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Stabilization of Metal contaminants in Municipal Waste Leachate using Metal precipitant additives

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Abstract: The environment faces serious problems which may be caused by metal contaminants transported by municipal waste leachate(MWL). If not treated,municipal waste leachate can be a potential source of pollution of soil and water. This may affect the quality of water supply where increasing concentrations of metal cations in the water constitute a severe health hazard, mainly clue to their non-degradability and toxicity. This work deals with the removal of these pollutants using phosphate metal precipitant additives. In this method, complexation reaction between metal cations and efficient complexing agent (stabilizer) in a liner of landfill will prevent from passing the pollutants trough the liner, hence increasing the metal retention. Metal precipitant additives that used in this work are sodium tripolyphosphate (STPP) that is inexpensive and has high usage in industry.

Contaminants in MWL were determined by flame atomic absorption spectroscopy (FAAS). The results showed that the concentration of iron, zinc, nickel, magnesium and manganese, were high and are contaminants of municipal waste leachate.

Concentrations of these contaminants are 32, 0.1, 0.68, 11.5 and 2.14 μg ml $^{-1}$ respectively.

Introduction

Human activities always generate solid wastes. Solid wastes are usually handled by processes such as, collection ,transportation, sorting, recycling and disposal at dumping sites. As a result, the dumping sites become concentrated with wastes and may affect the environment (1).

The generation of leachate is caused principally by precipitation percolating through waste deposited in a landfill. Once in contact with decomposing solid waste, the percolating water becomes contaminated and if it then flows out of the waste material it is termed leachate. Additional leachate volume is produced during this decomposition of solid waste producing a wide range of materials including methane, carbon dioxide and a complex mixture of organic acids, aldehydes, alcohols, simple sugars, heavy metals and metal cations.

Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. Heavy metals are dangerous because they tend to bioaccumulation. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Some heavy metals are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted.

MWL was sampled at landfill in Shiraz and was chemically characterized by using flame atomic absorption spectrometer (FAAS) and PH meter. Parameters measured were pH, heavy metals (Zn, Ni, Mn, Co, Cu, and Ag) and major cations (Mg, Fe). pH value recorded for untreated MWL was 7.33

and results showed that concentration of 5 cations were high .

This study was conducted to creation of a liner in the bottom of landfill for prohibition of influx of metal contaminants transported by leachate in soil. This filter is made of mixture of soil and a complexing agent. Complexation reaction between metal cations and efficient complexing agent (stabilizer) will prevent from passing the pollutants trough the soil, hence increasing the metal retention.

One stabilization agent of recent interest is orthophosphate (PO_4^{3-}). It is used commercially to stabilize a variety of hazardous and industrial wastes (2-5).

This agent combines with over 30 elements to form about 300 naturally occurring minerals (6, 7). The use of PO_4^{3-} to immobilize metals has been advocated for industrial wastewaters (8, 9) and lead-contaminated soils [4, 10].

This study was conducted to evaluate STPP as a chemical immobilization treatment in a leachate column described in ASTM D 4874-95. STPP is inexpensive and is used in water softening, industrial cleaners, food uses, detergent, emulsifier of oil and grease, peptizing agent, deflocculating agent in oil well, sequester in cotton boiling.

The column test was carried out by passing the leachate through a bed of soil and complex agent (STPP) contained in a column (11-14).

Materials and Methods

Analytical materials and apparatus

Standard solutions of metal cations and stabilizer were made of manganese(II) chloride, zinc(II) nitrate, magnesium(II) nitrate, iron(II) nitrate, zinc(II) nitrate, nickel (II) nitrate and sodium tripolyphosphate that were obtained from Merck as analytical reagent grade materials and were used without further purification. All dilute solutions were prepared from double-distilled water. The concentration of cation solutions and stpp solution were 10^3 and 10^5 μg ml^{-1} respectively.

Apparatus that used in this study were PERKIN ELMER UV-VIS spectrophotometer, Sens AA flame atomic absorption spectrometer.

Chemical analyze of untreated municipal waste leachate

The metal cations in untreated municipal waste leachate then dilution and centrifuge determined by flame atomic absorption spectrometer (FAAS). Concentrations of 8 metal elements are shown in table1. This results show that Zn, Ni, Mn, Mg and Fe are metal contaminants in MWL.

Evalution of complexation reaction between stabilizer and contaminants

The complexation ability of stpp with contaminant*s* has been investigated using Uv/Vis spectrophotometric technique.

Measurements were done at pH 7.33, 1(using Hcl 1M), 9(using NaOH 1M) and room temperature. In this technique, complexing agent added to cation solution in several series. In each series, 0.1 ml STPP solution added to cation solution. Peak shift in spectra are signifier of existence of complex formation. Spectra in various PH show that complexation reactions between metal cations and stabilizer in PH< 7 are perfecter than complexation reactions in alkaline PH too.

For example, Figures 1 until 3 show the nickel cations and Ni-TPP complex spectra in water solution. In this figure, peak shift is distinct.

Column test

The column test was carried out by passing the leachate through a bed of soil and stabilizer contained in a column. Passing the leachate is conducted in an up-flow mode. Column (r =2, L=8cm) was uniformly packed with dry soil or soil-stabilizer mixtures. The soil that used for filling column was sand and the mineralogy of soil is shown in table2. Column packing was performed in approximately 30 g increments that were tamped by hand with a plastic dowel.

Three stabilizer / soil ratio (0.7/100, 0.5/100, 0.2/100 w/w) used for filling column were made of adding 12.4 ml STPP solution 10^5, 7.285×10^4 and 2.9×10^4 μg ml^{-1} to 180 g dry soil respectively.

Table1. Concentrations of metal contaminants in MWL

Sample	Concentrations (μg ml^{-1})							
	Fe	Zn	Ni	Mg	Mn	Co	Cu	Ag
MWL	0.16	0.005	0.02	1.15	0.15	0	0.0003	0

Table 2. The mineralogy of soil

Minerals	Content(g) in 1000g soil
SiO2	41.20
Al2O3	9.55
Fe2O3	4.72
TiO2	0.76
CaO	22.70
MgO	2.72
Na2O	0.62
K2O	1.96
SO4	0.07
P2O5	0.13

Table 3. Void ratio for columns with varied soil / stabilizer ratios

Sample	STPP/soil ratio	STPP volume (ml)	Con of STPP (μg ml^{-1})	Dry soil weight (g)	γd	e
S1	0/100	-	-	160.07	1.59	0.676
S2	0.7/100	12.4	100,000	180.66	1.79	0.485
S3	0.5/100	12.4	72,850	180.66	1.79	0.485
S4	0.2/100	12.4	29,000	181.03	1.80	0.482

Table 4. Hydraulic conductivity of columns with varied stabilizer / soil ratios

Experiment	Column type	Passed liquid type	K (cm s-1)
W-No chem-T1	dry soil	water	5.1E -4
L-No chem-T2	dry soil	leachate	4.7 E -4
L-0.7/100 STPP-T3	soil-stabilizer (0.7/100 w/w)	leachate	7.61 E -5
L-0.5/100 STPP-T4	soil-stabilizer (0.5/100 w/w)	leachate	4.08 E -5
L-0.2/100 STPP-T5	soil-stabilizer (0.2/100 w/w)	leachate	1.98 E -5

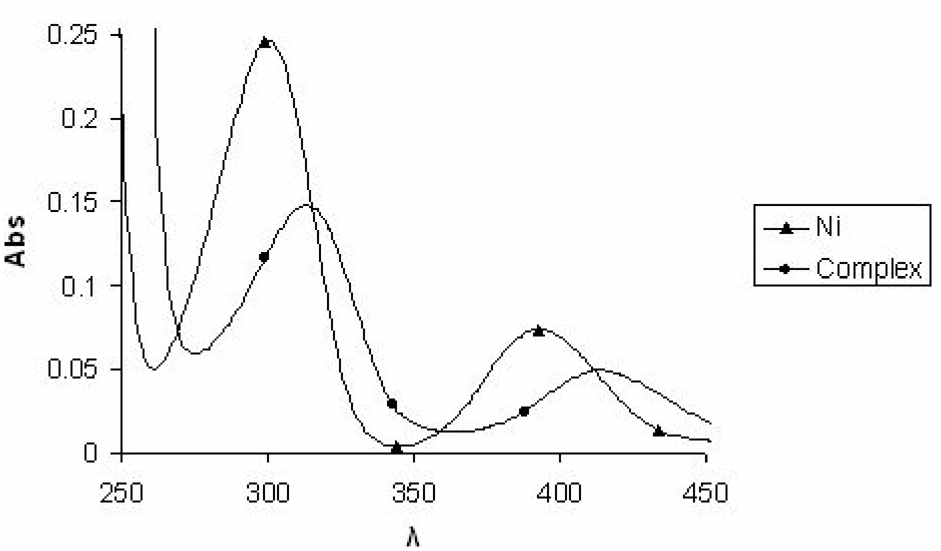

Fig.1. the UV-Vis spectrums of Ni^{2+} and Ni-TPP in pH=7.33

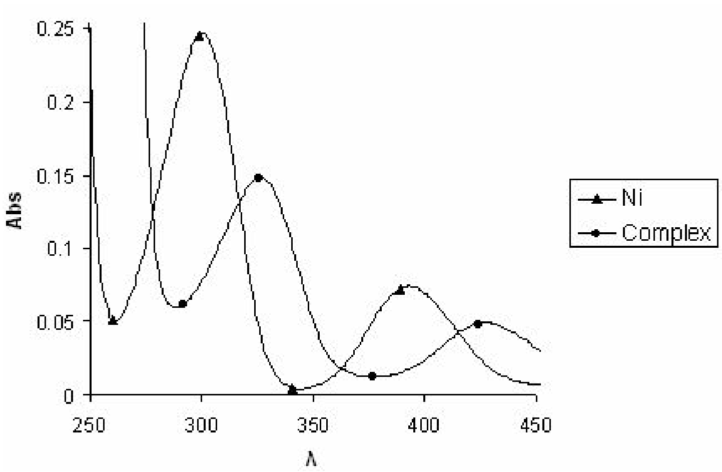

Fig.2. the UV-Vis spectrums of Ni^{2+} and Ni-TPP in pH=1

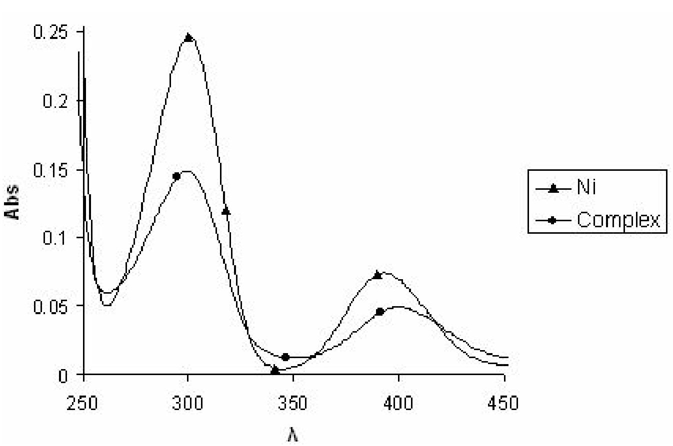

Fig.3. the UV-Vis spectrums of Ni^{2+} and Ni-TPP in pH=9

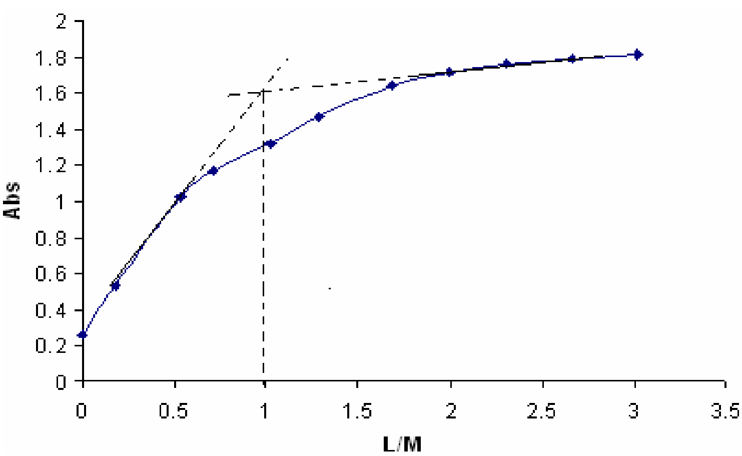

Figure4. The mole - ratio method

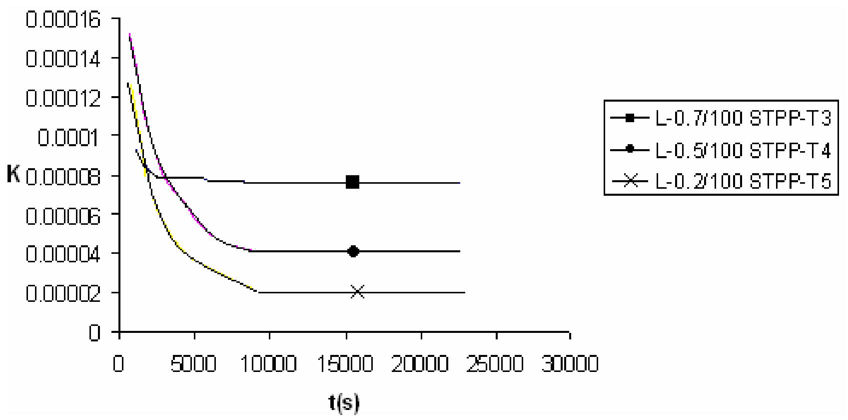

Figure5. Hydraulic conductivity of columns with varied stabilizer / soil ratios

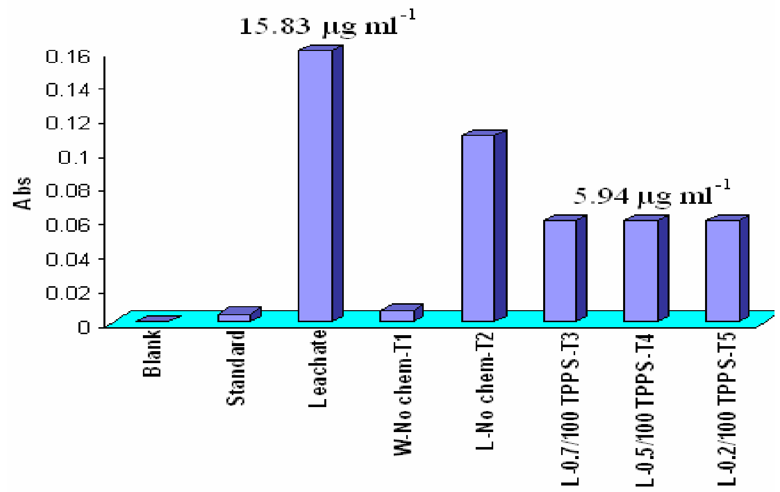

Figure6. Absorbance graphs of iron contaminant in treated leachate
Stabilization percent = 62.5%

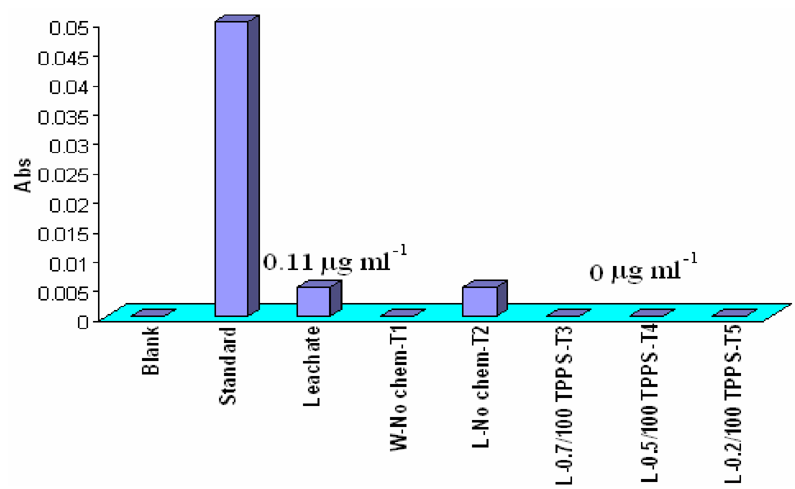

Figure7. Absorbance graphs of zinc contaminant in treated leachate

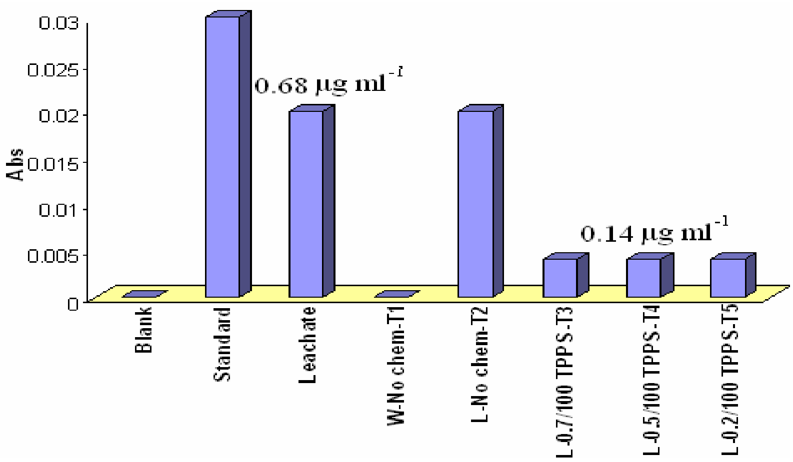

Figure8. Absorbance graphs of nickel contaminant in treated leachate

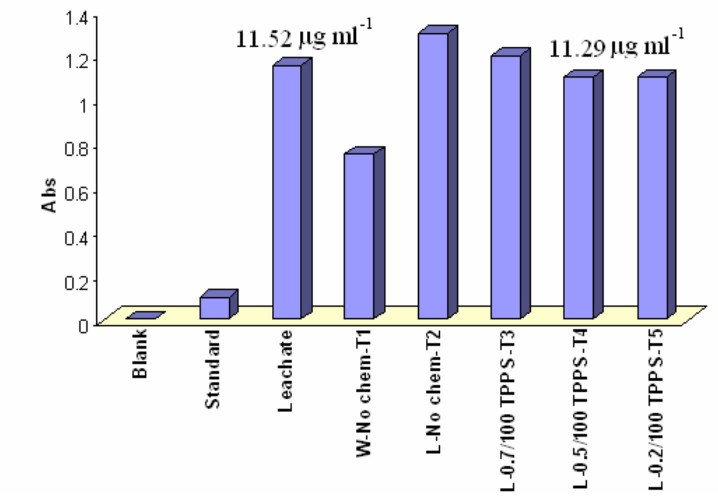

Figure9. Absorbance graphs of magnesium contaminant in treated leachate

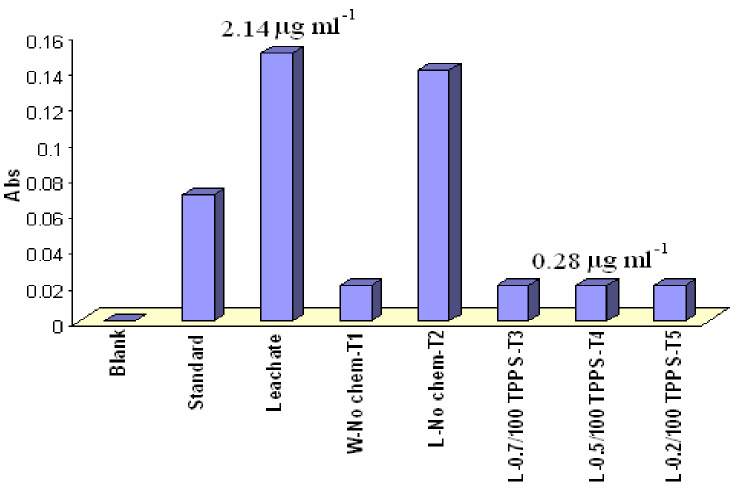

Figure10. Absorbance graphs of manganese contaminant in treated leachate

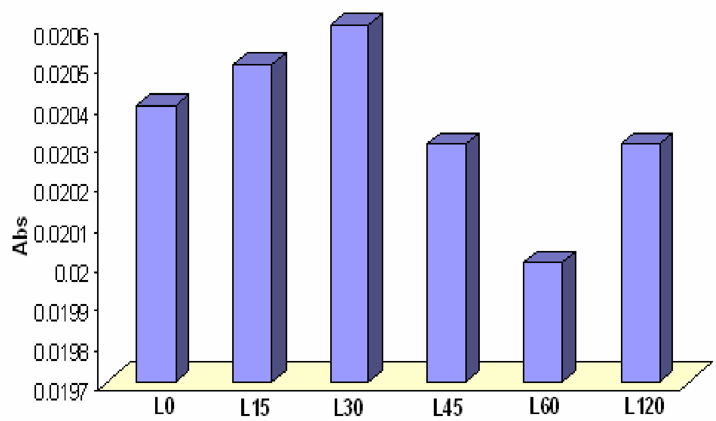

Figure11. Absorbance diagrams of nickel contaminant present in sampled leachates in varying time

Results and Discussion

The stoichiometry of the complexes

The stoichiometry of the complexes was obtained by mole ratio method and the stoichimetry of the all complexes that is studied in this work were obtained 1:1.

For example mole ratio graph of complexation reaction between nickel solution and STPP are shown in figure 4.

Calculation of void ratio

Void ratio (e) for columns with varied stabilizer / soil ratios calculated by below formula and results are shown in table 4. In this method for evolution of efficiency of columns with varied stabilizer / soil ratios must conditions of all columns be similar and void ratio for each column is same, hence for creation of varied stabilizer / soil ratios, equal volume of stabilizer solutions with various concentrations added to specific amount of dry soil.

- γ_d = weight of dry soil / column volume
- $\gamma_d = Gs\ \delta w / 1 + e$
- e= void ratio
- γ_d =specific weight of soil
- γ_W = specific weight of water = 1gf/cm^3
- Gs=2.67

Hydraulic conductivity data

Hydraulic conductivity (k) for leachate passed through columns with varied stabilizer / soil ratios measured using the constant head technique. Results of varied experiments are shown in table4 and for comparison of these results; they are depicted in figure 5. These results show that with increment stabilizer/soil ratio, hydraulic conductivity decrease.

Chemical analyze of treated municipal waste leachate

Then passing leachate through the column, metal cations in treated leachate were determined by flame atomic absorption spectrometer. Absorbance of contaminants in leachates passed trough columns with varied stabilizer / soil ratios is shown in figure 6 until 10.

Results presented here illustrate that none chemical reaction occurred between dry oil and leachate and amount of metal cations except Mg in passed leachate through the oil column didn't change saliently. but adding STPP solution as stabilizer to soil in olumn test method is an effective method of reducing metal solubility and mobility complexation reaction between metal cations and phosphate ligands and resulting omplexes precipitation in void volumes of soil cause to reducing amounts of Fe, Zn, Ni and Mn in treated municipal waste leachate but amount of Mg increased because of solution Mg present in soil in leachate. This results show that stabilizer / soil ratio (0.2/100 w/w) is optimum ratio in this method too.

Hydraulic conductivity data

Results of chemical analyze of iron

Absorbance graphs of iron contaminant in leachates passed trough columns with varied stabilizer/soil ratios are shown in figure 6. this graph are shown that:

- Stabilization percent of iron contaminant in treated leachate is 62.5% that 35% of this percent stabilized by soil.
- T1diagram are shown that a little amount of iron present in soil dissolved in leachate.
- Comparison between T3, T4 and T5 are shown that stabilizer/soil ratio (0.2/100 w/w) is optimum ratio in this method.

Results of chemical analyze of zinc

Absorbance graphs of zinc contaminant in treated leachate are shown in figure 16. Results presented here illustrate that:

- Stabilization percent of zinc contaminant in treated leachate is 100%.

- Comparison between diagrams of leachate and T2 are shown that the soil can not stabilize zinc alone.
- Optimum stabilizer/soil ratio for stabilization of zinc is 0.2/100 too.

Results of chemical analyze of nickel

Absorbance graphs of iron contaminant in leachates passed trough columns with varied stabilizer/soil ratios are shown in figure 17. In this figure:

- Comparison between leachate and T3 are shown that Stabilization percent of nickel contaminant in treated leachate is 80%.
- Comparison between diagrams of leachate and T2 demonstrate that the soil can not stabilize zinc alone.
- Comparison between T3, T4 and T5 are shown that optimum stabilizer/soil ratio is 0.2/100.

Results of chemical analyze of magnesium

Absorbance graphs of magnesium contaminant in treated leachate (figure18) are shown in figure 18. in this graph:

- T1 diagram are shown that a lot of Mg contaminant present in the soil that used in this method dissolved in double-distilled water passed through soil column.
- Therefore amount of Mg do not decreased saliently because of dissolution of Mg present in soil in treated leachate and this method is not effective method for stabilization of magnesium contaminant present in municipal waste leachate.

Results of chemical analyze of manganese

Absorbance graphs of zinc contaminant in treated leachate are shown in figure 19. In this graph:

- Comparison between leachate and T3 are shown that Stabilization percent of manganese contaminant in treated leachate is 87%.
- None saliently chemical reaction occurred between dry soil and leachate and stabilizer/soil ratio (0.2/100 w/w) is optimum ratio in this method too.

Evaluation of time influence on the metal contaminants stabilization

For this purpose, samplings of treated leachate were done in each 15 min then leachate issue of column apparatus.

Absorbance diagrams of nickel contaminant present in sampled leachates in varying time that passed through column apparatus (stabilizer/soil ratio 0.2/100) are shown in figure 11 and number of samples is demonstrator of sampling time.

This figure is shown that complexation reaction and stabilization process occur very fast and are not time consuming. These results are same for another columns and metal contaminants too.

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