Concentrations of Plant Nutrients and Heavy Metals in Sludge from Kombolcha Textile Factory, North Central Ethiopia

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Abstract

Waste effluents from textile industries have been reported as a major environmental threat because of large amounts of water and dyes involved in the manufacturing processes. A study was carried out to quantify concentrations of plant nutrients and heavy metals in textile sludge. Samples were collected from Kombolcha textile factory, located in north-central Ethiopia. Nitrogen, phosphorus, and potassium were determined following standard procedures. Subsamples were dry digested for extraction of micronutrients and heavy metals. The concentrations of micronutrients and heavy metals were determined by ICP-OES with a radial plasma test tube. Results revealed that nitrogen, phosphorus, and potassium contents of textile sludge were 1.665, 0.29, and 0.358%, respectively. The mean concentrations of heavy metals in mg/kg were Cu (846.25) Fe (17340.60), Zn (597.73), Ni (30.83), Co (6.66), Mn (1165.43), Cr (71.01), Cd (2.25), Hg (2.96), Sn (60.03), Pb (27.70), As (10.72)). All the heavy metals concentrations, except Pb and Cr in the sludge samples, were higher than the acceptable ranges set by WHO to use the sludge as a fertilizer in agricultural soil. Based on the results from this study, it can be concluded that pre-treatment processes in order to reduce concentrations of heavy metals are mandatory before the sludge to be used as a soil conditioner or fertilizer for agricultural production.

Keywords: *Fertilizer, Macro and micronutrients, Textile Effluents, Toxic metals*

Introduction

Textiles being the essential necessitate of human being undoubtedly, textile industries have great trade and industrial significance. The textile industry involves the processing of raw materials and fabric into finished cloth involving various stages of processes and operations consuming large quantities of water and various types of chemicals and dyes (Adinew, 2012). In addition, the input of a wide range of chemicals and dyestuffs, which are generally organic compounds of complex structure is required for those processes (Gaber et al.,2011).

Uses of wide ranges of chemicals and dyestuffs and discharge of effluents in the processes of manufacturing have placed textile industries in the kind of most polluting industries in the world. Typically, textile effluents contain dissolved organic and inorganic substances, colloidal or suspended forms and it is typically colored due to the presence of residual dyestuffs. In addition, it is often contaminated with non-biodegradable organics termed refractory materials. Detergents are typical examples of such materials. Textile wastewater from dyeing and finishing processes is the major cause of environmental pollution. As a consequence; textile waste effluents cause grave environmental problems and concerns. Being one of the biggest industries, Textile, and dyeing, are now observed as a major environmental risk in the industrial area of Ethiopia and they contribute vast amounts of sludge in wastewater treatment processes (Mehari and Mulu, 2013). The final removal of industrial sludge in the country has become a critical issue due to public concern and the limited land for waste disposal. The most effective line of management is to reuse or reduce the quantity of sludge produced by various industrial processes. If a reduction is not practicable, then the reuse is the most alternate management option of sludge as to be considered (Aziz e*t al.* 2012). Although characteristics of sludge depend on the wastewater treatment process and sludge stabilization methods, it contains substantial amounts of toxic heavy metals (Singh *et al*.,2004)

Heavy metals are very unsafe because of their toxic nature to the organism, elongated natural half-lives, and their perspective to be accumulated in different body parts (Manaham, 2005). Too much accumulation of heavy metals in agricultural soils through the application of textile wastewater may not only result in soil contamination but also affect food quality and safety (Wilson and Pyatt, 2007). Heavy metals such as Cd, Pb, Cu, Zn, and Ni have carcinogenic or toxic effects on human beings and the environment (Muchuweti and Lester,2006)

Heavy metals like cadmium, copper, zinc, chromium, and iron have also been found in the dye effluents. As all of them are not enclosed in the final product, they may be thrown away and caused disposal problems. Huge quantities of unused materials including dyes in the wastewater generated during various stages of textile processing with inappropriate waste management practices i.e. straight discharge of wastewater into an environment that can affect ecological status by causing various adverse effects(Muchuweti and Lester,2006). Subsequently, this can lead to contamination of surface and groundwater; affect public health and atmosphere due to diffusion of bad odor problems from wastes. It is usually expected that the textile effluents contain highly toxic dyes, salts, acids, alkalis, and bleaching agents (Udom and Agbim, 2004). If applied to soils, the actual toxicity of heavy metal will affect the organic matter, pH, and biological properties of soil. The health effects of exposure to heavy metals depend on the quantity and length of coverage, *i.e*. the volume of contaminated soil or food consumed over time (Wong and Min, 2002)

Land application of textile sludge can be an excellent solution, whereas it is a lucrative retention method for treatment plants and also can provide a complimentary fertilizer for agricultural lands (Kocasoy and Sahin, 2007). Analysis of plant nutrients and organic matter contents in textile sludge conducted in Bangladesh indicates its potential application as a fertilizer (Kocasoy and Sahin, 2007). This provides an economical alternative for the final disposal of the textile sludge (Kocasoy and Sahin, 2007). But heavy metals in textile sludge are always an issue restricting its use as fertilizers. So, pre-treatment of textile sludge earlier to the land application is likely to be a possible and practical means for reducing heavy metal contents. Similarly, characterization of the sludge in terms of heavy metals and plant nutrients content is vital to use textile sludge as complementary fertilizer for agricultural production. So the objective of this study was to assess plant nutrients and heavy metals content in textile sludge in order to use as organic fertilizer for agricultural production.

Materials and Methods

Study Area Description

The study area is located in northern central Ethiopia at 380 km north of Addis Ababa and has an elevation ranging from 1842-1915 m.a.s.l. It has a latitude and longitude of 11º 5' N 39 º 44 'E. It is characterized as a sub-humid climate with bimodal rainfall distribution. The main rainy season is from July to September while March to October is the period for a small amount of rainfall.

Sludge Sampling and Sample preparation

Textile sludge samples were collected from Kombolecha textile factory from sludge discharge thank. The collected samples were subjected to basic sample preparation procedures, air drying, and grinding. The air-dried sludge samples were ground well with a mortar and pestle to get the final ground powder and kept for analysis. The concentration of nitrogen, phosphorus and potassium in textile sludge analysis result is presented in Table 1.

Laboratory analysis

Nitrogen

Three samples of textile sludge of weight 1.000 g were weighted and transfer into a dry Kjeldahl flask. Kjeldahl tablets (selenium tablets) were added to each Kjeldahl flask containing the samples. Then 10.00 ml of concentrated sulphuric acid was added and flasks were placed on the heating device inclining the neck at an angle of about120^{o}. Heating was continued for 180 minutes until the solution has become colorless or clear. Few boiling chips and 150.0 ml of distilled water were added to the digested mixture in the Kjeldahl flask. Then45.0 ml of 45%NaOH (aq) was added and the mixture was heated until it boiled. In the distillation step, a Boric acid solution (20.0 ml) and five drops of the Bromo cresol green indicator were added to conical flasks. Distillation was carried out using (Indicate apparatus used for distillation). Distillates were collected in flasks containing boric acid solution. Titration was carried out using 0.5 M H_2SO_4 (aq) solution against sample distillates and blank sample for determination of ammonium nitrogen.

Determination of phosphorus

The sludge samples which were prepared for analysis weighted on an analytical balance and calcinated in a muffle furnace. The residuals ashes after calculations were dissolved in 6 N HCl and filtered into 250 ml volumetric flasks, then filled up to the mark with distilled water. The calibration curve was created using a standard phosphate solution of potassium dihydrogen phosphate (KH_2

Determination of potassium

Potassium standards were prepared from potassium chloride (1.9070 g). Sludge samples (5.g, were placed in a crucible and keep in a
samples were digested to ashes. Then samples were cooled to room temperature. Conc. HCl (2.5ml) was added and keep in a steam bath for about 30 minutes and filtered into a 100.0 ml flask. Total potassium contents of these three samples were determined using AAS.

Digestion methods

The determination of metals was proceeded using the dry digestion method (Haynes, 1980) using a muffle furnace by placing 1.25g samples into a high-form porcelain crucible. After digestion, the residuals were wetted with a small amount of distilled water, and then5 ml of 6 N HCl was added. The aliquot of the final solution was placed into an ICP test tube and all measurements were performed with spectra across optical emission spectrometer The detection limits for the selected heavy metals were 1.00 mg/kg (Ellis *et al*., 1975).

Table 1. Concentration of nitrogen phosphorus and potassium in textile sludge

Nutrients	Contents (%)
Nitrogen	1.665
Phosphorus	0.29
Potassium	0.355

Results and discussion

Comparison of Nitrogen, Phosphorus and Potassium Contents of Textile Sludge with Their Respective Chemical Fertilizer and Manure

The percentage of most important nutrients (N, P, and K) in textile sludge were compared with common organic manure and chemical fertilizer in Table 2. The concentration of N in textile sludge is higher than its content in all organic manures listed in Table 2. However, the concentration of P in textile sludge is typically lower than its content in all manures except in compost. Phosphorus in textile sludge is almost equal to its content in compost. This suggests textile sludge is as good as compost considering only its P content. The concentration of K is lower than its content in all manures listed, but the amount is better to be used with zero K chemical fertilizers.

Plant micronutrients and heavy metals

Heavy metals are of great significance in geochemistry and ecotoxicology because of their toxicity at low levels and tendency to accumulate in human organs (Aziz et al. 2012). The current study indicated that the average concentration of lead in the sludge samples was 27.01 mg kg-1, (Table 3). This result revealed that examined sludge samples contained a relatively lower amount of Pb. According to the US Environmental Protection Agency (EPA) guidelines, the background of Pb in sludge to use a fertilizer in agricultural soil is 100 mg kg-1 (Aziz et al. 2012). So the concentration was acceptable for only over the short term on a site-specific basis (Kempster and Van, 1991).

Table 2. Comparison of N, P, and K of textile sludge with some commonly used chemical fertilizers and organic sources of plant nutrients.

Manures/ chemical fertilizers	Nitrogen (N) %	Phosphorus (P) %	Potassium(K)%
Textile sludge	1.665	0.29	0.355
Cow dung	0.5-1.5	0.4-0.8	0.5-1.9
Poultry manures	1.6	1.5	0.85
Farmyard manure	0.5-1.5	0.4-0.80	0.5-1.9
Compost(general)	0.4-0.8	0.3-0.6	0.7-1.0
Urea	46	-	-
Ammonium sulphate	21	-	-
Diammonium phosphate	18-21	20	-

The average concentration of cadmium of the sludge samples was 2.25 mg kg-1 (Table 3). The permissible level of Cd in textile sludge to be used as fertilizer in agricultural soils set by US Environmental Protection Agency (EPA) is 0.6 mg kg-1.Even natural background level of $^{-1}$ (Mehari and Mulu, 2013). So, the values of Cd found in the present investigation were higher than the critical value set by the international guidelines and other researchers. Some cadmium compounds are able to leach through soils to groundwater. Therefore, the use of the investigated sludge, with regard to its Cd concentration, as a soil conditioner or fertilizer can cause severe environmental pollution. In addition, Cadmium is strongly adsorbed by soil clay minerals and co-precipitated with iron and manganese oxides and oxy-hydroxides. For these reasons, cadmium has a limited vertical movement in neutral to alkaline soils. Its availability to plants increases at low pH levels and with increasing chloride concentrations. Plant availability of cadmium decreases when the concentration of organic matter is high. Cadmium can be expected to be retained in the soil surface layers because of its strong sorption by the soil exchange complex. It is highly unlikely that cadmium can be economically removed from sludge. Cadmium can be most conveniently removed by raising the pH and precipitating the insoluble cadmium salts after the addition of lime or iron salts in the pH range of 8.5 - 11.5 (Berman, 1980). However, this range of pH value is not suitable for normal growth of most plants.

The concentration of Zn was 597mg kg-1 in the sludge samples, which was higher than those of permissible levels in textile sludge given by different guidelines and nations. The maximum Zn value in light soil used in cultivation in India given by (Wong and Min, 2002), was 100 mg kg-1. The entry natural background values of Zn in crop soils and paddy soils in $^{-1}$ At higher concentrations it causes toxic responses by inducing iron deficiency. So the pretreatment of sludge to reduce Zn concentration should be proceeded by applying agricultural lime in order to raise (or maintain) soil pH to neutral to slightly alkaline; or huge quantities of organic material and switch to a crop that is more tolerant to zinc (Page and Chang, 1990)

The Cu content in the sludge samples was 846.25 mg kg-1 which was also extremely higher than that of the kg-1). Some well-documented studies revealed that heavy metals such as zinc (Zn) and copper (Cu) are the principal elements restricting the use of sludge as fertilizer for agricultural purposes (Udom and Agbim, 2004). Copper is an essential plant micro-nutrient and is an important component of several plant enzymes. Copper deficiency symptoms occur in plants grown in soil that have a low copper concentration. Approximately 6 mg/kg of copper in the soil is the lower limit for healthy plant growth. Copper toxicity is usually associated with soil concentrations in the range of 150 - 400 mg/kg. Depending on plant species, copper toxicity occurs in nutrient solutions at concentrations between 0.1 and 1 mg/kg. This research work indicates that the concentration of Cu was found higher than the safe limit. Thus the application of agricultural lime with sludge in order to raise (or maintain) soil pH to neutral to slightly alkaline and ample phosphate fertilizers or iron salts are important as reported by Page and Chang (1990).

The average concentration of chromium (Cr) in the samples was 71.01 mg kg-1. The maximum content of Cr reported by Zorpas et al. (2008) in soil used in cultivation was 100 mg kg^{-1}. The natural background of Cr in agricultural soils based on the 90 mg kg^{-1}. The Cr content in textile sludge obtained from the present study was lower than the permissible levels recommended by the above sources. Chromium has no known plant physiological function and is not an essential plant nutrient, but at low concentrations, it has been found to have a beneficial effect on plant growth (Devereals and Fujii, 1990).

Extensive term contact 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 textile sludge to use as fertilizer in agricultural soils in different countries varying from 289.3-338.5 mg kg^{-1} (Dai *et al.,* 2007). The Fe content in sludge obtained from the present study was17340.6 mg kg-1 which is higher than the permissible value described by SEPA and the above researcher. Iron-rich sludge can cause a number of problems; an iron coating sludge sample application on land may be deposited on plant leaves or fruit. It could be in the form of light brown spotting, a silvery coating, or a thick black coating. This interferes with normal photosynthesis, transpiration, and respiration and may lead to damage and eventual plant death. So, sludges should be pretreated before applying as a source of fertilizer or be applied with agricultural lime in order to raise (or maintain) soil pH to neutral to slightly alkaline.

Since cobalt is retained strongly by soils, it is likely to be accumulated to phototoxic concentrations before equilibrium between sorption and desorption reactions are reached, cobalt can be removed by precipitation at alkaline pH, with lime, or by flocculation and co-precipitation with a ferric salt. Alternatively, ion exchange can be used (Page and Chang, 1990). Plants vary in their sensitivity to manganese and toxicity has been observed at a fraction of a mg/kg in a nutrient solution. The concentration of Mn was 1165.44 gm/kg and highly accumulated in the sludge. Excessive manganese in the sludge can cause manganese toxicity if applied to the soil without pretreatment. Thus, as mentioned above pretreatment or application of agricultural lime with sludge, in order to raise or maintain soil pH to neutral to slightly alkaline is mandatory (Page and Chang, 1990). Other toxic elements contents of sludge (Ni, Co, Hg, Sn, As, and B) were higher than the permissible values set by Rodríguez-Eugenio et al., (2018) SEPA/FAO (Table 3).

Table 3. Concentrations of micronutrients and heavy metals in textile sludge samples from Kombolcha textile factory

Parameter	Result (mg/kg)	SEPA/FAO limit
Lead	27.70	100.00 Mg/kg
Cadmium	2.25	0.60 Mg/kg
Zinc	597.73	300.0 Mg/kg
Copper	846.25	100.00 Mg/kg
Chromium	71.01	100.00 Mg/kg
Iron	17340.60	338.50Mg/kg
Nickel	30.83	1.00Mg/kg
Cobalt	6.66	5.00Mg/kg
Manganese	1165.44	50.00Mg/kg
Mercury	2.96	1.00Mg/kg
Tin	60.03	5.0 Mg/kg
Arsenic	10.72	10.00Mg/kg
Boron	27.75	15.00Mg/kg

Conclusion

The results revealed that analysis of textile sludge in terms of principal plant nutrients namely nitrogen, phosphorous, and potassium was highly victorious. More significantly, experimentally found average nitrogen content in textile sludge (1.665%) was considerable compared to nitrogen content present in commonly used manure. Secondly, average phosphorus (0.29%) and potassium (0.358%) content were approximately analogous to amount of phosphorus (0.3%-0.6%) and potassium (0.5%) concentrations found in common manure. From the results of the elemental analysis of textile sludge, it can be affirmed that levels of heavy metals were generally higher than the standards, except Pb and Cr. The concentrations of Cd, Zn, Cu, Ni, Co, Mn, Hg, and Fe in the sludge samples were beyond the safe limit set by SEPA limits whereas Pb and Cr were found within the safe limits of the respective heavy metals. From this study, it could be concluded that a pre-treatment process should be carried out in order to reduce concentrations of heavy metals in sludge to use as complementary organic fertilizer or should be applied with agricultural lime to raise or maintain soil pH to neutral to slightly alkaline. These are mandatory before the sludge can be used as a soil conditioner or fertilizer for agricultural production.

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