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Analysis of some heavy metals and physicochemical parameters of textile sludge sample in the Bahir Dar textile industry, Northern Amhara, Ethiopia

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ABSTRACT

The present study was conducted to characterize the solid sludge from the Bahir Dar textile industry.The concentration of heavy metals (Cr, Cd, Zn, Fe, Pb, Cu and Mn) in the samples were found to be 37.433-50.967, ND, 244.8-279.9, 2868.633-2886.667, 4.567-7.83, 242.767-282.133 and 160.9-212.8 (mg/Kg) respectively. The range of the pH, EC (%), OM (%), OC (%), MC (%), VS (%) and FS (%) in the sludge samples were found to be in the ranges of 7.317-7.771, 1.466-1.872, 12.302-12.778, 7.136-7.412, 9.211-11.576, 44.598-47.778 and 52.222-55.402 respectively. The results of the heavy metals in the textile sludge sample showed that the concentration levels of Cu metal was above the standard guide lines for maximum limit proposed for agricultural soil set by FAO /WHO and in the case of other metals (Pb, Zn, Mn, Fe, Cr), their concentration levels were found below the standard guide lines for maximum limit proposed for agriculture soil set by this organization, but the concentration levels of Cd was not detected in this present study. Finally, the study concluded that pre-treatment process for reducing the amount of some heavy metal is mandatory before the sludge can be used as a soil conditioner / fertilizer in the agricultural soil.

***Keywords*:** Textile sludge, contaminated soil, heavy metals, physicochemical parameters, FAAS

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1. INTRODUCTION

Textiles being the basic needs of human being undoutly, textile industries have great economic significance which involves processing of raw materials and fabric into finished cloth involving various stages of processing and operations consuming large quantities of water and various types of chemicals and dyes [1, 2].

Textile industries have been placed in the category of most polluting industries in the world. Usually textile effluents contain dissolved organic and inorganic substances, colloidal or suspended forms and it is typically colored due to the presence of residual dye stuffs [3, 4]. Industrial activities lead to the generation of large amounts of sludge, the disposal of which is a serious environmental issue because it contains harmful level of pollutants including heavy metals [5]. Sludge is the separated semi solid part obtained after effluent treatment in the Effluent Treatment Plant (ETP).

Textile sludge is an inevitable by-product of textile wastewater treatment process [6] and which consists of a cluster of organic and inorganic complex with high concentrations of heavy metals such as Fe, Cu, Cd, Zn, Cr etc. Sludge can become a problem if they are improperly managed or disposed. Untreated coloured and toxic effluents are directly discharged into the nearby rivers, lakes, and streams. Contamination from industrial activities or by products can increase the natural levels of heavy metals in soil.

Heavy metals disposal is a big concern due to their being non-biodegradable and their tendency to bioaccumulation. Therefore, they can affect human and animals' health, and also environmental quality [7]. Heavy metals are elements with high atomic weights that are generally toxic in relatively low concentrations to plant and animal life. Heavy metals enter the environment by natural and anthropogenic means. Such sources include: natural weathering of the earth's crust, mining, soil erosion, industrial discharge, urban runoff, sewage effluents and pest or disease control agents applied to plants, air pollution fallout, and a number of others [8].

2. EXPERIMENTAL

2. 1. Description of Sampling Area

Bahir Dar, the capital of Amhara National Regional State, is situated on the southern shore of Lake Tana, the source of Blue Nile River, approximately 565 Kms northwest of Addis Ababa at an altitude of 1801 m.a.s.l, having latitude of 11º 35' N and longitude of 37º 24' E. The average elevation in the town is about 1795 m.a.s.l with "Woina Dega" type of agroecological zone.

The town covers an area of about 16,000 hectares. The study area experiences average annual rainfall that ranges from 1200 to 1600 mm and it has mean annual temperature of 26 °C. It is a rapidly expanding town with commercial centers, small industries, and residences in all sectors of the town.

The textile factory (480,000 square meters) located at the edge of head of Blue Nile River discharges its effluents but not solid sludge directly into head of Blue Nile River [9]. Location of the study area is shown in Figure 1.

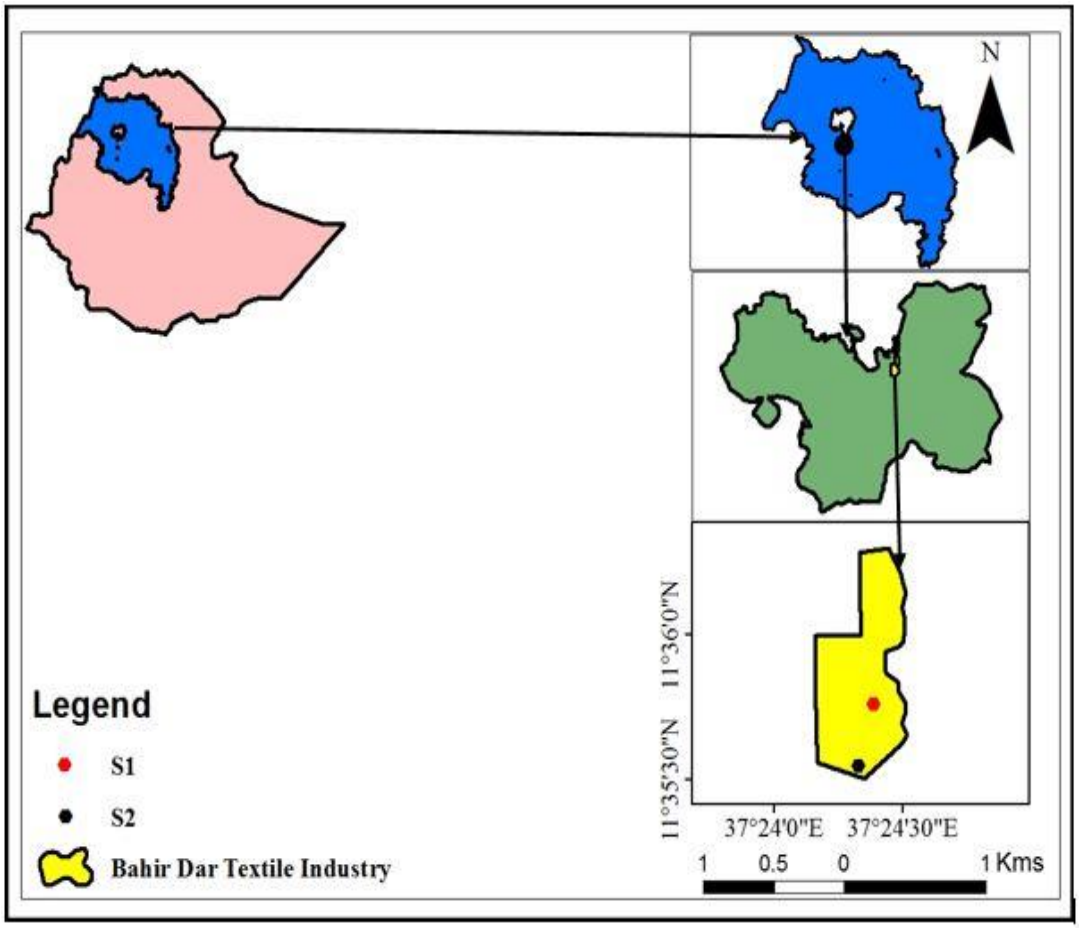

Figure 1. Map of the study area

2. 2. Apparatus and Instruments

The following equipment's were used in this study: Electronic analytical balance (AA-200DS, Denver Instrument Company) was used for weighing samples of sludge prior to digestion. Atomic Absorption Spectrophotometer (AA-500AFG, UK) equipped with deuterium back ground correctors and Hallow Cathode Lamp of each metal was used for the analysis of heavy metals. PH (CPI-Sol, ELMEIRON) meter was used for the determination of the pH of sludge samples. Digestive furnace (model: KDN-20c, China), Kjeldahl tubes fitted with reflex condenser were used in Kjeldahl digestion block apparatus to digest sludge sample, their spiked samples and blank solutions.

2. 3. Chemicals and Reagents

HNO_3 (65.0 %), UNI-CHEM® Chemical reagents, India), $HClO_4$ (70.0-72.0 %), UNI-CHEM® Chemical reagents, India) and H_2O_2 (35.0 %, UNI-CHEM® Chemical reagents, India) were used for the sample digestions. 1000 ppm stock standard solutions of the heavy metals Fe, Zn, Mn, Cu, Cr, Cd, and Pb were used to prepare calibration standard solutions and $ZnSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$, K_2CrO_4 (99.5 %), UNI-CHEM® Chemical reagents, India),

$Pb(NO_3)_2$ (99.5 %), $Cd(NO_3)_2$ (97 %), UNI-CHEM®, NICE, Chemicals Pvt. Ltd, India), $MnSO_4 \cdot H_2O$ (99 %), UNI-CHEM®, NICE, chemicals Pvt. Ltd, India) were used to prepare spiking standard solutions. $K_2Cr_2O_7$, H_2SO_4 and Fe $(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (UNI-CHEM® Chemical reagents, India) were used for determination of carbon contents and organic matter.

2. 4. Sampling Procedures

2. 4. 1. Cleaning of Sampling Equipment's

Polyethylene bags and bottles for sludge sampling were thoroughly washed with tap water and detergent, rinsed with distilled water. After that, all containers were well-rinsed with distilled water routinely and air dried.

2. 4. 2. Sludge Sampling

The sludge samples from sampling sites of Bahir Dar Textile Industry, Southern shore of Lake Tana Amhara, Ethiopia were collected into polyethylene bags that was pre-treated with diluted nitric acid and rinsed with deionized water. Three sludge samples were randomly collected from each of the two sub-sites in the industrial areas and pooled together to obtain a composite sample. Finally, two sludge samples one from each stated sites were transferred in to polyethylene bags. Two sludge samples were collected at distance of 200 meters from sedimentation tank of the treatment process designated as S1 and disposal area of sludge designated as S2 by using glass (inert) sampling equipment. The sampled sludge was air dried within a period of one week at room temperature, ground with porcelain mortar and pestle, passed through 0.5 mm sieve, and then kept in clean polyethylene bags for further analysis.

2. 5. Sample Pre-treatments

The dried sludge sample was first passed through a 0.5 mm sieve eliminating roots, stones, plastics, grass and other impurities. The sample was then powdered to fine sizes using mortar and pestle and thoroughly mixed to achieve homogeneity. The powdered sludge sample was then sieved mechanically to obtain fractions that are less than 50 μm.The sludge sample after these steps was stored in the polyethylene plastic containers (bags) (have the advantage of lighter weight and greater durability) until they was analysed.

2. 6. Procedures

2. 6. 1. Preparation of Standard Stock Solutions

The standard stock solutions of Zn, Cu, Cr, Pb, Cd, Fe and Mn were prepared by dissolving the appropriate amount of the respective metal salt, 4.3987 g of $ZnSO_4 \cdot 7H_2O$, 3.9295 g of $CuSO_4 \cdot 5H_2O$, 3.7348 g K_2CrO_4, 1.5980 g of $Pb(NO_3)_2$ and 2.1032 g of $Cd(NO_3)_2$, 7.162 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and 3.118 g of $MnSO_4 \cdot H_2O$ in 1000 mL volumetric flask and filled to the mark with distilled water to prepare a 1000 ppm stock solution of respectively.

2. 6. 2. Working Intermediate Metal Standard Solutions

For the determination of metals in sludge sample, 10 mg/L intermediate standard solution in 100 mL volumetric flask was prepared from 1000 mg/L stock solution.

2. 6. 3. Standard Solutions for Calibration

The calibration standard solutions were used to calibrate the instrument response with respect to the analyte concentration. For calibration of the flame atomic absorption spectrophotometer a series of blank and five standard solutions were prepared for each metal from their respective working standard solutions (10 mg/L). The calibration standard concentrations were within the working linear range of the instrument used for analysis.

2. 6. 4. Spiking Metal Standard Mixture Solution

For the spiking processes of the sludge sample, a mixture of standard solution containing 2 mg/L of each Zn and Mn, 2.023 mg/L Cu, 9 mg/L Pb, 2.25 mg/L Cd, 4.5 mg/L Cr and 3.375 mg/L Fe was prepared. This mixture of standard solution was obtained by taking 0.1 mL of each Mn and Zn, 0.101 mL Cu, 0.225 mL Cr, 0.113 mL Cd, 0.169 mL Fe, 0.45 mL Pb of each metal stock standard solution (1000 mg/L) in to 100 mL volumetric flask and diluting to the mark with double distilled water.

2. 7. Sample Preparation for Sludge Analysis

A concentration of heavy metals in sludge samples was expressed as mg /kg of dry matter. The sludge sample was air dried for a period of one week, ground with a clean porcelain mortar and pestle and passed through a 0.5 mm sieve. The sludge sample was kept in polythene packets for further analysis.

2. 8. Determination of Physicochemical Parameters of Sludge

In general three replicates from each of the prepared sample were taken for the determination of physicochemical characteristics of the sludge samples. The parameters determined include: pH, electrical conductivity, moisture content, volatile and fixed solids, organic matter and organic carbon.

pH and Electrical Conductivity (mS/cm)

The pH and electrical conductivity were measured by means of a pH-meter (CPI-Sol, ELMEIRON) and conductivity meter (ELMEIRON® Zabrze-Grzybowice, CC-101, POLAND), respectively. Deionized water (100 mL) was added to 10 g of sludge and mixed thoroughly in beaker. This solution was stirred continuously in a shaker for 30 min and then was allowed to settle and the supernatant was used for the pH and EC measurements. Then the pH and EC were measured directly.

Moisture Contents (%)

Moisture content (%) was measured by drying the sample at 105 ±1 ºC in hot air oven for 24 hours. A sludge sample (0.5 g) was taken in to evaporating dish and the sample was oven dried at 105 ºC for 24 hrs. The difference in weights before and after drying gives the moisture content. The loss in weight corresponds to the amount of water present in the sludge sample. The formula below was used to calculate the percentage of moisture content in each of the sludge samples [10].

$$\text{Moisture content (MC) (\%)} = \frac{\text{Loss in weight on drying (g)}}{\text{Initial sample weight (g)}} \times 100 \quad \ldots\ldots \quad (2.1)$$

The corresponding moisture correction factor (mcf) for analytical results or the multiplication factor for the amount of sample to be weighted in for analysis was:

$$\text{Moisture correction factor (mcf)} = \frac{100 + \%\ \text{moisture}}{100} \quad \ldots\ldots\ldots \quad (2.2)$$

Volatile Solids and Fixed Solids (%)

Volatile solids (%) and fixed solids (%) of dried sludge were determined by igniting the sample. A sludge sample (5.0 g) was taken in to evaporating dish and the sample was igniting in igniting furnace at 600 ±5 ºC for 2 hrs. The difference in initial and final weight of dried sample represents the volatile content of the sample. The fixed solids (%) and volatile solids (%) from the formula below:

$$\text{Volatile solids, as \% total solids} = \left(\frac{A-B}{A-C}\right) \times 100 \ldots\ldots\ldots\ldots\ldots\ldots \quad (2.3)$$

$$\text{Fixed solids, as \% total solids} = \left(\frac{B-C}{A-C}\right) \times 100 \ldots\ldots\ldots\ldots\ldots\ldots \quad (2.4)$$

where: A = weight of sample plus dish before burning, mg,
B = weight of sample plus dish after burning, mg, and C = weight of dish, mg.

Organic Carbon and Organic Matter Contents (%)

The organic carbon content of the sludge samples were determined by the same procedure as soil samples. Finely ground sludge sample (0.5 g) was passed through 0.5 mm sieve without loss, and added into 500 mL conical flask. Then 10 mL of 1.0 N $K_2Cr_2O_7$was added into the flask with pipette and it was swirled. In which 20 mL conc. H_2SO_4 solution was added rapidly with a burette and then, it was swirled gently until sludge and reagents was mixed more vigorously for one minute. The reaction was allowed to proceed for 30 min on asbestos sheet to avoid burning of table due to release of intense heat due to reaction of sulphuric acid and 200 mL distilled water was added slowly and allowed to cool. Before titration of the sample, 10 mL of concentrated orthophosphoric acid was added. Just before titration, 1 mL ferroin indicator was added into the conical flask that contains digested solution. Excess $K_2Cr_2O_7$ was titrated with 1 N ferrous ammonium sulphates till the colour flashes from yellowish green to greenish and finally brownish red indicated the end point of the titration. Simultaneously blank test was run without sludge.

$$\text{Organic carbon \%} = \frac{N \times (V1 - V2) \times 0.39}{S} \times \text{mcf} \ldots\ldots\ldots\ldots\ldots\ldots \quad (2.5)$$

where: N = Normality of ferrous ammonium sulfate (FAS)
V1 = Volume of 1 N FAS required to neutralize 10 mL of 1 N $K_2Cr_2O_7$ i.e. blank reading (mL).
V2 = Volume of 1 N FAS needed for titration of sludge sample (mL)
S = Weight of air-dry sample (g)

0.39 = 0.003 × 100 % × 1.31 (0.003 is the milliequivalent weight of carbon in g). It is assumed that only 77 % of the organic matter is oxidized and a fraction of 100/77 = 1.31. Sludge organic matter contains (58 %) of organic carbon, the percentage of organic carbon multiplied by 100/58 = 1.724 which gives the percentage of organic matter i.e.

$$\text{Organic matter (\%)} = \text{Organic carbon (\%)} \times 1.724 \quad \ldots\ldots\ldots \quad (2.6)$$

2. 9. Laboratory Sample Analysis

2. 9. 1. Cleaning of Laboratory Glassware

All the glass wares and apparatus used through the entire analysis were first washed with tap water and detergent .Next, rinsed with distilled water and followed by 10 % (v/v) HNO_3 solution. Finally, rinsed again with distilled water and air dried to ensure that free from contamination.

2. 9. 2. Digestion of Sludge Samples

For the digestion of sludge samples, exactly 0.300 g of powdered sludge of each sample was accurately weighed on a digital analytical balance of ±0.001 precision and transferred quantitatively in to Kjeldahl digestion flask. Freshly prepared mixture of conc. HNO_3 (0.500 mL), H_2O_2 (0.500 mL) and conc·$HClO_4$ (6.500 mL) was added to the sample. The sample was swirled gently to homogenize the mixture then the sample was fitted to a reflux condenser and digested continuously for 2:00 hours on a Kjeldahl digestion block by setting the temperature dial at 230 ºC. Each sludge sample was digested in triplicate and hence a total six digest were made for two sludge samples. Then it was cooled to room temperature for 10 min without removing the condenser from the flask and for 10 min after removing the condenser. To the cooled solution deionized water was added to dissolve the precipitate formed on cooling and to minimize dissolution of filter paper by the digest residue while filtering with Whatman filter paper.

The Kjeldahl digestion flasks were rinsed subsequently with deionized water in to 50 mL volumetric flasks. And finally the volumetric flasks were made up to the mark with deionized water. The digestion gave a clear colorless solution and it was transferred in to 50 mL polyethylene bottles. Analysis of the levels of heavy metals was done at the University of Bahir Dar research laboratory using Flame Atomic Absorption Spectrophotometer.

2. 9. 3. Digestion of the Blanks

Estimation of the metal concentration of the blank is important for the determination of the LOD and LOQ of the analytical method used during the study. For the analysis of sludge samples three reagent blank samples was prepared. All the digested samples were stored in refrigerator until analysis using FAAS.

2. 9. 4. Method Validation

The proposed method was validated by evaluating different parameters as limit of detection (LOD), limit of quantitation (LOQ), accuracy (in terms of recovery) and precision (in terms of repeatability) [11].

2. 9. 4. 1. Limit of Detection

Limit of detection (LOD) is the minimum concentration of analyte that can be detected but not necessarily quantified with an acceptable uncertainty. LOD for each metal was determined from analysis of three replicates of method blanks which were digested in the same digestion procedure as the actual samples [12]. LOD was calculated as:

$$LOD = 3 \times S_{bl.} \quad \text{.....} \quad (2.7)$$

where: S_{bl} is the standard deviation of the method blank.

2. 9. 4. 2. Limit of Quantification

Limit of quantification (LOQ) is the lowest concentration of analyte that can be determined with an acceptable level of uncertainty. LOQ was obtained from analysis of three replicate of method blanks which were digested in the same digestion procedure as the actual samples. LOQ was calculated as ten times the standard deviation of the blank:

$$LOQ = 10 \times S_{bl} \quad \text{.....} \quad (2.8)$$

where: Sb_l is the standard deviation of the method blank [12].

2. 9. 4. 3. Precision and Accuracy

Precision is the extent of the consistency of results as they are obtained during repeated applications a specified determination method. It was evaluated regarding repeatability by estimating the relative standard deviation (RSD) of the recovery percentage for each spiked level. Accuracy was evaluated through recovery studies of sample spikes. Triplicate samples were prepared and triplicate readings were obtained.The relative standard deviations of the sample were obtained as:

$$RSD\ (\%) = \frac{\text{Standard deviation}}{\text{Mean vaue}} \times 100 \quad \text{.....} \quad (2.9)$$

The percentage recoveries of the analyte were calculated to evaluate the accuracy of the analytical procedure. Recovery was then calculated as:

$$\text{Recovery } (\%) = \frac{\text{Conc.in spiked sample} - \text{Conc.in unspiked sample}}{\text{Amount added}} \times 100 \text{.....} (2.10)$$

2. 9. 5. Heavy Metal Analysis of Sludge Samples

The digested sludge sample was analysed for copper (Cu), cadmium (Cd), manganese (Mn), chromium (Cr), lead (Pb), iron (Fe) and zinc (Zn) by atomic absorption spectrometer (AAS) after all parameters (lamp alignment, wave length and slit width adjustment) were optimized for maximum signal intensity and sensitivity of the instrument. The wavelength and slit width were selected and adjusted at the beginning of each analysis and kept constant up to the end of the analysis. Triplicate determinations were carried out on each sample.

The concentration of sample in mg/L was converted to mg /Kg using the formula [13]:

$$\text{Concentration in mg/kg} = \frac{\text{Concentration in mg/L} \times \text{volume in litre}}{\text{Mass of sample in kilogram}} \quad (2.11)$$

The operating conditions for FAAS employed for each analyte are given in Table 1.

Table 1. Instrumental operating conditions for determination of metals in sludge sample by using FAAS

	FAAS Working Conditions				
Element	Wavelength (nm)	Slit Width (nm)	Lamp Current (mA)	Oxidant/Fuel	Detection limit (mg/L)
Cu	324.75	0.4	5.0	Air/Acetylene	0.0018
Mn	279.48	0.4	5.0	Air/Acetylene	0.0030
Cr	357.87	0.4	5.0	Air/Acetylene	0.0018
Cd	228.80	0.4	5.0	Air/Acetylene	0.0070
Fe	248.33	0.2	5.0	Air/Acetylene	0.0046
Zn	213.86	0.4	5.0	Air/Acetylene	0.0060
Pb	283.31	0.4	5.0	Air/Acetylene	0.0020

2. 10. Statistical Analysis

One-way analysis of variance (ANOVA) was used to evaluate the significant differences in the mean values of physicochemical parameters and heavy metals among groups of soil and sludge samples. A probability level of $P < 0.05$ was considered statistically significant. All statistical analyses were done by Microsoft Office Excel-2007, IBM SPSS Version 20 and Origin 8.1 software packages. Pearson's product moment correlation r was used to express the relationship between levels of heavy metal concentrations. Data were expressed as mean ± standard deviation (SD) of three replicate experiments.

3. RESULTS AND DISCUSSION

3. 1. Determination of Physicochemical Parameters of Sludge samples

The results of the determination of some selected physicochemical parameters of the sludge are shown in Table 2 and Figure 2.

pH

The pH of the studied sludge was varying from 7.317 to 7.771, which was weakly alkaline in nature. It was slightly lower than to the average value range given in the literature 8.02 to 9.0

[14]. Other data reported that smaller pH values 6.27 [15]. The results of one-way ANOVA ($p < 0.05$) indicated that the pH values are significantly differing between the studied sludge samples.

Electric conductivity

The electrical conductivity (EC) value was reported to be as high as 13.4 mS/cm [13]. Other data obtained EC in the textile sludge ranging from 2.12 to 6.63 mS/cm [14]. The electrical conductivity values in the present study (1.466 to 1.872 mS/cm) were lying below the data range [14, 16]. The electrical conductivity values in the present study indicated the presence of low concentrations of ionic compounds in the sludge samples. Statistical test of significance using one-way ANOVA revealed significant differences ($P < 0.05$) between the values of EC in the sludge samples obtained from the two sites. The difference in the electrical conductivity values could be attributed to differences in the soluble salt and ionic compound content of the sludge.

Table 2. Selected physicochemical properties of sludge samples (mean ± SD, n = 3).

Properties	S1	S2
pH	7.771 ± 0.067	7.317 ± 0.015
EC(mS/cm)	1.466 ± 0.013	1.872 ± 0.003
OM (%)	12.778 ± 0.051	12.302 ± 0.025
OC (%)	7.412 ± 0.018	7.136 ± 0.015
MC (%)	9.211 ± 0.104	11.576 ± 0.214
VS (%)	44.598 ± 0.319	47.778 ± 0.116
FS (%)	55.402 ± 0.319	52.222 ± 0.116

Volatile and Fixed Solids

The values of volatile solids (VS) and fixed solids (FS) also in present study were again comparable to the literature data. The total volatile solids in the sludge were varying from 44.598 to 47.778 % and fixed solids were 55.402 to 55.222 %. While in one case the volatile content was found to be high as 80 % as reported [17]. Statistical test of significance using ANOVA revealed significant differences ($p < 0.05$) between the values of volatile and fixed solid in the sludge samples obtained from the two sites.

Organic Matter and Organic Carbon

The studied sludge contains high organic matter (OM) and the average OM value of sludge samples was 12.540 %. Organic matter is the measure of carbon based material in the sludge. In the literature obtained approximately similar OM values for their studied sludge [18].

Organic carbon contents were found to be in the range of 67.3 to 76.0 % as reported [16]. The organic carbon content in the studied sludge was varying from the 7.412 to 7.136 %. This result indicates that the Organic carbon content was low in the present study as compared to the literature above [19]. Statistical test of significance using one-way ANOVA revealed significant differences ($p < 0.05$) between the values of OM and also the values of OC in the sludge samples.

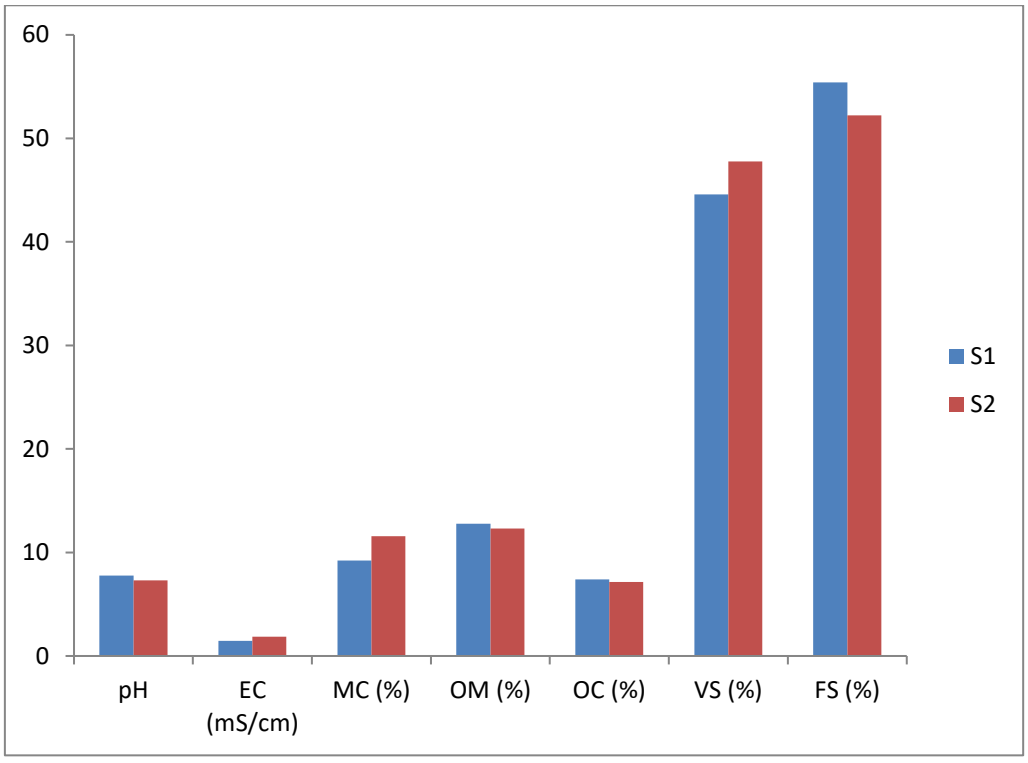

Figure 2. Mean values (mean ± SD, n = 3) of physicochemical parameters of sludge samples

Moisture Content

The sludge used in the literature was of different moisture content varying from 75 to 80 % [19]. The moisture content in the present studies was from 9.211 to 11.576 % as shown in the Table 2. This result indicates that the moisture contents were low in the present study as compared to the literature above [19]. Statistical test of significance using one-way ANOVA revealed significant differences ($P < 0.05$) between the values of MC in the sludge samples.

3. 2. Calibration of the Instrument

In this study, atomic absorption spectroscopic standard solutions containing 1000 mg/L were used for preparing intermediate standard solutions (10 mg/L) in 100 mL volumetric flask. As the values are given in Table 1, appropriate working standards were prepared for each of the metal solution. Each of the sets of serial dilutions was then aspirated one after the other into the atomic absorption spectrometry. Immediately after calibration using the standard solutions, the

sample solutions were aspirated into the FAAS instrument and direct readings of the metal concentration was recorded. Three replicate determinations were carried out on each sample.

The same analytical procedure was employed in the determination of elements in each six (three for each soil and sludge) digested blank.

3. 3. Method Validation

3. 3. 1. Limit of Detection (LOD) and Limit of Quantification (LOQ)

LOD and LOQ for each metal were determined from analysis of triplicates of method blanks which were digested in the same digestion procedure as the actual samples. For the present study, three reagents blank solutions were digested for sludge sample and each of the samples were analyzed for metal concentrations of Mn, Fe, Cu, Zn, Cr, Pb and Cd by FAAS. The standard deviations for each element were calculated from blank measurements.

Table 3. Limit of detection (LOD) and limit of quantification (LOQ) of sludge matrix spike samples for the determination of metals.

Elements	LOD (mg/L)	LOQ (mg/L)
Cu	0.042	0.14
Cr	0.066	0.22
Zn	0.015	0.05
Mn	0.066	0.22
Pb	0.030	0.10
Cd	0.057	0.19
Fe	0.048	0.16

From Table 3, the limit of detection (LOD) values for all the metals analyzed in the sludge samples ranged from 0.015 mg/L for Zn to 0.066 mg/L for Mn and Cr and the limit of quantification (LOQ) values for all the metals analyzed in this samples also ranged from 0.05 mg /L for Zn to 0.22 mg/L for Mn and Cr.

3. 3. 2. Accuracy and Precision

The results of accuracy and precision were evaluated through recovery tests. Accuracy of the method was determined by matrix spike recovery studies and precision was expressed as relative standard deviation (RSD) of replicate results.

In this study, the recovery test was done by spiking a suitable known quantity of metal standard solution in to a test portion of the sample. For doing so, each sample was spiked in

triplicates and the spiked and non-spiked samples were digested and analyzed using the same analytical procedure [20].

The recovery values of the triplicate analysis of matrix spike sludge sample was calculated using equation 2.10 and RSD values are were calculated using equation 2.9.

Table 4. Percent recovery of metals in sludge samples (mean ± SD, n = 3)

Elements	Conc. in unspiked sample (mg/L)	Amount added (mg/L)	Conc. In spiked sample (mg/L)	Recovery (%)	RSD (%)
Cd	ND	0.18	0.171 ± 0.016	95.000 ± 1.240	1.310
Cu	2.821 ± 0.031	0.16	2.974 ± 0.049	94.444 ± 1.635	1.731
Zn	2.799 ± 0.044	0.16	2.955 ± 0.001	97.500 ± 3.651	3.745
Cr	0.374 ± 0.002	0.36	0.722 ± 0.072	96.667 ± 1.140	1.180
Pb	0.457 ± 0.009	0.72	1.147 ± 0.059	95.833 ± 3.204	3.343
Mn	2.128 ± 0.007	0.16	2.273 ± 0.047	90.625 ± 3.229	3.563
Fe	28.860 ± 0.404	0.27	29.144 ± 0.429	94.815 ± 1.643	1.733

From Table 4, the percentage recovery of the metal analysis in the sludge samples were ranged between 90.625-97.5 % and the RSD values ranged between 1.180-3.745 %. The matrix spike recovery obtained in this study falls within the normal acceptable range of 90-110 % for a good recovery study. The high percentage recovery obtained from the study validates the accuracy of the method and the reliability of the levels of metal concentration in this study. The RSD values of the samples were < 10 %, indicating that the proposed method was precise.

3. 4. Concentration of Heavy Metals in Sludge Samples

This study was also focussed on heavy metals such as Cu, Mn, Cd, Pb, Zn, Fe and Cr, which are commonly found in the textile effluent due to the usage of metal complex dyes and other chemicals. The mean concentrations of the heavy metals in the sludge samples were given in Table 5 and Figure 3.

The value of Cd was not detected in the studied sludge. However, other studies reported that the average Cd metal concentrations in textile sludge were 1.13 and 6.27 mg/kg [21, 22] respectively. The levels of Copper in the studied sludge samples were varying from 242.767 mg /kg and 282.133 mg/kg in S1and S2 respectively, which was also much higher than that of in China (≤ 35 mg/kg) and India (20 to 30 mg/kg). More recently reported higher concentration (290 mg/kg) of Cu [21]. On the other hand, much lower concentration of Cu was reported 1.3 mg/kg [22] as compared to the values of present study. So, some well documented studies

disclosed that heavy metals from which copper (Cu) is the principal elements restricting the use of sludge for agricultural purposes [23-25].

The average concentrations of Zn recorded in the studied sludge sample was 262.35 mg /kg. The maximum Zn value in light soil used in cultivation in India was 100 mg/kg [26]. The threshold natural background value of Zn in crop soils and paddy soils in China is ≤100 mg /kg. In this study the Zn contents in sludge sample was than those of permissible levels in China and India. So that, sludge that contains this heavy metal needs further treatment process before used as fertilizers or soil conditioners. The concentration levels of chromium in this study were 37.433 and 50.967 mg/kg in the sampling sites of 1 and 2, respectively and these, result were lower than maximum content of Cr allowed in soil used in cultivation (100 mg/kg) [23]. In this case, there is no need of further treatment processes for reduction of Cr concentrations in this studied sludge.

Table 5. Heavy metal concentrations (mean ± SD, n = 3, mg /kg dry weight) in textile sludge samples

Heavy Metals	Site1	Site2
Cd	ND	ND
Cu	242.767 ± 1.528	282.133 ± 3.099
Zn	244.800 ± 4.613	279.900 ± 3.600
Cr	37.433 ± 0.058	50.967 ± 4.734
Mn	212.800 ± 0.721	160.900 ± 0.721
Pb	4.567 ± 0.920	7.833 ± 1.419
Fe	2886.667 ± 21.391	2868.633 ± 12.404

N.B: ND = Not Detected

The present study found that the average concentration of Mn in the sludge sample was 186.85 mg/kg. This result revealed that examined sludge samples contained relatively lower amount of Mn than that of agricultural soil (2000 mg/kg) and that of the recommended value by FAO /WHO [27]. However, other literature reported that very high levels of Mn metal concentration in textile sludge was 3974.1 mg/kg [22], which was higher than the values that recommended by FAO/WHO [27]. The average value of Mn in the present study was found in the range of uncontaminated soil in India, 100 to 4000 mg/kg [28], which makes the studied sludge suitable or safe for land application as Indian rule.

As shown in Table 4, the sludge samples contained Pb concentrations from 4.567 to 7.833 mg/kg. The FAO/WHO permissible limit of lead in soil is 100 mg/kg [27] and the maximum content of lead in light soils for cultivation was 50 mg/kg [23]. The threshold natural background value of Pb in crop soils and paddy soils in China was 50 mg/kg [29]. So, Pb

concentration in this sludge is not significant potential threat for contaminations of soil when this sludge is used as fertilizer.

In the present study, the concentrations of iron in the sludge samples were ranging from 2868.633 to 2886.667 mg/kg. Iron had the highest concentration amongst the studied metals. Long term exposure of iron from the sludge into soils may contaminate it and change the soil structure and thus make it harmful for cultivation. The concentrations of Fe in agricultural soils in India varying from 289.3 to 338.5 mg/kg dry weight [30]. So, this indicates that there is a need for further treatment process to reduce Fe content from the sludge as Indian rule.

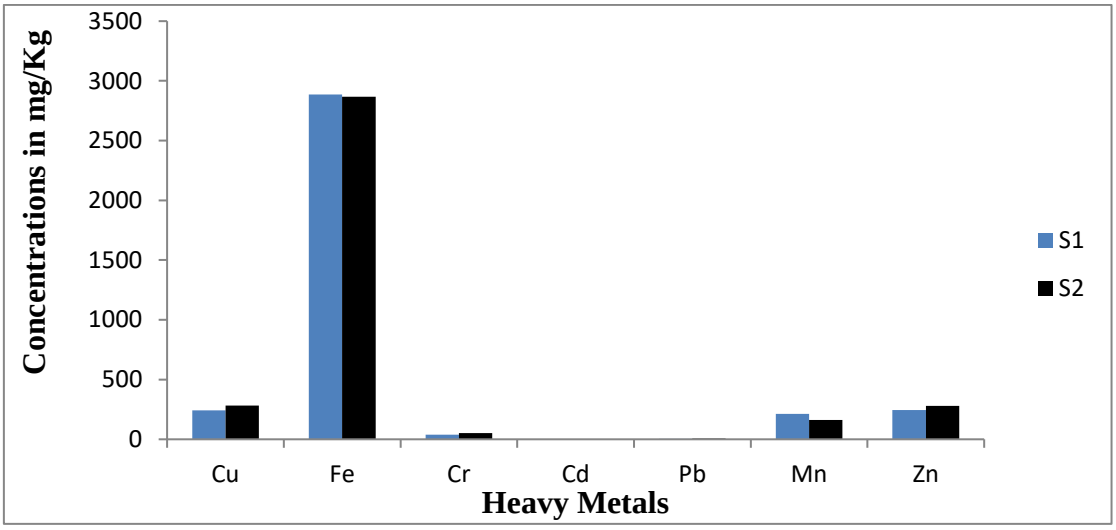

Figure 3. Mean concentrations (mean ± SD, *n* = 3) of heavy metals in sludge samples

Table 6. Comparison of heavy metal concentrations in textile sludge with the standard of [27] and other country rule [29] (mg /kg).

Heavy Metals	Present Study (Mean)	FAO /WHO	In China
Pb	6.2	100	50
Cd	ND	3	20
Cr	44.2	50	90
Cu	262.45	100	35
Zn	262.35	300	100
Mn	186.85	2000	NA
Fe	2877.65	5000	NA

N.B: NA = Not Analysis and ND = Not Detected, Source: In China [29] = USEPA (2005)

In general, the concentration levels of Cu and Zn in the textile industry sludge were above the standard guidelines for the maximum limit proposed for agricultural soil in China and in the case of Pb and Cr, their concentration levels were found below the standard guidelines for maximum limit proposed for agriculture soil in China [29].

However, the concentrations of Mn and Fe were not recognized by this organization. The concentrations of heavy metals were within the regulatory limits of FAO /WHO rules except Cu metal and its concentration found above the limit [27] and Cd metal was not detected in the present study.

In one-way analysis of variance (ANOVA), the results showed that there was no significant differences ($p > 0.05$) in the concentrations of Fe among the analyzed sludge samples while there were significant difference ($p < 0.05$) in the concentrations of others heavy metals (Cr, Cu, Pb, Zn, Mn) except Cd was not detected. In general, the mean concentration of heavy metals in sludge sample collected from all sampling site were decreased in the order of: Fe > Cu > Zn > Mn > Cr > Pb.

3. 5. Pearson's Correlation Analysis

Pearson's correlation coefficient was used to examine the relationship between the various heavy metals in sludge sample from all the sample sites. From the Table 7 showed that the correlation matrix of the relationshipbetween heavy metals concentration of sludge samples. Other studied reported that high correlation coefficient (near +1 or −1) means a good relation between two variables, and its concentration around zero means no relationship between them at a significant level of 0.05% level, it can be strongly correlated, if $r > 0.7$, whereas r values between 0.5 and 0.7 shows moderate correlation between two different parameters [31].

3. 5. 1. Correlation of Heavy Metals in Sludge Samples

Table 7. Metal to metal correlation coefficient matrix (r) of sludge samples.

	Mn	Cr	Zn	Pb	Cu	Cd	Fe
Mn	1						
Cr	-0.92297	1					
Zn	-0.9788*	0.94845	1				
Pb	-0.8543	0.94772	0.90715	1			
Cu	-0.9929**	0.94201	0.9806*	0.87656	1		
Cd	-	-	-	-	-	-	
Fe	0.34584	-0.42408	0.33367	0.60939	0.39247	-	1

* Correlation is significant at the 0.05 level (2-tailed); ** Correlation is significant at the 0.01 level (2-tailed)

The correlation between the metals in the sludge samples was investigated using Pearson correlation matrices. As it can be seen from the Table 7, the results of the correlation

coefficients showed strong positive correlation between Zn and Cr (r = 0.948), Pb and Zn (r = 0.907) and Cr (r = 0.948), Cu with Cr (r = 0.942), and Cu with Zn (r = 0.980) and Pb (r = 0.877). This strong positive correlation shows that the elements are closely associated, thus suggesting their common origin.

There were also strong negative correlation between Cr with Mn (r = -0.923), Zn with Mn (r = -0. 979), Pb with Mn (r = -0.854) and Cu with Mn (-0.993). There was also moderate positive correlation between Fe with Pb (r = 0.609). The other heavy metals have weak negative or positive correlation with Fe indicating that the presence or absence of one element affect in lesser extent to the other.

4. CONCLUSIONS

The sludge samples from textile industry were characterised for different physicochemical parameters and levels of heavy metals. The characterisation data indicates that the sludge have slightly alkaline in nature, volatile solids varying from 44.598 to 47.778 % and a less variability in the values of organic carbon (7.13 to 7.412 %). The concentration levels of some heavy metals (Cu, Zn) were above the standard guide lines for maximum limit proposed for agricultural soil in China and in the case of Pb, and Cr, their concentration levels were found below the standard guide lines for maximum limit proposed for agriculture soil, except Cd metal not detected in the present studies and Mn and Fe metals concentration were not recognized by this organization [29]. The study conclude that pre-treatment process for reducing the amount of some heavy metal is mandatory before the sludge can be used as a soil conditioner or fertilizer in the agricultural soil.

In general, the mean concentration of heavy metals in sludge sample collected from all sampling site were decreased in the order of: Fe > Cu > Zn > Mn > Cr > Pb. From the present study one can observe that there is a possibility of contaminant in the soil of industrial areas where industrial contribution is major effect. This study recommends further investigations on the contamination of the soil by heavy metals and their health implication on the peoples fed on the plant grown in this soil. This study might be repeated with GFAAS and ICP-OES to compare the heavy metal contents of the selected sample types.

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