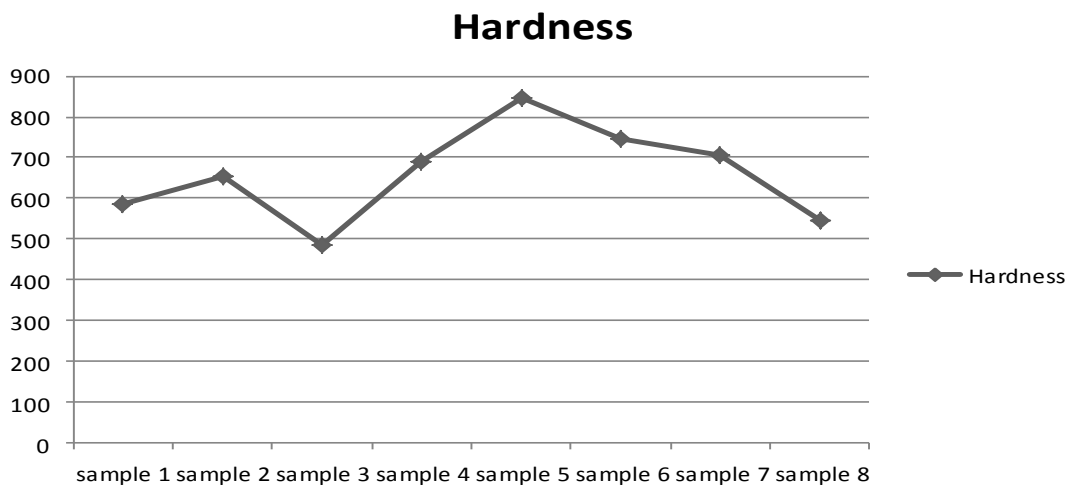
Hardness

Figure 4. Graphical representation of observed values of Hardness in mg/l as CaCO₃.

which are much below the permissible values of effluent discharge as recommended by Bangladesh Water Standard Control Board. Further, COD value of 108 which indicates a lower amount of organic compounds in wastewater collected from this area. The highest value of COD was recorded at 150 mg/l (Figure 6). All other locations were found to be within these values.

Heavy metals concentration in wastewater by AAS

The heavy metal concentrations in water samples of

BSIC and Kumarkhali textile area are summarized in Table 2, including mean metal concentrations with minimum and maximum values, guideline values by the various authorities, and world average background levels. This study revealed that the concentration of heavy metals in the water samples of Gorai river, where the effluents were directly discharged from various industries around Kumarkhali and BSIC industrial areas, was higher than the permitted heavy metal concentrations of various standards. The ranking order of mean metal contents in various zones was Mn> Cu> Pb> Cr> *C*d, thus, Mn was identified as the most abundant in the river water,
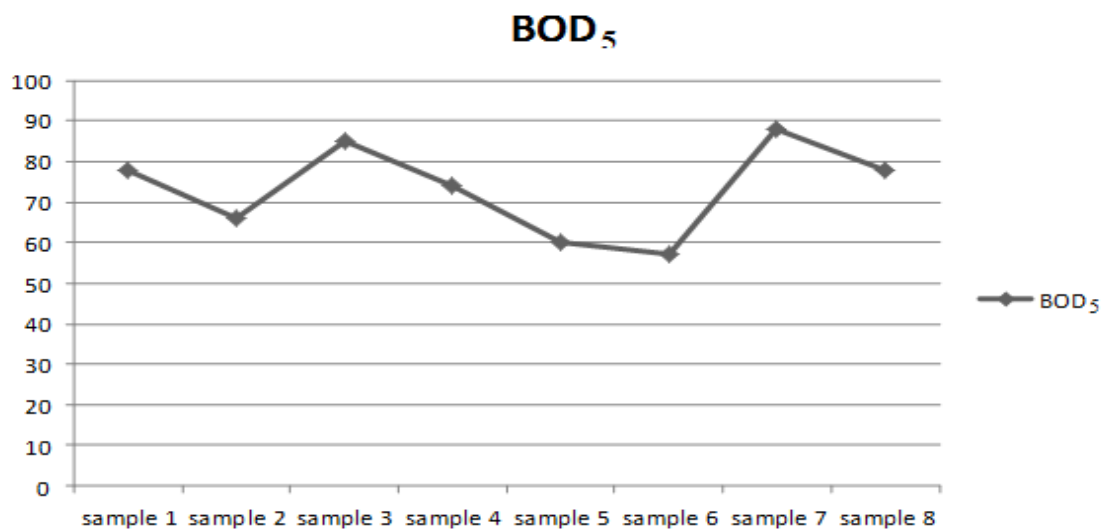
Figure 5. Graphical representation of observed values of BOD$_5$ in ppm.
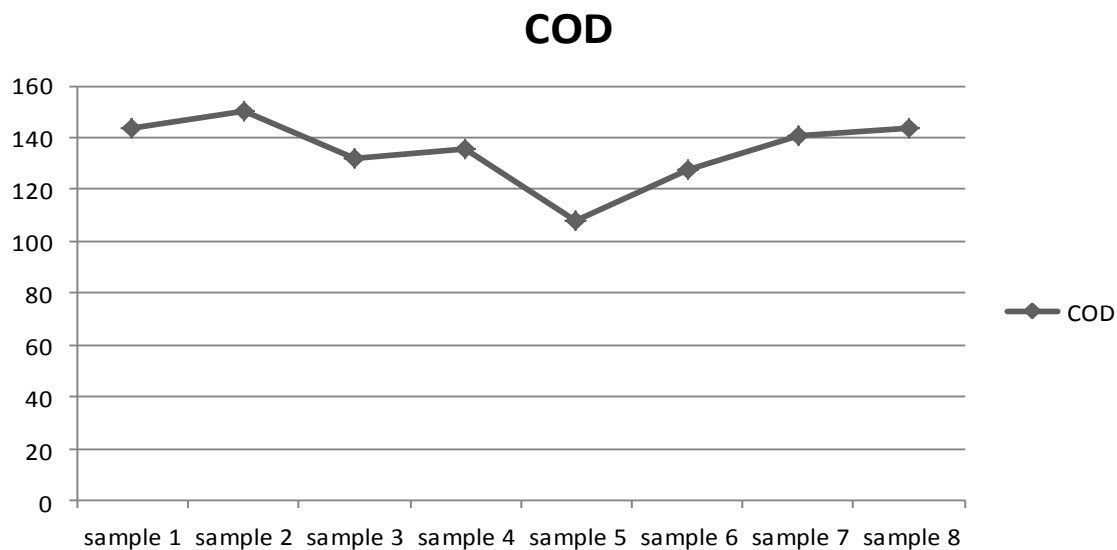
Figure 6. Graphical representation of observed values of COD in ppm.

followed by Cu and Pb, and the least was Cd.

This study reveals that most examined metals concentration in both BSIC industrial area and Kumarkhali textile zone water were generally higher than the reference values suggested by World Health Organization (WHO, 1993), with the exception of Cd and Cr.

However, the metal concentrations in all of the waste water samples were mostly below or close to the Bangladesh drinking water standards Environment Conservation Rules (ECR, 1997) with elevated levels of

Pb, Cd, and Mn concentrations, which could be due to an excess entry of effluents in the water bodies. The Mn concentrations in all of the studied water samples were found to be 0.68-0.72 ppm, which is higher than all prescribed limits (Table 2), and might be due to the fallout of industrial emissions and discharge effluents. Pb and Cu were found within the limit from 0.0045 to 0.0085 and 1.33 to 1.58 ppm, respectively. Besides, contamination of Cd and Cr identified as below detective level (BDL). The contents of all metals in BSIC industrial area and Gorai River water were higher than the respective world

Table 2. The heavy metal concentration in water samples and comparison with water quality guidelines (in ppm).

Station	Pb	Cd	Cr	Cu	Mn	Reference
BSIC industrial area, Kushtia (mean)	0.0085	BDL	BDL	1.58	0.68	This study
Kumarkhali textile area (mean)	0.0045	BDL	BDL	1.33	0.72	This study
Bangladesh drinking water standards	0.05	0.005	0.05	1.0	0.10	ECR (1997)
World Health Organization	0.01	0.003	0.05	2.0	0.50	WHO (1993)
Background concentration world average	0.0002	0.00002	NG	0.001	0.006	Klavins et al. (2000)

*BDL= Below Detection Limit; *NG= Not Given.

average background concentrations.

Conclusions

As a highly dense and growing industrial area, Kushtia is becoming polluted as the effluents are descending their way to the Gorai river and canals. The pH value showed that the effluents disposed are of great corrosion characteristics. The hardness of wastewater samples in this area was quite high. The BOD, COD values indicate that the levels of contamination are increasing; although, the heavy metal contamination was below the standard limit. If proper steps cannot be taken, then contamination in aquatic system will be increased day by day. That is why, it is high time to take proper precautions and strong monitoring so that the environment can be sustained in its original state.

Conflict of Interests

The authors have not declared any conflict of interests.

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