

Heavy Metal Removal from a Contaminated Soil using Chemical Reagents

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Abstract— The study was conducted to understand the feasibility of remediation of heavy metals (HM) from contaminated soil using tartaric acid, citric acid and Ethylene Diamine Tetra Acetic acid (EDTA) solution. The chemical reagents used for the study are environment-friendly extractants, which are less expensive. The soil samples are collected from three different stations surrounding Titanium Travancore Pvt. Ltd (TTPL) industry during the months of August and September of the year 2016. As an initial study the collected soil samples are taken for physical and chemical analysis. It was noted that the sample was acidic in nature. It was noted that the collected soil sample has very low organic and nutrient contents. The sample was then mixed with tartaric acid, citric acid and EDTA solutions in separate open beakers and kept for three months. At the end of the study, it was recorded that the concentrations of HMs in the soil samples mixed with tartaric acid has reduced drastically compared with other two mixes. Also the soil heavy metal concentration was high in the station near the waste and effluent discharging points compared to that in the other two stations of the study area.

Keywords— Heavy Metal(HM); Contamination; Remediation; TTPL; EDTA

I. INTRODUCTION

India is a developing and fast growing country in every field in the world. As part of its growth, the number of industries and companies are multiplying day by day. All free lands are occupied by multi-national companies and industries. In Kerala, TTPL industry is a leading producer of titanium dioxide which is situated at Kochuveli nearer to Arabian sea. TTPL industry produces good quality of titanium dioxide which are used in cosmetics, toothpastes, body lotions, paints, etc. But the problem is as part of the production of titanium dioxide varying byproducts or wastes are emitted and discharged from the industry. Such wastes are dumped in an open land inside the TTPL industrial area. The main discharges from the industry are solid sludge, effluent, red gypsum and white gypsum. Solid sludge is dumped in an open land and effluents are discharged to the nearby sea through open drains without any treatment. Red gypsum and white gypsum are accumulated in company area itself. By the accumulation of these waste materials in the industrial area, the soils in that area and nearby area are getting contaminated. For the production of titanium dioxide scrap iron blocks are also used. The wastes or fine particles of scrap iron after industrial process are also dumped along with solid sludge in the industrial area itself, which causes HM contamination in the soil and reduces the soil strength and nutrient contents

from the soil. Thus understanding these problems in the area a remediation technique is to be implemented to prevent future contamination and also to reduce the present contamination intensity in the area near TTPL industry.

II. OBJECTIVES OF STUDY

- To evaluate the intensity of contamination in and near the TTPL area.
- To implement a best remedial measure for the soil contamination using environment friendly reagents.

III. MATERIALS USED

A. Soil

The soil sample selected for the study was collected from TTPL and from its nearby areas. Sample 1 (S1) was collected from TTPL waste disposing point were solid sludge, metal scraps and small quantity of effluents are dumped. Sample 2 (S2) was collected from Vettucaud. Sample 3 (S3) was collected from Kochuveli. Accurate locations of three samples are mentioned in table I.

TABLE I. DESCRIPTION OF SAMPLING STATIONS

| STATIONS | LOCATIONS | DESCRIPTIONS |
|----------|----------------|--------------|
| S1 | N 08°30'01.9" | Titanium |
| | E 076°54'06.7" | |
| S2 | N 08°29'39.7" | Vettucaud |
| | E 076°54'05.6" | |
| S3 | N 08°30'15.8" | Kochuveli |
| | E 076°53'41.2" | |

Selected soil sample consist of all types of soil particles including gravels, fine sand, medium sand, coarse sand, silt and clay. Correct percentages of soil classifications which are calculated from sieve analysis results are mentioned in table II.

TABLE II. SOIL CLASSIFICATION

| TYPE | PERCENTAGE(%) |
|---------------|---------------|
| Gravel | 18 |
| Fine sand | 12 |
| Medium sand | 42 |
| Coarse sand | 15 |
| Silt and Clay | 13 |

The basic soil properties like specific gravity, liquid limit, plastic limit, moisture content, field density are obtained by using Pyconometer, Casagrande apparatus, Oven dry method, Sand replacement, etc with reference to IS codes. The obtained values are recorded in table III.

TABLE III. SOIL PROPERTIES

| PARAMETERS | TESTS | S1 | S2 | S3 |
|----------------------|----------------------|-----|-----|-----|
| Specific gravity | Pyconometer | 4.8 | 3.5 | 3.3 |
| Liquid limit (%) | Casagrande apparatus | 52 | 48 | 43 |
| Plastic limit (%) | Atterbeg limits | 35 | 32 | 28 |
| Moisture content (%) | Oven dry method | 29 | 25 | 23 |
| Field density(g/cc) | Sand replacement | 3.1 | 3.4 | 2.8 |

B. Tartaric acid

Tartaric acid is represented as $(\text{CHOH.COOH})_2$. Powdered tartaric acid was used for heavy metal removal from soils. About 25g of tartaric acid powder was mixed with 150ml of distilled water. Thus tartaric acid solution was prepared. It is a clear and colourless solution. Contents in tartaric acid are mentioned in table IV.

TABLE IV. TARTARIC ACID CONTENTS

| CONTENT | PERCENTAGE(%) |
|---------------|---------------|
| Assay | 99 |
| Sulphated ash | 0.05 |
| Chloride | 0.002 |
| Sulphate | 0.02 |
| Iron | 0.002 |
| Lead | 0.001 |

C. Citric acid

Its basic equation is $\text{C}(\text{OH})(\text{COOH}).(\text{CH}_2.\text{COOH})_2.\text{H}_2\text{O}$. Powdered citric acid is used for the study. About 25g of citric acid powder was mixed with 150ml distilled water to form citric acid solution.

TABLE V. CITRIC ACID CONTENTS

| CONTENTS | PERCENTAGE (%) |
|---------------|----------------|
| Assay | 99.5 |
| Sulphated ash | 0.1 |
| Sulphate | 0.015 |
| Iron | 0.005 |
| Heavy metals | 0.001 |
| Oxalate | 0.02 |

D. EDTA Solution

EDTA solution is an anti-coagulant solution. The EDTA solution used for remediation is of 5% W/V (Weight/Volume). It is a colourless and clear solution, which was collected from Kanton laboratories.

IV. METHODOLOGY

A. Soil Sample Preparation

The soil samples collected from field are kept on room temperature for drying. The clods seen in the soil sample was broken with a wooden mallet and again kept for drying in room temperature. Organic matters like tree roots, wooden pieces and large size solid wastes are removed from the sample by sieving through 4.75mm sieve. Then the remaining soil samples have been sieved through 2mm sieve and the soil particles passing through 2mm sieve are used for various soil tests.

B. Determination of organic matter

Soil sample weighing 5g was taken in a dry 500ml conical flask. Then a 10ml of potassium dichromate solution was added to the conical flask through a burette and again a 20ml of concentrated sulphuric acid was added to the flask. The mixture was swirled for 1 minute. Then the flask was kept on a heat insulating surface for 30 minutes and allowed it for oxidation. After 30 minutes 200ml of distilled water along with 10 ml of ortho-phosphoric acid added and 1 ml of indicator was also added into it. The mixture was shaken well. Then ferrous sulphate solution was added to the flask from second burette with 0.5ml increment, while the flask was swirled well until the solution colour changes from blue to green. Then again 0.5ml potassium dichromate was added to change the colour again back to blue. Then again ferrous sulphate solution was added drop by drop with continues swirling until solution colour changes from blue to green. The total volume of ferrous sulphate solution used was noted. Then using equations mentioned in IS code 2720 (Part XXII) – 1972 amount of organic matter was determined.

C. Remediation

Remediation of soil sample is done with tartaric acid, citric acid and EDTA solution. 500g of soil sample sieved through 2mm sieve was taken for remediation. 500g of soil samples was mixed with 300ml of tartaric acid, citric acid and EDTA solutions in three different open beakers and kept for one month for remediation. After one month the soil sample was kept for drying in air at room temperature and chemical analysis for each sample was done separately.

D. Chemical analysis

Chemical analysis for each sample was done by referring the standard procedures from IS codes and there results are calculated using the equations from IS codes for soil analysis.

V. RESULTS AND DISCUSSIONS

Chemical characteristics of soil samples from three different stations around the TTPL industry was mentioned in Table VI. A series of parameters like pH, Cd content, Cu content, CEC, organic matter, sulphates, nitrates, etc are determined using various tests. While comparing the values of these parameters obtained from three different stations like S1, S2 and S3 showed that the contamination concentration was high at station 1 that is at S1 which is the sample collected TTPL industrial area. As distance increases from the industry contamination intensity reduces. This study concluded that TTPL industry at Kochuveli is polluting the area around it in large concentrations, also heavy metal contents in the soil at TTPL industry is high.

TABLE VI. CHEMICAL CHARACTERISTICS OF SOILS IN THE STUDY AREA

| PARAMETERS | S1 | S2 | S3 |
|--------------------------|--------|--------|--------|
| pH | 5.2 | 6.1 | 6.3 |
| Cadmium, Cd (mg/Kg) | 3.9 | 2.5 | 1.6 |
| Copper, Cu (mg/Kg) | 41.4 | 18.2 | 20.1 |
| Lead, Pb (mg/Kg) | 57.3 | 32.1 | 28.3 |
| Zinc, Zn (mg/Kg) | 208 | 118 | 107 |
| CEC (cmol/Kg) | 16.4 | 13.2 | 10.1 |
| Conductivity(mS) | 0.15 | 0.08 | 0.13 |
| Chlorides(mg/L) | 58.4 | 49.4 | 49.1 |
| Organic Carbon(%) | 0.72 | 0.35 | 0.81 |
| Organic matter(%) | 1.0 | 0.51 | 1.40 |
| Total nitrogen (mg/g) | 1.13 | 0.3 | 0.8 |
| Sulphates (mg/g) | 0.15 | 0.08 | 0.06 |
| Nitrates (mg/g) | 0.0019 | 0.0023 | 0.0017 |
| Phosphates (mg/g) | 0.012 | 0.044 | 0.038 |
| Sodium (mg/g) | 0.72 | 1.3 | 0.98 |
| Potassium (mg/g) | 0.14 | 0.45 | 0.41 |
| Calcium (mg/100g) | 24.03 | 15.02 | 18.04 |
| Magnesium(mg/100g) | 0.034 | 0.031 | 0.04 |
| Total phosphorous (mg/g) | 0.61 | 0.29 | 1.8 |

Note: CEC – Cation Exchange Capacity

Soil Characteristics of the remediated soil at station 1 is recorded in table VII. Since the soil at S1 contains high concentrations of contamination it was taken for remediation process. Environmental friendly chemicals are taken for remediation. Thus the study resulted that soils mixed with tartaric acid has quick reactions with the contaminants in the soil and it reduced the contents of heavy metals in soils other than citric acid and EDTA solutions. But citric acid and EDTA are also good reagents for heavy metal remediation from soil. These reagents have changed the values of pH of soils from acidic state to neutral state with a remediation period of one month.

TABLE VII. PHYSICAL AND CHEMICAL CHARACTERISTICS OF REMEDIATED SOIL FOR S1 AFTER ONE MONTH

| PARAMETER | USING TARTARIC ACID | USING CITRIC ACID | USING EDTA SOLUTION |
|---------------------|---------------------|-------------------|---------------------|
| Specific gravity | 2.6 | 2.4 | 2.7 |
| Organic matter (%) | 1.8 | 0.81 | 1.2 |
| Cadmium, Cd (mg/Kg) | 2.1 | 3.7 | 4.1 |
| Lead, Pb (mg/Kg) | 38.2 | 40.1 | 37.3 |
| Copper, Cu (mg/Kg) | 28.6 | 32.5 | 30.2 |
| Zinc, Zn (mg/Kg) | 98.3 | 112 | 145 |
| pH | 6.7 | 6.3 | 6.8 |

VI. CONCLUSIONS

- The results obtained in this study showed that TTPL industry is causing high concentrations of heavy metal contamination in its area.
- Contamination causing from the TTPL area is spreading to the nearby soils also, which will cause various health and environmental problems in future.
- The TTPL industry is spreading the contamination to the nearby aquatic lives also by discharging acidic effluents to the nearby sea.
- The remediation study recorded that the chemicals used for HM remediation is environmental friendly.
- Tartaric acid is the best reagent among the selected three reagents for HM remediation.
- Contamination intensity reduces as distance from the industry increases.

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