Quantification of Toxicity of lead from Sewage-Sludge samples used for Vegetation in Dombivli MIDC, Maharashtra, India

Bambardekar Yogini and Anand Neena
Department of Chemistry, Smt.C.H.M. College, Ulhasnagar, Maharashtra, INDIA

Abstract

Application of sewage sludge is common as a soil amendment on productive vegetation land. Sludge builds up the soil organic matter content effectively like compost; it thus improves soil structure and capacity of water retention. At the same time significant amount of nutrients are supplied to the soil. Depending upon the sources, sewage sludge composition is highly variable. Unfortunately, sludge originating from urban wastewater source contain relatively higher concentrations of non-nutrient metals Some of the elements are potentially toxic to plants growing on soil that is treated with sludge., Households are the major sources as well; lead, copper, zinc, iron are all leached from domestic pipes. The vegetation land is mainly utilized for cultivating variety of routine vegetables that are consumed by local residents. The concentration level of heavy metal lead present in selected sections of sludge was ascertained using liquid-liquid extraction coupled with photometric technique. Hexane-2,5-dione-bis(ethylene diamine) HDBE, novel derivative that forms deep yellow complex with lead which is quantitatively extracted into chloroform at PH4.4 respectively. Concentration of reagent required for complex formation and full color development is very low ($0.8cm^3$ of 0.1% HDBE). Beer's law is obeyed in the detectable range 0.4-5.0ppm for Pb(II)

Keywords: sludge, vegetation, HDBE, lead, complexation.

Introduction

Metals and alloys have become an integral part of today's modern life. Disposal of metal as scrap without proper processing is becoming a major threat to the environment. Rapid urbanization and industrialization pose many challenges to the ecosystem, and the bulk materials in the form of wastes from domestic use and industries, have been and will continue to be discarded on the land. Many of these wastes include metals, are disposed off in the sewerages without the operator's knowledge[1].

Sludge applied with appropriate treatment not only supplies nutrients through organic wastes but also enhances the quality of soil .Unfortunately, majority of landfills undergo sludge application which is untreated. These practices certainly lead to degradation of soil structure due to over accumulation of unwanted metals[2].

Some of the open lands in MIDC PHASE-1 area in highly polluted city like Dombivli were developed as vegetation lands for cultivation of vegetables like cabbage, tomatoes, radish and spinach[3]. T he vegetation belts developed in MIDC is surrounded by mainly residential area and variety of small and medium scale industrial units mainly which extensively involve use of heavy metals like cadmium and lead[4]. Landfills, over the period of time accumulate reasonable amount of unwanted heavy metals through waste disposal in the form of sewage-sludge (solid and liquid) which eventually enter the soil system

and therefore contribute greatly to this risk potential[5-6].

Industrial effluents from surrounding areas, atmospheric pollutants often get discharged into sewers[7]. Along with organic wastes, many other poisonous trace metals get added to sewerage system. Some of these substances can be highly toxic to humans and/or animals so it is necessary to control the concentrations of potentially toxic elements and their rate of application to the soil[8].

During application of sludge to the vegetation land, the concentrations of potentially toxic elements like lead can be determined in soil samples taken to a depth of 0-15.0 cm. The maximum concentration limit of lead should not exceed the limits set out as per sewage sludge guidelines, EPB296, (June2004)[9]. Max. acceptable concentration of lead in vegetables is 10 mg/kg[10].

Material and Methods

Apparatus and instruments: Glassware made up of standard Pyrex or corning were calibrated and used throughout the analysis. An analytical balance of 0.001 g sensitivity was used for weighing. pH measurements were taken with an Elico Li 120 Ph meter and absorption spectra were recorded using Schimadzu UV2100 spectrophotometer.

Sample collection and leaching: Selected portion of landfill was demarked into five sections viz. A, B, C, D, E as under:

Section	Area (Sq.m)	No. of samples taken	
		0-15cm	**15-30cm**
A	128	3	3
B	210	3	3
C	465	5	5
D	320	3	3
E	280	3	3

Preparation of Real Samples: Soil samples: At each site, three replicated samples were taken from the surface soil, composite and represented samples preserved in an acid prewashed cleaned polyethene bags and subsequently treated and analyzed separately. The soil samples were collected at 0-15 cm and 15-30 cm depth from three portions at each section with interval of 10cm in each portion. The soils were collected in airtight plastic bags. They were air dried, mechanically ground and sieved through 2mm sieve. To determine the total concentration of metal content of the soil, 1.0g of the sieved sample was heated with 20ml conc. HNO_3 at 30^0C to dampness. Then 50 ml of 70% $HClO_4$ acid was added into the sample and heated on wire guage until a complete digestion was observed. After cooling, the digested residue was filtered through a whatman filter paper into a 50ml volumetric flask and made up to mark with distilled deionized water.

Reagents and solutions: Preparation of working standards: HDBE Reagent: A novel chelating ligand for lead was prepared by combination of diketone and primary amine. A buff colored solid product was obtained after monitoring all reaction conditions which was purified by recrystallisation. Characterization was carried out using IR and NMR. 10ml of each digested sample was analyzed for Pb using stock lead solution which was prepared by dissolving 1.598g of Lead nitrate with double distilled water in a 1000ml volumetric flask. Working standard was prepared by dilution of 10 cm3 stock solution to 100 cm3 with double distilled water and then standardized immediately prior to analysis.

Methodology for extraction and photometric studies: i. Addition of reagent: 1.0 cm^3 of 1% solution of HDBE reagent was added to 1.0 cm^3 of an aqueous solution containing 0.1 mg of Pb(II), ii. An appropriate PH was adjusted (6.4) keeping the total volume to 10.0 cm^3. iii. The solution was transferred to a separatory funnel and equilibrated with 10.0 cm^3 of preselected solvent chloroform. iv. After shaking, the two phases were allowed to separate. Organic layer was collected in 10.0 cm3 standard flask to record the absorbance at suitable wavelength for investigation of various parameters of spectrophotometric study 5.An aqueous phase collected was used to determine concentration of pb (II) by standard method.

Results and Discussion

In a slightly alkaline medium HDBE forms with lead(II) ions a bright yellow complex soluble in chloroform. The 4.3-4.6 pH range is optimum range for the extraction of this complex. The spectrophotometric method of determining microgram amounts of lead consists of the extraction of Pb(II)-HDBE by using solvent chloroform. The basic masking agents are cyanides which form stable complexes with Ag, Hg, Cu, Zn, Cd, Ni and Co, thus preventing their reaction with HDBE.

The absorbance of the coloured Pb(II) –HDBE complex is measured at $\lambda = 545nm$

Reagent concentration and Optimum pH: The extraction of complex has been investigated over the pH range 1-10. The maximum extraction was observed at pH 4.4, further the percentage extraction decreases with increase in Ph.

With other factors constant, increasing volumes of 0.1% reagent solution were added to an aliquot of sample solution containing 100 µg of lead at respective Ph. The absorbance remained fairly constant above 0.8 cm^3 indicating the optimum value of reagent concentration for full colour development as 0.8 cm^3

Determination of Colour Stability of extracted complex: The absorbance of colored extracted complex remained constant upto 28 hrs. at room temperature which is adequate for analytical applications. Throughout the experiment, for the reason of practical convenience, absorbance measurements had been carried out within one hour of extraction.

Calibration plot: The calibration curve was plotted for the range of concentrations from 0.00 to 0.09 mg. For this purpose from 0.0 to 9.0 ml of working solution of lead(II) was measured into the separatory funnels, water was added to 10.0 ml and the same procedure as in the case of the determination of lead was used.

Table-1
Optimization of practical parameters

Equilibration temperature	35^0C
Equilibration time	3 min.
Working pH	4.4
Reagent conc.	0.8 cm3 of 0.1% HDBE
Aqueous phase	10.0 cm^3 containing 0.5cm^3 of 0.1% HDBE
Organic phase	10.0 cm^3 chloroform
Wavelength	545 nm

Table-2
PH of selected sections

Sample section	pH
A	5.7
B	6.0
C	7.7
D	7.9
E	6.7

pH is considered as a significant ecological factor affecting the rate of adsorption, With increasing pH, the solubility of most metals decreases due to their increased adsorption at surface level. Higher pH values may result in greater retention of metals at surface and their lower solubility in the soils of study area. Thus ascertaining Ph of each section under study becomes the primary task of the work. High soil pH can stabilize soil toxic elements, resulting in decreased leaching effects of those elements.
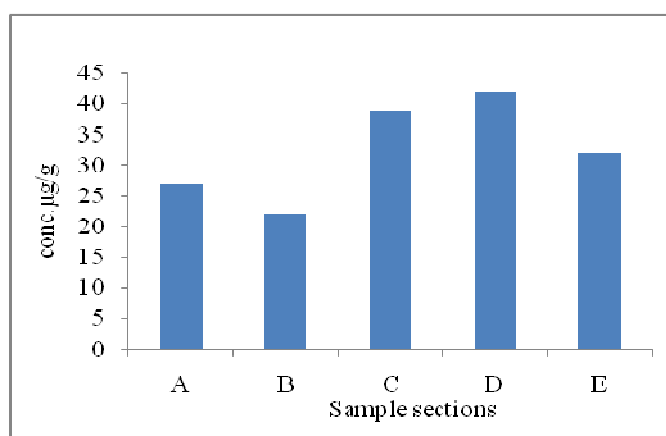
Table-3
The average of triplicate determinations of metal Pb(II) concentration in Soil at various sampling sites is presented in μg/g

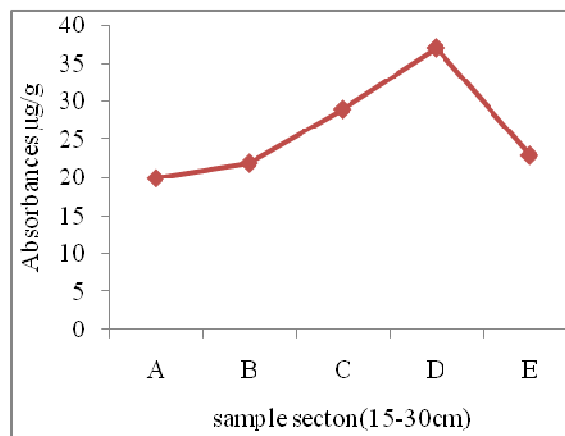| Sample section	Conc. of Pb(II) in μg/g	
	(0-15cm)	(15-30cm)
A	27	20
B	22	22
C	39	29
D	42	37
E	32	23
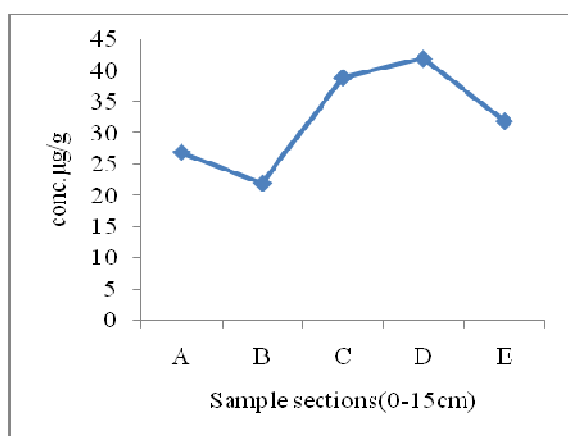
Figure-1
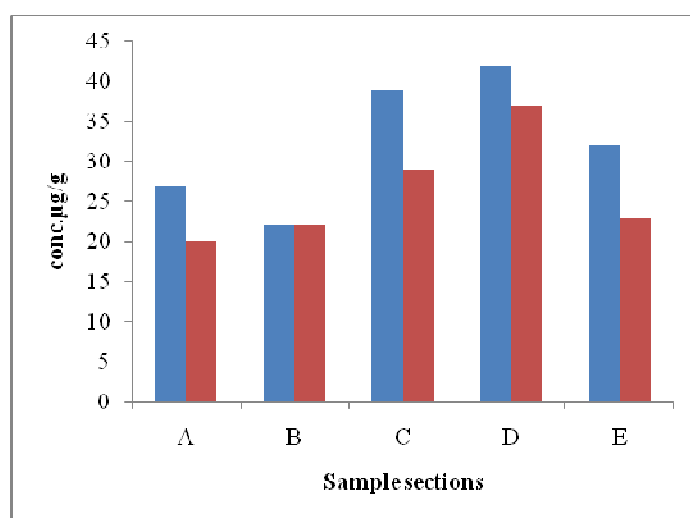**Comparitive Conc. of Pb(II) at 0-15 cm depth**

Figure-2
Comparitive Conc. of Pb(II) at 0-15 cm depth

Figure-3
Comparative conc. of Pb(II) at 15-30 cm depth

Figure-4
Comparative conc. of Pb(II) at 15-30 cm depth

The high mean value of the concentrations attested to the overall high level of contaminations of this metal in the section D with higher Ph value 7.9

Conclusion

Concentration of toxic heavy metal lead can be precisely ascertained in laboratory using coupled technique like chelation-extraction and spectrophotometry. The upper limits of lead in a region with higher pH values indicate the maximum retention of metal due to lowered solubility. Subsequently it decreases the mobility of toxic metal deep into the soil. A correlation can be found out between the toxicity level of metal in vegetables or crops grown on soil areas and higher pH values. Lower limits of lead in soil sections with acidic pH suggest possibility of mobilization of Lead in soil due to lesser adsorption at surface level and possibility of absorption of lead by roots of vegetables. That would be further scope of studies.

A uniform national policy for sludge application in agriculture is need of the hour. This must include the division of responsibilities in authorities and provide for their collaboration. Realistic standards must be adopted to safeguard public health and prevent adverse environmental impacts. Provisions should be made of trained staff and resource organizations well acquainted with the responsibility for assessing, executing, functioning and monitoring sludge use schemes.

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