



Assessment of Heavy Metals in Borkena River in South Wollo Ethiopia

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Abstract

Trace elements concentration in Borkena River was investigated, as they can deteriorate water quality. Levels of Lead (Pb) and Cadmium (Cd) in river water and industrial effluents taken from 3 industries found in Kombolcha were determined by differential pulse anodic stripping voltammetry. The river water down the site, where effluents join, had significantly higher concentration of Pb and Cd than did the water above the drainage system. The concentration of Pb and Cd in river water down the site where effluents join were found to be above the permissible limit values of WHO and FAO. The highest contributor was KOSPI: BGI and Textile was the second and third interns of Pb content. The water supply for domestic purpose and irrigation from the river down the site where the drainage system joins were note safe.

Keywords: Heavy metal analysis, Borkena River, Anodic Striping Voltammetry, Industrial Effluents

1 Introduction

Generally industrial or municipal wastes, containing different chemicals, are disposed to water bodies such as lakes, oceans and rivers as water is considered as universal solvent [1]. The chemical contamination of drinking water leads to health problems primarily through chronic exposure, as it may persist for years before detection [2]. In many countries the major chemical pollutant of surface water comes from industrial and municipal sewages as municipalities of cities lacks sufficient waste treatment facilities [3]. Sometimes the corrosion of the urban water supply system also contributes heavy metal contamination of water [5]. The preservation and maintenance of natural water resources is a burning issue. The quality of water resources is deteriorating day by day due to continuous discharge of municipal and industrial effluents. On the other hand, the demand for safe water is increasing continuously due to the increase in population, living standard and industrialization [6]. The discharges from many industrial wastes contain various organic and inorganic water contaminants including higher level of toxic heavy metals like Pb, Cd, Zn, Cu and others. Among the various water bodies river water is the most exposed for pollution due to the direct discharge of municipal and industrial effluents to rivers. Under ground water in the vicinity different drain systems also can be polluted by toxic metals contamination from industrial, domestic, mining and others waste discharges [3-5]. Among the various metal ions Pb, Cd and Hg are toxic at all concentration level and have no known functions. The metal ions of Cu, Zn, Co and Fe are required for physiological and cellular activities but toxic above a certain level [7, 8]. Toxic metals as they are non-

degradable and bio-accumulative, cause tissue degradation in nature [9, 10].

In literature different method has been suggested by author as well some standard method are also available in which Voltammetric is one of them. Voltammetric method was first introduced by Heyrovsky in 1922, it also known as Polarography. Polarography is a special case of voltammetry referring to the current voltage measurement acquired using a dropping mercury electrode (DME) with a constant flow of mercury drops. Voltammetry today represents a refined technique that offers wide limits of detection and is used for trace analysis [3]. Voltammetric techniques offer a number of analytical advantages in environmental analysis [11, 12]. These includes, applicability to a wide range of substances, high sensitivity with a linear concentration range of analyse (10^{-12} to 10^{-1} M), tremendous number of useful solvents and electrolyte, ease of automation, the capability of determining more than one species at a time, a well-developed theory which allows to reasonably estimate the values of unknown parameters, and the ease with which different potential wave forms can be generated and small currents are measured. With impactive impression toward the analyses pollution, it was decided to dected the heavy metal in Broken River by Voltammetric method. The river originates from Tosa Mountain, which is located few kilometres from Dessie town in South Wollo of Amhara region, Ethiopia, and flows down to Kombolcha. Borkena River crosses the plane of Kalu, Kemissie and finally joins to Awash River in Afar region. Thousands of people are dependent on the water of Borkena River and play vital role. The river is used for irrigation, drinking and common household purposes in the towns including Kombolcha, Harbu, Dawa Chefa and Kemisie.

The main objective of this study is to investigate the pollution potential of industrial effluents on the river by considering the targeted toxic metal pollution status of the river and point sources of the effluents.

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2 Material and methods

2.1 Material

2.1.1 Chemicals

Nitrate salts of Pb^{2+} and Cd^{2+} (Blulux), concentrated HNO_3 (LOBA), NaOH (Blulux), sodium acetate (Blulux), acetic acid (Blulux) and distilled water were used through the experiment.

2.1.2 Apparatus

Voltammetric determination of Cd^{2+} and Pb^{2+} was performed with BAS 100B, electrochemical analyzer connected with Dell computer. Three-electrode electrochemical system consisting of a glassy carbon working electrode (radius = 1.5 mm), a platinum wire as counter electrode and an Ag/AgCl reference electrode were used. The glassy carbon electrode was polished with alumina (0.05 μ M) and rinsed with distilled water after each run. To measure the pH of solutions a Jenway digital model 3305 pH meter with a combination of glass electrode were used. Plastic bottles (HDPE), filter paper, electrochemical glass cell were used in the experiment.

2.2 Methods

2.2.1 Preparations of Standard Solutions

- Lead (Pb):** A 0.1599 g of $Pb(NO_3)_2$ was dissolved in 200 mL of distilled water; 10 mL of concentrated HNO_3 was added and the solution was diluted to the mark of 500 mL volumetric flask.
- Cadmium (Cd):** A 0.2744 g of $Cd(NO_3)_2 \cdot 4H_2O$ was dissolved in 200 mL of distilled water, 10 mL of concentrated HNO_3 was added and the solution was diluted to the mark of 0.5 L volumetric flask. The prepared stock solutions were containing 200 mg/L of the targeted metal ions. Standard solutions were prepared by series of dilutions of the stock solutions daily.
- Acetate Buffer:** A 0.1 M acetate butter (pH = 4.5) was prepared by dissolving 8.2 g of sodium acetate in 0.8 mL of distilled water and by adding 5.75 mL of acetic acid (CH_3COOH). The pH of the buffer solution was adjusted by adding drops of concentrated HNO_3 or NaOH. The HNO_3 was also used to acidify the sample which prevents adsorption of the metal ions on the wall of the container. Distilled water was used to prepare solutions and to clean equipments.

2.2.2 Sampling

From five sites, a total of seventeen composite samples were collected in clean high density polyethylene (HDPE) bottles within a week. Seven industrial effluent samples were collected from the outlet of the tankers of KOSPI, BGI and Textile factories according to the schedule of discharge for a week. In order to study the net contamination potential of the industrial wastes at Kombolcha on the river, two sets of samples (five bottles for each) were collected from sites; i) Borkena Before the drain system of Effluents join the river (BOBE); ii) Borkena After the drain system of effluents join the river (BOAE). During sampling, the bottles were first filled and rinsed three times with the sample before collecting some for analysis and a grab sample at each site was collected within 12 hours of a day with 30 minutes intervals. Besides, tap water sample from physical chemistry research laboratory of Bahir Dar University was probed for the toxic metals ions of Pb and Cd.

2.2.3 Sample Preparation

The samples were filtered through 0.45 μ m membrane filter into a beaker and acidified by adding concentrated HNO_3 to the pH of 2. The acidified filtrate was cooled in a refrigerator until analysis to avoid variation in composition [13- 17]. Substantial concentrations of organic materials in samples hinder the electro chemical analysis of metal ions by forming stable complexes with metal and by adsorbing on the electrode surface. To avoid the interference acid digestion of the samples was used. A 50 mL of the acidified sample and 10 mL of concentrated nitric acid in an Erlenmeyer flask was heated on a hot plate for 2 hours. The light-colored solution was cooled and filtered into 50 mL volumetric flask and diluted to the mark. These digested samples were preserved in refrigerator for analysis.

2.2.4 Procedures

In a typical differential pulse anodic stripping voltammetry, 10 mL of a 0.1 M acetate buffer and 10 mL of sample were transferred to a clean cell. After the operating parameters of DPASV have been adjusted the solution was sprayed with nitrogen for 5 min. The operating parameters are given in Table 1.

Table 1: Operating parameter of Voltammetry

S.No	Parameters	Description
1	Mode	Differential Pulse
2	Calibration	Standard Addition
3	Purge Time	180s
4	Deposition Time	300s
5	Quite Time	30s
6	Depositions Potential	-1V
7	Pulse Amplitude	50mV
8	Pulse Width	50ms
9	Initial Potential	-1V
10	Final Potential	-0.2V
11	Sweep Rate	15mV/s

The metal ions of Pb and Cd were deposited by reduction at - 1.0 V on a bare glassy carbon electrode surface. The deposited metals were oxidized by scanning the potential of the electrode from -1.0 to - 0.2 V using differential pulse model.

The voltammogram of the sample were recorded and the procedure was repeated after addition of standard solution of the targeted metal ions. The quantification and determination of sensitivity for Pb (II) and Cd (II) were accomplished by standard addition to the sample. The peak currents of each metal in the sample, and after standard addition were recorded for calibration and quantification. This method was preferred as the sensitivity of differential pulse stripping voltammetry analysis varies between samples of different ionic strength [5, 10, 18].

The activity coefficient and the diffusion current constant of metal ions vary with the matrix of the solution. As the rates of diffusion and the activity coefficients of the analyses vary with composition of the sample, the signal produced by a given analyse changes as the matrix changes. The sensitivity, the magnitude of peak current produced per 1pp, of metal ion in standard and samples of different composition can vary substantially [13, 19-20]. A basic issue that must be considered for all calibration procedures is the matrix effects on the analyse signal. The advantage of standard addition method in both qualitative and quantitative analysis is that all measurements, ($E_{1/2}$, ip), are made in

the same matrix [19]. Hence, as the calibration –curves, as well as, the sensitivity of analyses is strongly affected by the matrix of the solution standard addition method is preferred over the method of calibration using standard solution alone [18, 19].

3 Results and Discussion

3.1 Mechanism of Voltammetric

The common characteristics of all Voltammetric techniques is the application of a potential (E) to an electrode and monitoring of current for chemical analysis. In voltammetry method the potential is varied or the current is recorded over a period of time (t). Thus the current response is used to qualitatively and quantitatively characterize the electro-active species. The current (i) is plotted as a function of an applied potential wave form. The magnitude of the peak current (ip) is proportional to the concentration of the analysis. In each Voltammetric waves, the current increases at the reduction or oxidation potential of the analysis. The measure of the peak currents forms the basis of quantitative analysis. The maximum current is proportional to concentration and the rate of diffusion of analyses from the solution to the electrode surface. The potential at which the diffusion current reaches half of the limiting values is known as the half-wave potential ($E_{1/2}$). It is characteristic of the particular electro- active species involved and used for qualitative analysis of metal ions [18,19]. Half wave potential ($E_{1/2}$) for reduction of metal ions can be expressed by equation (1)

$$E_{\frac{1}{2}} = E^{o'} + \frac{RT}{2nF} \ln \frac{D_M}{D_O} - \frac{RT}{nF} \ln KC_L^m$$

Where; E^o is the standard reduction potential, n is number of electrons, D_M is diffusion coefficient of oxidized specie, D_O is diffusion coefficient of reduced specie. When current is generated because of reduction or oxidation reaction at the WE, a counter reaction takes place at the CE. The analyses in the bulk diffuse to the surface of the WE and undergo reduction or oxidation reaction. The current generated due to this reaction provides chemical information about the analyse. The fundamental principles and applications of the various types of Voltammetric techniques are derived from the same electrochemical theory [21]

3.2 Analysis of Industrial Effluent Samples

3.2.1 Textile Effluent Samples

Three samples collected on different days at the point source of textile effluent site were probed for Pb (II) and Cd (II). Only Pb was found at detectable concentration. In Fig. 1 the DPAS voltammogram for Pb obtained from standard addition in the textile sample. The net current of Pb (II) value in the sample was 12.75 μ A and the reduction potential was observed at - 0. 44 V. The peak current was increasing proportionally with the concentration of Pb in standard addition.

The successive addition of standard solution did not bring significant potential peak shifts or any other changes to the voltammogram, except an increase in peak currents. The peaks of Pb (II) were reasonably symmetric with narrow bas widths. The calibration curve of the peak current as a function of Pb (II) concentrations in solution during standard addition was linear with correlation coefficient (R) = 0.993 as shown in Fig. 2. From the intercept of this line with concentration axis at zero

current signals, the concentration of Pb (II) in the sample can be calculated.

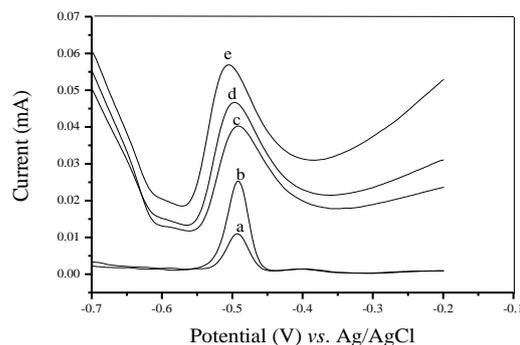


Fig.1: Differential pulse anodic stripping voltammogram for textile effluent sample spiked with standard Pb (II) solution: a) 10 mL of acetate buffer + 10 mL of sample, b) a +100 μ L of 10 mg/L standard Pb solution, c) a + 150 μ L of 10 mg/L standard Pb solution, d) a + 200 μ L of 10 mg/L standard Pb solution, e) a + 250 μ L of 10 mg/L standard Pb solution.

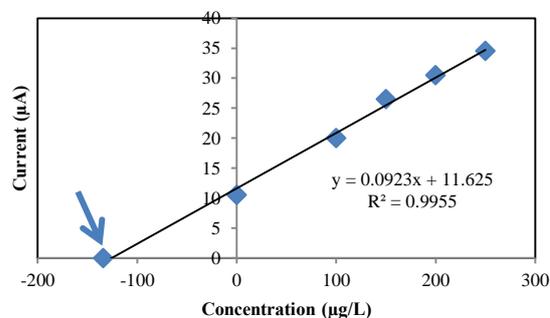


Fig.2: Plot of peak current as a function of concentration for Pb (II) obtained by standard addition method in textile sample.

In the three samples from the same site similar peak currents and average Pb (II) concentrations were obtained. The average Pb (II) concentration determined from the intercept and R value of the calibration plot was $134 \pm 3 \mu\text{g/L}$.

3.2.2 BGI Effluent Samples

Based on the waste disposal schedule, after the waste has been passed the treatment system three effluent samples were collected at a point source of BGI. These different samples were analyzed for detection of Pb (II) and Cd (II) by differential pulse anodic stripping Voltammetry. From the three samples only Pb (II) was found. In Fig. 3 the DPAS voltammogram of Pb in three BGI effluent samples. The voltammogram of each sample were broad with different peak currents as indicated in the figure. The reduction potential of Pb (II) was observed at - 0. 42 V and the average peak current was 23 μ A. The magnitude of the peak currents of sample two was higher than that of sample three and sample one. But the sensitivity for Pb (II) in each sample was identical.

Based on their peak currents, sample two has the highest Pb (II) concentration and sample one has the least. The average concentration of Pb (II) calculated from the sensitivity determined by single standard addition method and from the peak currents of each sample was found to be $241 \pm 5 \mu\text{g/L}$. The sensitivity of the technique for Pb in these samples was $95.2 \text{ nAL}/\mu\text{g}$ and current produced by 1 $\mu\text{g/L}$ of Pb in the solution. To determine the sensitivity a single standard addition

method was used: the current produced before and after spiking with 10 mg/L of Pb solution were recorded and the proportion was set from the change in concentration and current produced. The plot of peak current for function of concentration shown in Fig. 4.

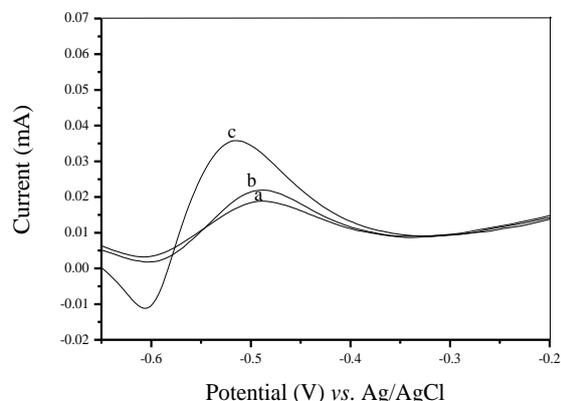


Fig.3:Differential pulse anodic stripping voltammograms for three BGI effluent samples in 0.1 M acetate buffer at pH = 4.5; a) sample 1 b) sample 2 c) sample 3

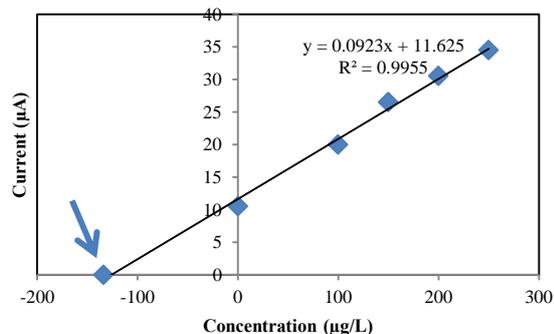


Fig.4: Plot of peak current as a function of concentration for Pb (II) obtained by standard addition method in BGI sample.

In the three samples from the same site similar peak currents and average Pb (II) concentrations were obtained. The average Pb (II) concentration determined from the intercept and R value of the calibration plot was $241 \pm 5 \mu\text{g/L}$.

3.2.3 KOSPI Effluent Samples

A bottle of composite sample from the point source was analyzed for determination of Pb (II) and Cd (II). The DPAS voltammogram for KOSPI waste water sample obtained from standard addition technique is shown in Fig. 5. Both Pb (II) and Cd (II) were detected in this sample. The Cd stripping peaks in the sample, and after spiked with standard solution, were symmetric with narrow bas widths. The peak current increases rapidly during each spike. However, the Pb stripping peaks were asymmetric with slow increment of peak current as it can be seen in the voltammogram.

Though the sensitivities were different, the peak currents of both Pb and Cd were increased proportionally with the solution concentration. Fig.6 and Fig.7 show the standard addition curves of peak current versus concentration of Cd (II) and Pb (II), respectively.

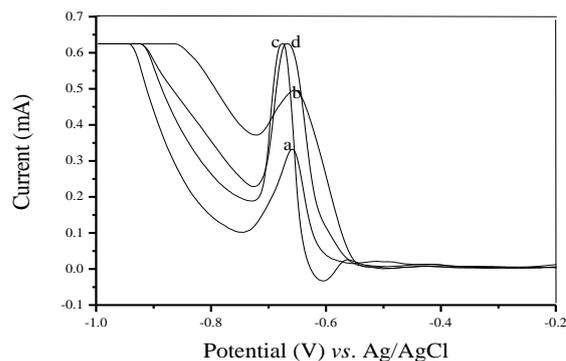


Fig.5:Differential pulse anodic stripping voltammogram for KOSPI waste water sample spiked with the standard solution of Cd (II) and Pb (II) (10 mg/L each) : a) 10 mL of acetate buffer + 10 mL of sample, b) a + 100 µL of 10 mg/L standard solution, c) a + 200 µL of 10 mg/L standard solution, d) a + 250 µL of 10 mg/L standard solution.

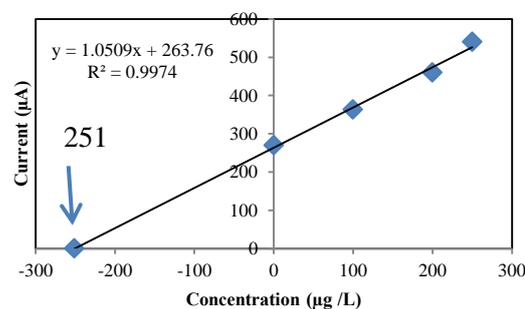


Fig. 6: Plot of peak current as a function of concentration for Cd obtained by standard addition method in KOSPI sample.

Good linearity of peak current and concentration of the standard added was observed for Cd (II). The concentration of Cd in the sample was calculated from the magnitude of intercept on the negative X-axis and from the linear regression correlation coefficient ($R = 0.998$). The quotient of the intercept and R value gives the concentration.

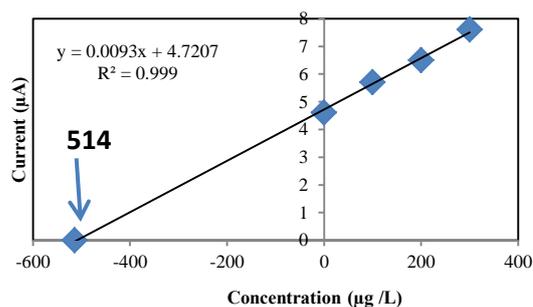


Fig 7: Plot of peak current as a function of concentration for Pb obtained by standard addition method in KOSPI sample.

The linearity of the response and added concentration of Pb (II) was observed with regression coefficient of 0.999. In the calibration, the sensitivity of voltammetry for Pb and Cd were $8.95 \text{ nA L}/\mu\text{g}$ and $107.5 \text{ nA L}/\mu\text{g}$, respectively. In this sample the Pb sensitivity was much less than that of Cd. From the intercepts and correlation coefficients of the two calibration graphs the concentrations of Pb and Cd in KOSPI sample were determined to be 514.4 ± 4 and $251 \pm 5 \mu\text{g/L}$, respectively.

3.3 The Borkena River Water Samples

The level of Pb and Cd were also measured in ten water samples of Borkena River. In order to see the net impact of the industrial wastes at Kombolcha two locations in the river were chosen on the basis of the reach of the industrial effluents into the river.

3.3.1 Borkena River before effluents joins the river (BOBE)

A total of five water samples from BOBE, were analyzed by DPASV. In these samples well-defined stripping peaks for Pb and Cd were observed. Fig. 8 shows the DPASV voltammogram for Borkena River water sample at the site before the industrial drain systems join the river. The peaks for both metals in the sample, as well after spiking, were symmetric with narrow base width. The reduction potentials for Pb (II) and Cd (II) were observed at -0.41 V and -0.56V with a corresponding maximum net current values of 0.47 and 0.8 μ A.

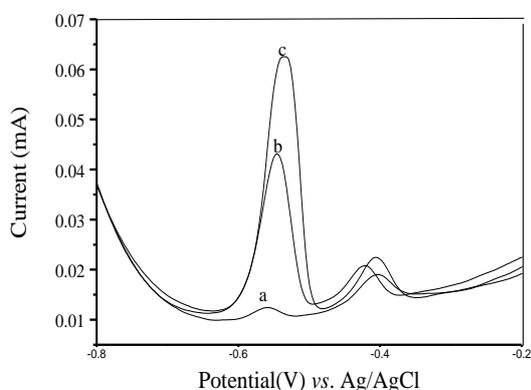


Fig.8: Differential pulse anodic stripping voltammogram for Pb and Cd in water sample of Borkena River, at the site before the effluents mix (BOBE), spiked with standard Pb (II) and Cd (II) solution : a) 10 mL of acetate buffer + 10 mL of sample, b) a + 100 μ L of 1 mg/L standard Pb and Cd solution, c) a + 150 μ L of 1 mg/L standard Pb and Cd solution.

The reduction potential of Cd (II) in these samples shift from the expected value, (-0.59 V) by a 0.03 V. But because of the complex formation and variation in activity coefficient, the reduction potential of metal ion can vary over one volt depending on the matrix of the solution [5, 12]. Besides as the surface coverage and adsorption of a metal deposit on the electrode change, the reduction potential of a given metal ion can vary with concentration. The most important advantage of electrochemical techniques to assure a given analyse at the observed potential is standard addition method [12]. As the analysis was done in the same matrix and from the increment of peak current with standard Cd addition, it is an obvious logic that the given analyse is Cd. The standard addition peak currents for both Pb (II) and Cd (II) were increased proportional to concentration. The linear relation of the peak currents and concentrations of added Pb (II) and Cd (II) are shown in Fig.9 and Fig.10 respectively.

The plot of peak currents against concentration of Pb (II) added was linear with regression correlation coefficient of 0.998.

Good linearity of peak current and concentration of Cd (II) was observed with correlation coefficient of regression 0.999. The concentration of each metal was calculated from the intercept on the negative x axis and

from the correlation coefficients. The concentrations of Pb and Cd are 21.7 and 3.95 μ g/L, respectively. The calibration curves of peak current as a function of concentration for each metal were linear with correlation coefficient R= 0.999.

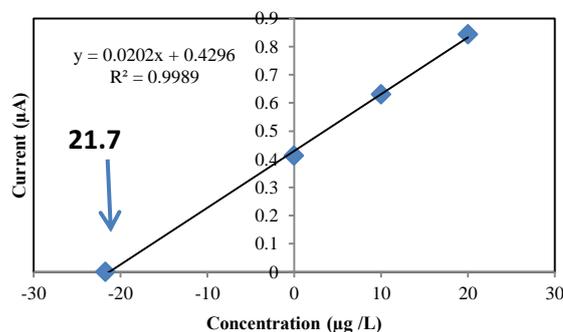


Fig. 9: Plot of peak current as a function of concentration for Pb obtained by standard addition method in BOBE sample.

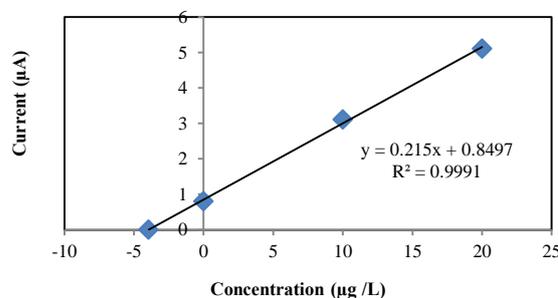


Fig. 10: Calibration plot of peak current as a function of concentration for Cd obtained by standard addition method in BOBE sample.

3.3.2 Borkena River after the effluents joins the river (BRAE)

Five water samples of Borkena River at the junction point of the river and the industrial effluent drain system were analyzed. Fig.11 shows the DPASV voltammogram of Pb and Cd in BOBE and BOAE samples

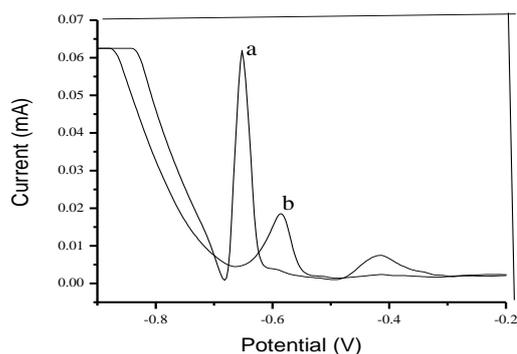


Fig. 11: Differential pulse anodic stripping voltammogram for Pb and Cd in water sample of Borkena River at two different sites a) BOAE b) BOBE

As it can be seen from the figure, the potentials of Cd and Pb in BOBE and BOAE samples show shift from each other. This is due to variation of the matrix of solutions in the two sets of samples. Though it is not possible to know the exact composition, the BOAE samples should contain several complexing agents disposed with industries wastes. However, both the

relative and the absolute reduction potential shifts observed are insignificant as compared with the maximum potential shift suggested from variation of matrix and concentrations [5,12 and 19]. Thereby it is logical to see that the reduction potential of a given metal ion in BOAE samples to be higher than in that of BOBE. Besides the potential, it is clearly indicated from the voltammograms that the peak currents of Pb and Cd in Borkena River after the effluent join the river are higher than that of BOBE samples. Based on the peak currents of oxidation, concentrations of each metal in BOBE and BOAE samples were determined to be 21.7 ± 2 and $333.5 \pm 4 \mu\text{g/L}$ for Pb and 3.95 ± 1 and $231.5 \pm 4 \mu\text{g/L}$ for Cd in the respective order.

3.4 Tap water Sample

The tap water sample was also collected from Bhirdar University for examine the heavy metal. The study is shown in Fig.12.

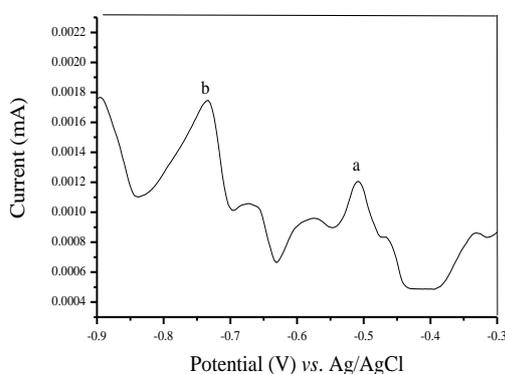


Fig. 12: Differential pulse anodic stripping voltammogram for Pb and Cd in sample of BDU tap water ; a) peak of Pb and b) peak of Cd.

The sensitivity for Pb and Cd determined by standard addition method were found to be $21.7 \text{ nAL}/\mu\text{g}$ and $202.4 \text{ nAL}/\mu\text{g}$, respectively. The calculated concentrations for each metal were $21.7 \pm 0.5 \mu\text{g/L}$ for Pb and $4.1 \pm 0.2 \mu\text{g/L}$ for Cd. The net currents of Pb and Cd found in the sample were $0.5 \mu\text{A}$ and $0.83 \mu\text{A}$ respectively. The concentration of Pb is greater than that of Cd unlike their peak current values. This is due to the sensitivity of the technique, that is, the magnitude of the current produced per $1 \mu\text{g/L}$ of each metal was lower for Pb than for Cd and hence the ratio of the peak current to the sensitivity (concentration) was greater for Pb.

3.5 Comparatively Study

Eighteen different samples were analyzed by differential pulse anodic stripping voltammetry. Seven waste effluent samples from three industries, ten river water samples, and one tap water sample were probed for Pb and Cd. The mean Pb and Cd contents of all samples were successfully determined. Both metal ions were found in KOSPI waste sample, in Borkena River water samples collected at two sites, before and after the effluents mix with the river and in tap water sample of Bihar Dar University. Only Pb was found in BGI and textile samples. The results of the experiments are summarized in Table 2.

Table 2: Concentration of heavy metal in different sample and limits

S.No	Type	Sample	Pb ($\mu\text{g/L}$)	Cd ($\mu\text{g/L}$)
1	Effluents	Textile	134 ± 3	Not detected
2		BGI	241 ± 5	Not detected
3		KOSPI	514.4 ± 4	251 ± 5
4	River Water	BOBE	21.7	3.95
5		BOAE	333.5	230.5
6	Drinking Water	Tap Water	23	4.1
7	Permissible Limits	WHO (Drinking)	50	10
8		FAO (Irrigation)	500	100

It is evident from the results that the concentrations of each toxic metal ion vary significantly in different drains depending on the nature of waste effluents. As it can be seen from Table 2 the highest concentration of both toxic metals, Pb and Cd, were released from KOSPI. Only Pb was found in BGI and Textile waste effluents. The least polluted effluent both in quality and quantity discharges out from textile.

The Borkena river water samples which were collected at two sites, (before and after industrial drain system joins the river) showed substantial difference in their Pb and Cd content. The concentrations of each metal ion in the river at the site just after the junction point of the drain system were found much higher than the other site.

It is apparent from the result that huge amount of toxic metal ions are released from various industrial drains at Kombolcha to Borkena River. The concentrations of metal ions determined in three industrial effluents are graphically compared in Fig. 13.

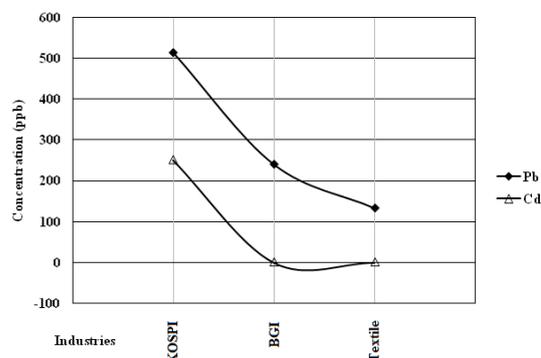


Fig.13: Comparatively study of heavy metal different industry

The sources of chemical contaminants of environmental matrixes occur when chemicals are used in industries and disposed with wastes. Agricultural

activities, such as use of excessive amount of fertilizers, pesticide and contaminated water for irrigation causes contamination of crops. Thus the Pb and Cd contamination of BOAE by industrial wastes at Kombolcha should come from their applicability in the nearby industries. Generally it is recognized that; cadmium is used in metal plating, coating, pigments stabilizer, and painting. Lead is used in painting dying, and welding activities. Thereby the possible sources of the contaminant Pb and Cd in KOSPI are wastes from painting, plating, stabilizing and welding activities of the steel products. In textile wastes from the use of dyes for textile products is the most supposed source. For BGI, the by-product of brewing crops, which have been harvested by application of fertilizers, pesticide and use of contaminated irrigation water, is the suspected source. Trace metals can be absorbed by roots of plants and can exist in adsorbed or complex forms with organic compound. As toxic level of Pb and Cd in drinking water or food results in profound disturbance to the normal biochemical and neurological process by crossing the cell membrane, the Borkena River water just as it reaches Kombolcha is dangerous to people and to any aquatic life [22-25].

4 Conclusions

The investigation of the contamination potential of industrial wastes on Borkena River was successfully accomplished in differential pulse anodic stripping Voltammetry on glassy carbon electrode. Based on the findings, Borkena River water gets polluted highly due to toxic metals Pb and Cd when it reaches Kombolcha. The quality of the river water is not safe for domestic use. The largest contributor of the pollutants Pb and Cd was Kombolcha steel products industry. Kombolcha brewery and Kombolcha textile factory was the second and third in their lead content, however, there are other factories which were not included in this work and may cause pollution. Such unregulated discharge of toxic metal containing waste effluents should be ceased to avoid farther pollution. Furthermore, the current effect of the contamination of Borkena River on human and aquatic life should be subject to full investigation. Finally this work is not complete and exhausted. But, it lights awareness and can be used as a foot step for full investigation of environmental pollution.

Reference

- 1- W. A. Bott, Stripping Voltammetry: Principles Discussion and Applications, West Lafay. 12 (1993) 141-146.
- 2- S.Yilmaz, M. Sadikoglu, G. Saglikoglu, S. Yagmur, and G. Saglikoglu, Determination of Ascorbic Acid in Tablet Dosage Forms and Some Fruit Juices by DPV, Int. J. Electrochem. 4 (2009) 288 – 294.
- 3- M. Jonathan Bruce, Voltammetric Analysis of Zinc, Cadmium, Lead and Copper in Marine waters, Meterohom Uk Ltd Water and waste water Asia, J. Electrochem. 6 (2005) 242-248.
- 4- P. Sharma, and S. Songara, Voltammetric Trace Determination of Sub - μg level Chlorate in Natural Water, Chemical Techn., 15 (2008) 504-506.
- 5- P. Sonthalia, E. McGaw. and Greg M. Swain, Metal ion analysis in contaminated water samples using anodic stripping Voltammetry and nanocrystalline Diamond thin-film Electrode, Analytica. Chemic. Acta., 522 (2004) 35-44.
- 6- A. Stephen, Heavy metal Analysis of liquid waste and Sediments from the Aliaga Petrochemical Plant, Aliaga Izmir Publication, 1996, 10-97.
- 7- V. Sychra, I. Lang, and G. Sebor, Analysis of petroleum and petroleum products by atomic absorption spectroscopy and related techniques, Prog. J of Ana. Chem. 4 (1981) 341-426.
- 8- W. Mertz, Accumulation of trace elements by Biological Matrix. Sci. 213 (1981) 1332 – 1338.
- 9- M. Tomar, Quality Assessment of Water and Waste Water, Lewis Publisher New York, 1999, 23-90.
- 10- M. H. Matloob, Determination of Cadmium, Lead, Copper and Zinc in Yemeni Khat by anodic Stripping Voltammetric, Eastern Mediterranean Health J., 901 (2001) 1-8.
- 11- T. Mathialagan and T. Viraraghavan, Adsorption of cadmium from aqueous solutions by perlite J. Hazardous Materials, 94 (2002) 291-303.
- 12- M.O. Akinola, K.L. Njoku, and B.E. Keifo, Determination of Lead, Cadmium and Chromium in the Tissue of an Economically Important Plant Grown Around a Textile Industry at Ibeshe, Ikorodu Area of Lagos State, Nigeria, Advances in Environmental Biology. 2 (2008) 25-30.
- 13- Saad A Al-Jilil, Saudi Arabian clays for lead removal in wastewater in wastewater, J.App. Clay Science 42 (2009) 671-674.
- 14- A. Hassan, and J. A. Mayouf, Comparative studies of the determination of Divalent Cd, Pb and Cu in the Boiling Medical herbs by Stripping Voltammetry and by Atomic absorption spectrometry, American J. of appl. sci., 6 (2009) 594-600.
- 15- I. Ali, C. K. Jain, Pollution Potential of Toxic metals in the Yamuna River at Delhi, India, J. Enviro. Hydro. 9 (2001) 1-8.
- 16- UNICEF, Hand book on Water Quality, Chemical contamination of water, VCH Publisher, UK, 2007, pp.19-32.
- 17- D. T. Sawyer, Electrochemistry for Chemists 2nd Edn., Interscience publication, Wiley, 1995, PP. 20 – 75.
- 18- P. H. Rieger, Electrochemistry 2nd Edn. Thomson Publication, New York, 1994, pp. 200-30.
- 19- F. W. Fifield, and D. Kealey, Principle and Practice of Analytical Chemistry 4th Edn., VCH Publications, New York, 1995, pp. 243-251.
- 20- I. Rubinstein, Physical Electrochemistry Principles, Methods and Applications, Marcel Dekker Publications, New York, 1995, PP. 4-24.
- 21- Paulo, J.S. Barberria and N. R. Stradiotto, Simultaneous determination of trace amount of zinc, lead and copper in rum by anodic stripping Voltammetry Talanta., 44 (1997) 185-188.
- 22- G. Somer, U. Unal and F.Edebiyat, A new and direct method for the trace element determination in cauliflower by differential pulse polarography, J. Science Talanta, 62 (2004) 323-328.
- 23- D. S. Stef, I.Gergen, and M. Harmanescu, Determination of the microelements content of some medical herbs, J. of Agroalimentary Processes and Techno., 15 (2009) 163-167.
- 24- A. Massadeh, F. Alali and Q. Jaradat, Determination of Copper and Zinc in different brands of Cigarettes in Jordan, Acta Chim. Slov., 50 (2003) 375-381.

- 25- S.A. Khan, L. Khan N. Akhtar, Comparative assessment of Heavy metals in Euphorbia helioscopia L, Pak. J. Weed J. Sci. Res., 14 (2008) 91-100.
- 26- A. Rejendran, V. Narayanan and I. Gnanavel Study on the Analysis of Trace Elements in Aloe Vera and in its Biological Importance, J. Appl. Sci. Res. 3(2007) 1476-1478.
- 27- D. A. Skoog, Fundamentals of Analytical Chemistry 8th Edn, UK Publications, D. M. West, F. J Holler, 2001,150-208.