

Geo-Chemical Exploration of Granite Mining Waste Using XRD, SEM/EDX and AAS Analysis

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ABSTRACT: *The purpose of the study was to investigate the mineralogical and Heavy Metals (HMs) present in the granite mining soils in Chimakurthy, India. The mineral exploration of mining soils were identified by X-Ray Diffractometer (XRD) pattern analysis. However, the morphological features and quantitative HMs were detected by Scanning Electron Microscopy/Energy Dispersed Spectroscopy (SEM/EDS). The relative concentrations of HMs measured by Atomic Absorption Spectrometry (AAS). In this study, the major minerals were identified as Quartz, Albite, Anorthite, K-Feldspars, Hornblende, Muscovite, Annite, Lepidolite, Illite, Clintonite, Enstatite, Ferrosilite, Kaolinite, Kyanite, Augite, and Phlogopite. Moreover, the presence of six HMs such as Chromium (Cr), Cobalt (Co), Nickel (Ni), Copper (Cu), Zinc (Zn) and Manganese (Mn), and their relative concentrations were measured. The concentrations of HMs in three groups of mining soils were in the range of Cr: 149-177 mg/kg (>100), for Co: 128-175 mg/kg (>50), for Ni: 166-204 mg/kg (>50), for Cu: 288-363 mg/kg (>100), for Zn: 433-548 mg/kg (>200) and for Mn: 714-769 mg/kg (<2000) as compared with maximum permissible levels set by standard organizations (WHO/FAO) limits. The results demonstrated that the HMs concentrations in mining soils were exceeded WHO/FAO limits except for Mn. The study is useful for assessment of environmental impact due to excessive deposition of mineral waste and assessment of the quality of investigated granites based on their mineralogical aspect, particularly in the production of granite stones.*

KEYWORDS: *Granite; Minerals; Heavy metals; XRD, SEM; AAS.*

INTRODUCTION

A large quantity of granite waste generated and accumulated at overburden (OB) dumps in the granite mining industry. The OB dumps are the most of possibly hazardous Heavy Metals (HMs) such as lead (Pb), arsenic (As), cadmium (Cd), zinc (Zn), copper (Cu) manganese (Mn), etc., which may have affected the local environment. Therefore, the physiochemical characterization for such contaminated soils are necessary and useful in the effective mitigation of toxic trace elements to improve

the environmental quality [1,2]. The granite stones are used in the construction of buildings, allied construction industry and decorative purposes, the construction of bridges, roads, interior/exterior of household walls and floor tiles for past decades [3].

The potential toxic metals usually are in polluted soils and could be accumulated into the human body via soil o crop to food chain or bioaccumulation or bio-magnification [4,5]. Generally, HMs existed in water

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bodies, soil source, sediment zones, aerosol, living species and that they have both natural and man-made activities [6].

Human or animal exposure to HM pollutants could be caused neurons-disorder, renal failure, cardiovascular complications and reproductive inhibition[7]. The concentrations of heavy metals and radio nucleotides of mining areas depend upon on geology and chemistry, and some of raw minerals usually exist in elevated concentrations of their own natural radioactivity [8]. In case of arsenic is a well-known toxin and carcinogen. It could be found in numerous geochemical forms, that vary in their bio-accessibility [9,10], since it's one amongst the foremost hazardous metal and affecting several countries in the world [11]. In case of radioactive toxic heavy metals like uranium, barium, caesium, radium, etc., even in small concentrations in rock beds, and soil origin, released into the environment due to numerous activities by means of mining, milling, and processing of metal ores. The mining sites may require long-term management and decontamination studies for further use, or reduce the risk to the public health and to the environment. The characterization, evaluation, and distribution were essential for the speciation of HMs and radio nucleotides within the soil [12]. Therefore, the chemical characterization for such contaminated soils are necessary and useful in the effective removal of toxic metals in order to improve environmental quality. Recently, many characterization studies were performed to assess the environmental impact and risk of mining and metallurgy industries based on their geochemical content and concentrations. The sequential acid digestion process was effectively used for determining HM content in the mining and tailing dumps, industrial waste disposal, municipal waste, sea beds, marine sediments and contaminated soils [13].

The knowledge of the physicochemical properties of mining soils is important to optimize its exploitation and useful for assessing appropriate damage to the environment due to excessive deposition of mineral waste. The study is useful to develop the strategies to mitigate environmental pollution during mining and excavation process.

In the present study, the granite samples obtained from a deposit site (mineral bench site, stock yard/mineral processing site and overburden dump yard) in Chimakurthy in Andhra Pradesh, India. The study

is divided into two sections. The first section focussed on experimental characterization of physiochemical. Subsequent section focussed on exploration of minerals, microstructure analysis by means of surface morphology and characterization of heavy metal content.

EXPERIMENTAL SECTION

Study area and soil sampling

The granite mining waste and agricultural soil samples have been collected from a mining and mineral extraction industry in Chimakurthy, Andhra Pradesh, India at coordinates: 15°34'0¹¹N, 15°36'0¹¹N, 79°48'0¹¹E, 79°50'0¹¹E. The study area and collection of soil samples were shown in Figs. 1 and 2. Locally, the granite is a black galaxy in physical form, geologically it is called *Gabbroic anorthosite* [14]. It is originated from igneous gabbro rock and Bronzite speck with Orthopyroxene mineral group [15]. The granite mining industrial area has a surface of 5 km², about 50 mining quarries are situated in Chimakurthy, where 20 surface soil samples (5-10 cm depth) were collected from three locations of mineral bench site, stock yard/mineral processing site and dump yard, using random sampling method. However, sequential sampling method was used to collect the agricultural soils in the vicinity of mining quarries for comparison of physiochemical properties between granite and agricultural soil samples.

Physiochemical characterization

Sieve analysis performed for the collected samples through a series of 4.75-0.002 mm mesh nylon fibre sieves by means of removal of any vegetation, large material, and fragments. Finally, soil sub-samples were homogenized well and kept in zip plastic bags at ambient conditions for further study [2,16,17]. The present study for chemical characterization, soil pH, redox potential, electrical conductivity, Total Dissolved Solids (TDS), zeta potential, moisture, porosity, organic and inorganic content were determined using standard protocols [9,11,18]. Soil pH and redox potential readings were recorded with a digital pH meter of glass electrode in a uniform suspension of soil with deionized distilled water in the ratio of 1:2.5 using Digital P^H meter MK VI, electrical conductivity, TDS were measured for the same extract diluted in the ratio of 1:5 using Systronics Conductivity TDS meter 308. Soils moisture determined by drying

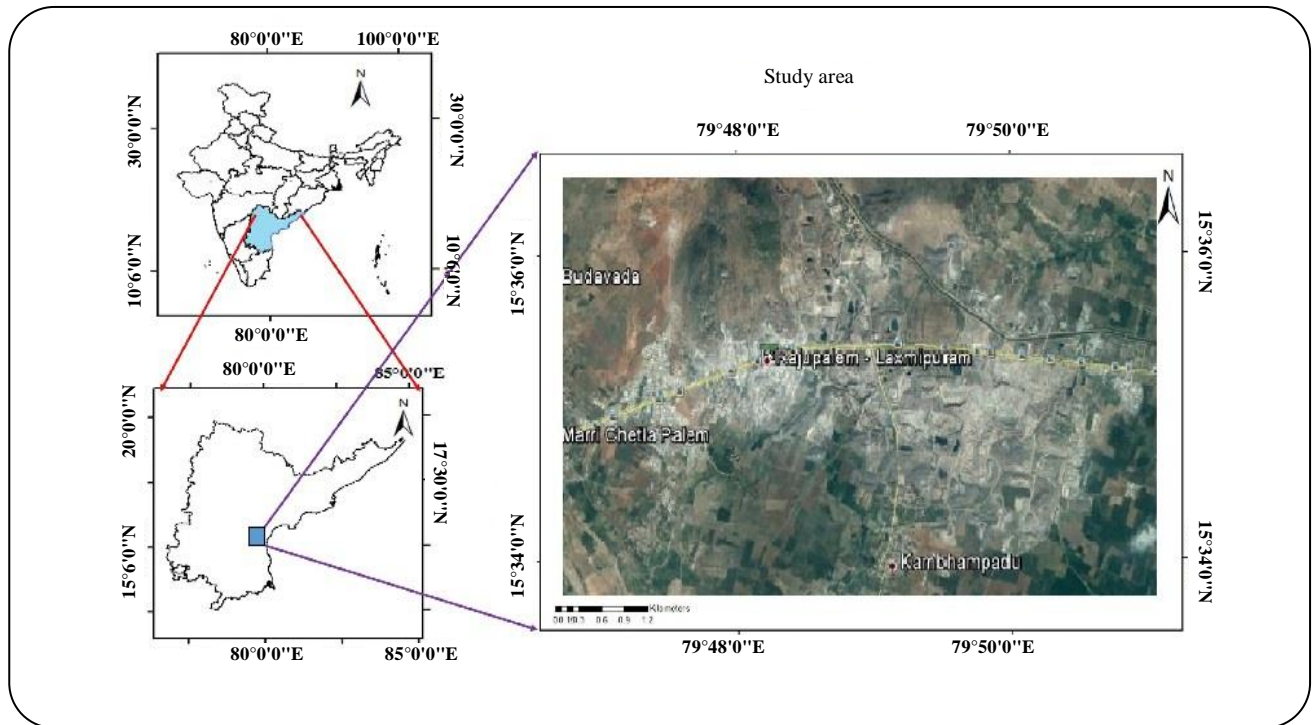


Fig. 1: The study area for collection of granite and agricultural soil samples.



Fig. 2: Soil sampling from mineral bench, stock yard, dump yard and agricultural land.

method using *Box furnace* at 125 °C for overnight. Finally, the organic and inorganic matter were determined by ignition method at 550 °C weight loss, in Box furnace for four hours using INDFURR Superheat furnaces controller [19].

Zeta potential (ζ)

The zeta potential (ζ) of the granite and agricultural farm soils were measured using zeta potential analyser (90 Plus Particle Size Analyser, Brookhaven Instruments Corporation, NY, USA, using Zeta Plus software). Zeta-potential is a dominating factor of a solid surface, which controls the magnitude, direction and movement of soli particles in dispersed liquid media under effect of known electric potential [20,21]. It can be used to characterize the nature of the electrostatic potential around the particle surface by mixing an aliquot of the sample with 0.001M potassium chloride (KCl) solution prior to analysis [22,23].

X-Ray Diffractometer (XRD)

The Debye-Scherrer-X-ray powder method was used to investigate the mineral composition of the granite mining waste and agricultural soil samples (BRUKER D8 Advance XRD machine). The XRD patterns for all soil-sub samples were taken with DIFFRAC Plus XRD software and set by the parameters such as Cu K α radiation at 1.56 Å, Ni-filter, lamp voltage at 40 kV, lamp current at 40 mA, 0.02° per step of registration, scan speed 1s per step, scanning rate 1° per minute [24–27]. Total scanning time was 40 minutes per sample and data recorded from 20 to 60° for granite clay samples.

Scanning Electron Microscopy followed by Energy Dispersed Spectroscopy (SEM-EDS)

Quantitative elementary analysis of granite and agricultural soil samples was characterized by SEM-EDX instrument (X-act, ZEISS, Oxford instruments, United Kingdom). The morphological features of particle microstructure were evaluated by SEM. Dried soil samples were coated with fine carbon layers to improve the secondary electron signal to enable or improve the images of samples under the scanning electron microscopy. Finally, the quantitate elementary analysis has been investigated with Aztec Energy EDS Software at an electrical field 10 keV for characterization of

metals, heavy metals, metalloids and any traces elements of radio nuclides [2,28].

Atomic Absorption Spectrometry (AAS)

Several studies have been determined the concentration of Heavy Metals (HMs) associated with contaminated soils and water by using Atomic Absorption Spectrometry (AAS), Inductively Coupled Plasma Optical emission Spectrometer (ICP-OES) and inductively coupled plasma-optical emission spectroscopy (ICP-AES) techniques [29-32]. Numerous studies used the flame type Atomic Absorption Spectrometry (AAS) in the measurement of HMs concentrations [33]. Representative soil sub-samples of fine powder one gram was weighed accurately and digested with acids (20 mL of HCl, HNO₃) and heated at 50°C over hot plate chamber for 30 minutes. Then, diluted with 100 mL deionised distilled water to acid digested samples and simultaneously filtered through 42 Whatman filter paper [34]. For chemical characterization, the liquid extracts were subjected to identify the concentration of HMs by means of AAS using Varian AA110 spectrophotometer. The process steps are involved in the acid digestion process is shown in Fig. 3.

Statistical analysis

In this study, we determined the mean, standard deviation, and standard error mean within the group of the soil samples. We applied simple statistical analysis to find the significant concentration of i^{th} HM within the group for all soil samples. The following formulae (Eqs. (1-3)) used for statistical analysis [35, 36]:

$$\mu = \frac{\sum x_i}{N} \quad (1)$$

$$\sigma = \sqrt{\frac{\sum (x_i - \mu)^2}{(N-1)}} \quad (2)$$

$$\sigma_{\mu} = \frac{\sigma}{\sqrt{N}} = \sqrt{\frac{\sum (x_i - \mu)^2}{N(N-1)}} \quad (3)$$

Where, x_i is the concentration of i^{th} HM, μ the mean of the concentration of i^{th} HM in the group, N is the sample size, σ is the standard deviation and σ_{μ} is the standard error mean (SEM), In this study, we considered the error

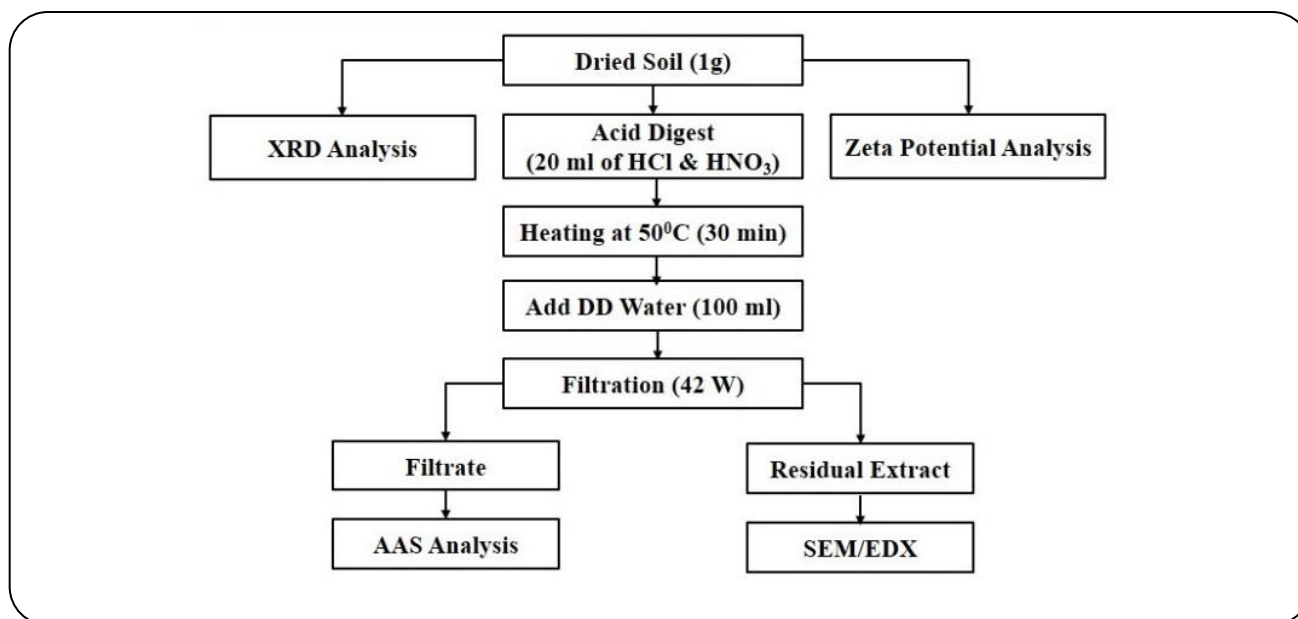


Fig. 3: The major steps involved in the acid digestion process of metals.

parameter ($p < 0.05$) was the more significant value of ith HM within the group.

RESULTS AND DISCUSSION

Physiochemical characteristics

The present study for physicochemical characterization, soil texture analysis, porosity, soil pH, Electrical Conductivity (EC), Redox Potential, Total Dissolved Solids (TDS), moisture, organic matter, inorganic matter, and zeta potential were determined using standard protocols. The physiochemical characteristics of four groups of soil samples were briefly discussed here and the data was reported in Table 1.

Soil texture analysis

In the mining soil samples of study area with percentages of gravel, sand, silt and clay ranges from (33% to 36%), (36% to 38%), (13% to 14%) and (11.5% to 14.2%) with the average percentages of 34.5%, 37%, 13.5% and 13% respectively. So the main texture of soil of the study area is gravel and sandy type, which is not best for green vegetation, whereas agricultural soil is sandy and silt loam type.

Porosity

Porosity is a good indication of the soil quality to know the permeability of water through pores of soil surface. It is measured of the soil samples using

permeability method. The porosity of the mining soils showed in the range of 0.38-0.45 with an average of 0.4, which is moderate to the permeability of the water through the soil, whereas, in case of agricultural soils have more porosity (0.52) due to presence of more organic and moisture content.

Soil pH

Soil pH is an important index used to measure the acidity and alkalinity of the soil and it provides a good identification of the soil chemical nature. At higher pH is usually found to be more alkalinity and lower pH indicates the more acidic. In this study, pH of the mining soil samples were found to be higher at 9.5-9.8 due to presences of alkali earth metals, alkali metals and the salts of metal hydroxides. The desired pH for good vegetation ranges from 5.5-6.8, whereas agricultural soil was found the slightly alkaline in nature with pH of 8.3, it might be the migration of mining soil species to nearby agricultural lands.

Electrical Conductivity (EC)

Electrical Conductivity (EC) measures the amount of electrical current a dissolved material in an aqueous solution can carry or its ability to carry a current. It can be measured in the units of Siemens per meter (S/m) or micro-Siemens/ TDS 640ppm scale ($\mu\text{S}/\text{ppm}$). It is the most common measurement of soil salinity. It is well

Table 1: Physiochemical characterization of mining and agricultural soils.

Soil characteristics		Mineral bench site	Stock yard	Dump yard	Agri. Land	Method
Gravel (>4.75 mm) (%)		33.25	34.70	36	12	Sieve analysis
Sand	Coarse (4.75-2.00 mm) (%)	13.92	13.72	12.81	12.97	Sieve analysis
	Medium (2.00-0.425 mm) (%)	13.01	13.22	13.06	14.47	Sieve analysis
	Fine (0.425-0.075 mm) (%)	12.82	10.85	11.91	15.10	Sieve analysis
Silt (0.075-0.002 mm) (%)		12.86	13.99	13.02	31.50	Sieve analysis
Clay (<0.002mm) (%)		14.10	11.48	14.12	12.90	Sieve analysis
Porosity		0.38	0.39	0.44	0.52	Permeability method
pH		9.7	9.5	9.8	8.3	1:2.5 soil/water slurry
Electrical Conductivity(μ S/ppm)		141.49	121.64	147.97	104.56	1:5 soil/water slurry
Redox potential		-179	-151	-181	-78	1:2.5 soil/water slurry
Zeta Potential		-36.1	-33.3	-26.5	-25.3	Electrokinetic method
TDS (mS/ppm)		199.41	136.41	173.18	103.14	1:5 soil/water slurry
Moisture (%)		0.49	0.85	0.92	1.61	Drying method at 125°C
Total Inorganic Matter (%)		98.15	97.14	97.57	93.45	Drying method at 500°C
Total Organic Matter (%)		0.97	1.13	1.44	4.58	Drying method at 500°C

explained that the conductivity 0.2 dS/m (12.8 μ S/ppm) - 0.8 dS/m (51.2 μ S/ppm) is the good for vegetation growth. In this study, we measured the EC of the soil samples by diluting with DD water in the ratio of 1:5 using Systronics Conductivity TDS meter 308. EC of mining soils were in the range of 121-148 μ S/ppm respectively, whereas, in the case of agricultural soil, it was 104.56 μ S/ppm. The more EC values indicate that the mining soils were attributed by excess salts and high level of salinity due to alkali earth metals. In case of agricultural soil was more salinity due to excess fertilization or might be the migration of mining soil species to nearby agricultural lands.

Redox potential

The transfer of electrons between chemical species determines the redox potential of an aqueous solution. It measures the tendency of the solution to either gain or lose electrons by introduction of a new species. A solution with a higher (more positive) reduction potential than the new species will have a tendency to gain electrons from the new species (i.e. to be reduced by oxidizing the new species) and a solution with a lower

(more negative) reduction potential will have a tendency to lose electrons to the new species (i.e. to be oxidized by reducing the new species). The redox potential of mining soils were in the range from -151mV to -181mV, by means of that the soil species (alkali metals, alkali earth metals and heavy metals) undergo loss of electrons and get to be oxidized in the redox reaction, whereas, in case of agricultural soil, redox potential was -78mV by means of that the less oxidized by loss of electrons than mining soils.

Total dissolved solids (TDS)

Total dissolved solids (TDS) measure the amount of inorganic and organic chemicals that dissolved in the water. It can be measured in parts per million mg/L or mS/ppm. In this study, we measured the TDS of the soil samples by diluting with DD water in the ratio of 1:5 using Systronics Conductivity TDS meter 308. TDS of the mining soils varied from 173.18 mS/ppm to 199.41 mS/ppm with an average of 169.7 mS/ppm. The more TDS values indicate that the mining soils were attributed by excess of salts and high level of dissolved minerals than agricultural soil (103 mS/ppm).

Moisture

Moisture content indicates that the amount of water present in the soil. The moisture content of soil can be expressed in percentage. The amount of water stored in the soil is not constant with time, but may vary with time to time. It is crucial for the growth of green vegetation. The moisture content of the mining soils was found to be ranged from 0.49% to 0.92% with an average of 0.75%. The moisture content of the mining soils has lower than agricultural soils (1.61%) due to presence of rocky mass material and sandy type.

Organic and inorganic matter

Soil organic matter is a complex mixture of organic components, ranging from recent plant residues to complex products of transformation processes and including the microbial biomass. It is the key role in the growth of the vegetation and plants. The organic matter of the mining soils was varied between 0.97-1.44 with an average of 1.2%. The organic matter of the mining soils was lower than agricultural soil (4.58%) due to presence of more inorganic content (97.6%) such as silicate minerals, metallic salts, heavy metal complexes, etc., moreover less amount of moisture and humus substances present in the soil.

Zeta potential

From Fig. 4a, b, c, d, shows the zeta potential values of four groups of a) Mining soils, b) Dump soils, c) Mine tailing soils and d) Agricultural soils. The zeta potential values can be used to determine the stability of soil particles by means of interface charged species in liquid dispersed media. In the case of mining and dump soil solutions gave a mean zeta potential values of -36.1 mV and -33.3 mV respectively, these indicate that colloidal stable dispersion of the particles under influence of electrical potential. In case of mine tailing and agricultural soil solutions gave a mean zeta potential values of less negative -26.5 mV and -25.3 mV respectively, these indicate that less colloidal stable dispersion of the particles due to anionic aggregation of particles.

From the acid digestion process, the fine solid extracts are collected and dried for estimating the mineral composition and associated metals for four different group soil sub samples. The dried fine powder samples

were subjected to X-ray diffractometer and pattern data were collected from 20 to 60° for granite powder samples and 20 to 70° for agricultural clay samples. In the present study, the XRD pattern of granite and agricultural soils presented in Fig. 5 and 6. Fig. 5 represent the XRD pattern analysis of four soils (mineral bench, stock yard, dump yard and agricultural soils in the 2θ range from 21° to 32° (numbers indicate the corresponding mineral compounds described in Table 2).

Fig. 6 represent the XRD pattern analysis of four soils (mineral bench, stock yard, dump yard and agricultural soils in the 2θ range from 32° to 45° (numbers indicate the corresponding mineral compounds described in Table 2). From the XRD data pattern analysis, the identified the major minerals are Quartz, Albite, Anorthite, K-Feldspars, Hornblende, Muscovite, Annite, Lepidolite, Illite, Clintonite, Enstatite, Ferrosilite, Kaolinite, Kyanite, Augite and Phlogopite in three groups of granite mining waste soils, whereas, in agricultural soils, the major minerals were identified as High-silica Quartz, Gypsum, Calcite, Magnetite, and Ferrosilite. The mineralogy of Boggalakonda Gabbro granite was studied and reported the almost same minerals [37]. Other studies on geochemical characterization for various types of granite mining soils are also reported same minerals [27, 38–40].

The details of the minerals name, chemical formula, and Joint Committee on Powder Diffraction Standards (JCPDS) identification numbers are provided in Table 2. The sharpness of the pattern with well match peak position and mean intensities that minerals contained in granite soils well crystallized. The results show the highly crystallized minerals are in the range from 26° to 30° (2θ). In the present study, it is observed that the Orthopyroxene group minerals such as Enstatite and Ferrosilite are enriched in *Gabbroic anorthosite* granite mining soils. From Fig. 7, The SEM images (a, b, d, e) and corresponding EDX spectrums (c, f) of Mineral bench soil (+X₁: Mica group-Annite, +X₂: Orthopyroxene group-Enstatite, +X₃: Mica group-Lepidolite, +H: water molecules) and stock yard soil (+X₁: Mica group-Annite, +X₂: Orthopyroxene group-Enstatite, +H: water molecules).

The white/brown portion is associated with Mica group minerals enriched with Annite mineral (+X₁), the black portion is associated with Orthopyroxene group mineral enriched in Enstatite (+X₂), streak white

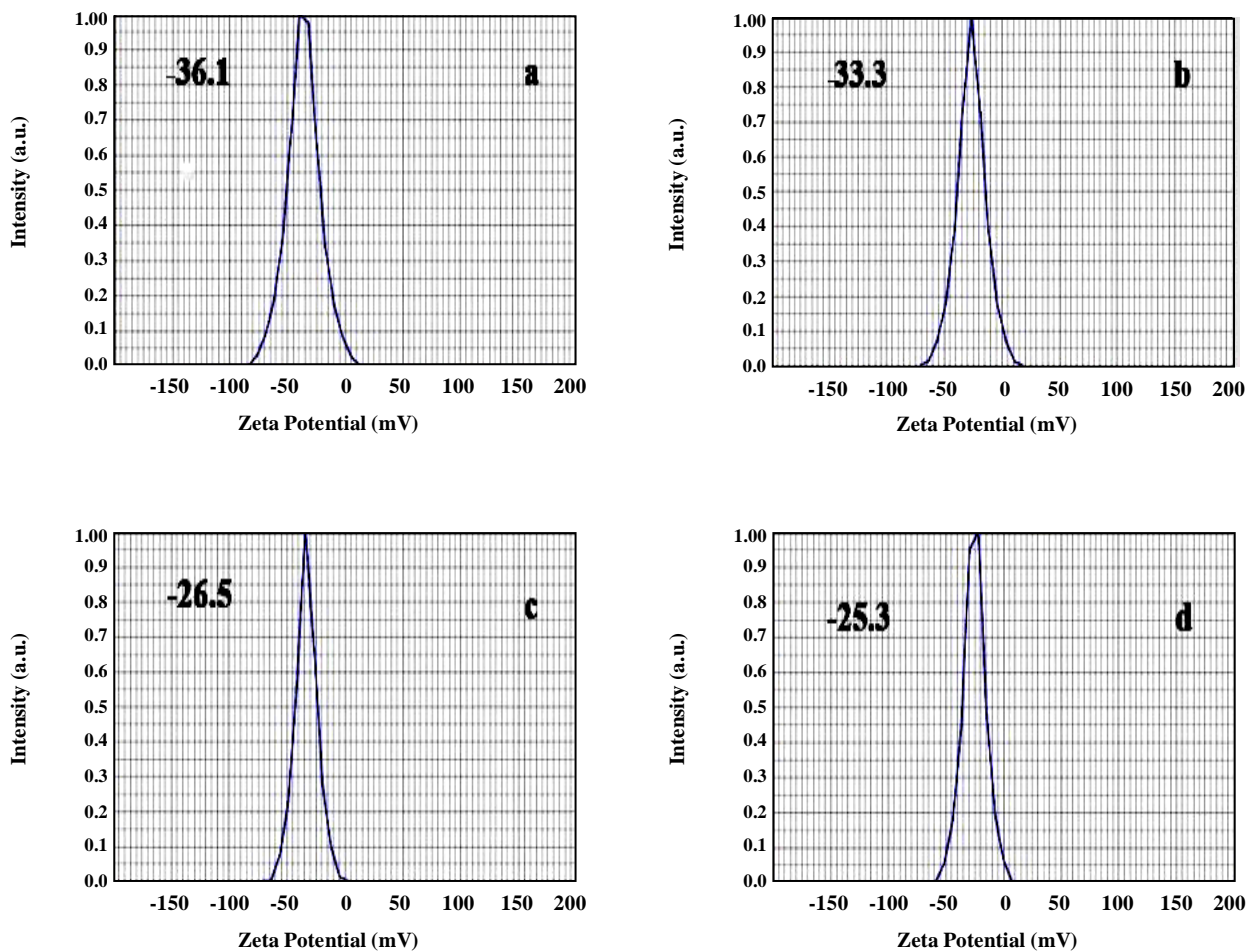


Fig. 4: Zeta potential of a) Mineral bench soil, b) Stock yard soil, c) Dump yard soil, d) Agricultural soil Identification of minerals.

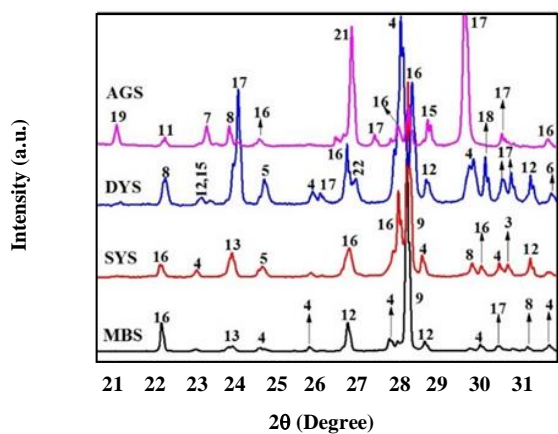


Fig. 5: The XRD pattern analysis of four groups of soils (mineral bench, stock yard, dump yard and agricultural soils) in the 2θ range from 21° to 32° (numbers indicate the corresponding mineral compounds described in Table 2).

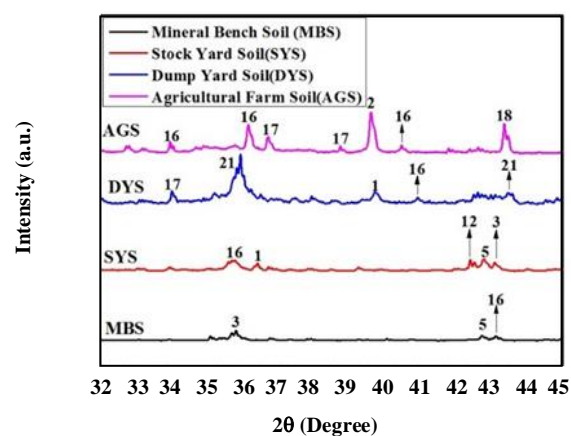


Fig. 6: The XRD pattern analysis of four groups soils (mineral bench, stock yard, dump yard and agricultural soils) in the 2θ range from 32° to 45° (numbers indicate the corresponding mineral compounds described in Table 2).

Table 2: Identification of mineral compounds in granite waste and agricultural soils using XRD pattern analysis.

Peak No.	Mineral Name	Chemical Formula	JCPDS Card No.	Soil Type
1	Quartz	SiO ₂	83-0539	Granite
2	High silica	SiO ₂	87-0703	Agricultural
3	Albite	Na Al Si ₃ O ₈	10-0393	Granite
4	Anorthite	CaAl ₂ Si ₂ O ₈	89-461/62/70/71/72	Granite
5	K-Feldspars	KAlSi ₃ O ₈	19-0931	Granite
6	Hornblende	Ca ₂ (Mg, Fe, Al) ₅ (Al, Si) ₈ O ₂₂ (OH) ₂	21-0149	Granite
7	Clintonite	Ca(Mg, Fe, Al) ₃ (Al, Si) ₄ O ₁₀ (OH) ₂	20-0321	Granite
8	Muscovite	K Al ₂ Si ₃ Al ₁₀ (OH) ₂	07-0032/06-0263	Granite
9	Annite	K(Fe, Mg) ₃ AlSi ₃ O ₁₀ (OH) ₂	02-0045	Granite
10	Phlogopite	K Mg ₃ AlSi ₃ O ₁₀ (F, OH) ₂	10-0495	Granite
11	Kyanite	Al ₂ O ₃ SiO ₂	02-1297	Granite
12	Lepidolite	K Li ₂ Al(Al, Si) ₃ O ₁₀ (F, OH) ₂	85-0389/38-0425	Granite
13	Illite	(K ₂ H ₃ O)Al ₂ Si ₃ AlO ₁₀ (OH) ₂	26-0911	Granite
14	Alamandine	Fe ₃ Al ₂ (SiO ₄) ₃	85-2495	Granite
15	Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	14-0164	Granite
16	Enstatite	Mg ₂ Si ₂ O ₆	86-0430	Granite
17	Ferrosilite	Fe ₂ Si ₂ O ₆	76-0889/91	Granite
18	Augite	Ca(Fe, Mg)Si ₂ O ₆	24-0201	Granite
19	Magnetite	Fe ₃ O ₄	89-6466	Agricultural
20	Calcite	CaCO ₃	87-1863	Agricultural
21	Gypsum	CaSO ₄ 2 H ₂ O	76-1746	Agricultural
22	Zinc sulfide	ZnS	89-2427	Granite

portion represents the mica group of Lepidolite (+X₃) and the surface on the microstructure contains white in colour that represents the moisture content (+H) of soil-sub samples.

From Fig. 8, the SEM images (a, b, d, e) and corresponding EDX spectrums (c, f) of dump yard soil (+X₁: Plagioclase group-Anorthite, +X₂: Orthopyroxene group-Enstatite and Ferrosilite, +H: Water molecules) and Agricultural farm soil (+X₁: Sulfate group-Gypsum, +X₂: Orthopyroxene group-Ferrosilite, +H: water molecules). The white/greyish portion is associated with Plagioclase group mineral enriched with Anorthite (+X₁), the black portion is associated with Orthopyroxene group minerals enriched with Ferrosilite and Enstatite (+X₂) and on the microstructure, the surface contains white in colour,

that represents the water or moisture content (+H) of soil-sub sample. In case of agricultural soils, the white/grey portion represents the sulphate group of Gypsum (+X₁), the black portion represents the Orthopyroxene group-Ferrosilite (+X₂) and the moisture content (+H) shows a surface white in colour on the surface of the microstructures.

Characterization of heavy metals

Concerning heavy metal analysis, SEM-EDX instrument was used to estimate the number of heavy metals present in the representative soil sub-samples of the four areas of mineral bench at mining site, overburden at dump site, mineral processing at dressing/stock yard and agricultural farm area. The presence of the main

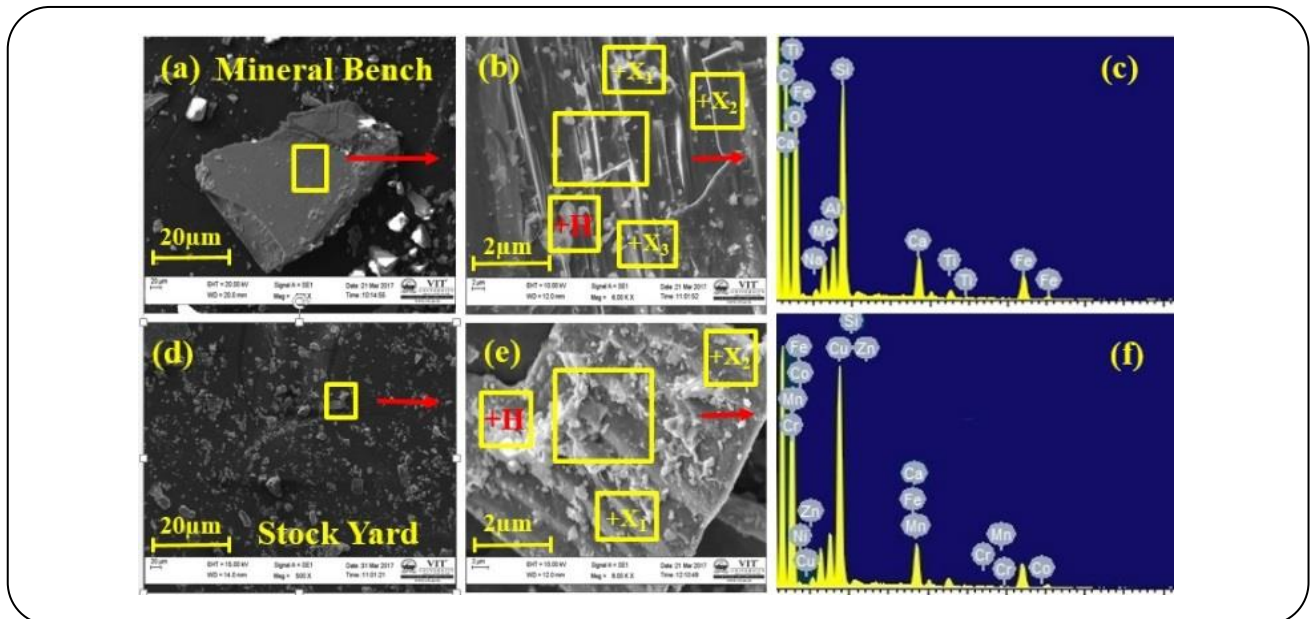


Fig. 7: The SEM images (a, b, d, e) and corresponding EDX spectrums (c, f) of Mineral bench soil (+X₁: Mica group-Annite, +X₂: Orthopyroxene group-Enstatite, +X₃: Mica group-Lepidolite, +H: water molecules) and stock yard soil (+X₁: Mica group-Annite, +X₂: Orthopyroxene group-Enstatite, +H: water molecules).

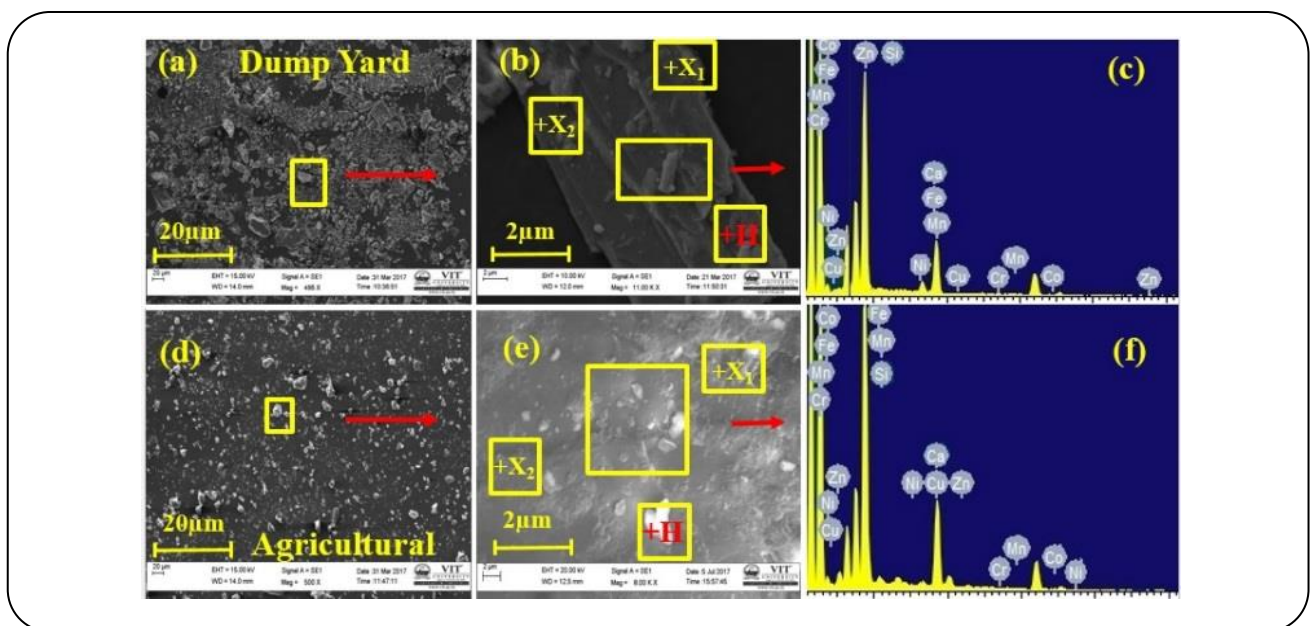


Fig. 8: The SEM images (a, b, d, e) and corresponding EDX spectrums (c, f) of dump yard soil (+X₁: Plagioclase group-Anorthite, +X₂: Orthopyroxene group-Enstatite and Ferrosilite, +H: Water molecules) and Agricultural farm soil (+X₁: Sulfate group-Gypsum, +X₂: Orthopyroxene group-Ferrosilite, +H: water molecules)

six heavy metals and their relative abundances are found, after energy diffraction X-ray spectrometer determination. From Figs. 5 (c, f) and 6 (c, f), the names of the heavy metals were found in EDS spectrum of granite and agricultural samples.

In this study, the heavy metals were identified as chromium (Cr), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn) and manganese (Mn) based on EDX elementary analysis. Kumar *et al.*, (2016), reported the heavy metals in the Gabbro granites and associated ultramafic rocks as

chromium(Cr), cobalt(Co), nickel(Ni), copper(Cu), zinc(Zn), manganese(Mn), gold(Au), silver(Ag) and platinum (Pt) were reported [37]. In other study, the reported heavy metals for *Rosa Porrino-type* granite were vanadium (V), chromium(Cr), nickel(Ni), copper(Cu), zinc(Zn), arsenic(As), selenium(Se), molybdenum(Mo), cadmium(Cd), barium(Ba), mercury(Hg), lead(Pb), manganese (Mn), uranium(U), rubidium (Rb), and strontium (Sr) respectively [41]. The heavy metal content in the present study well agreed with reported in literature for granite soils. The Mica group minerals are the main source of the metals, metalloids and heavy metals for all types of granite materials. However, the abundance and concentrations of metals vary due to various mineralogical, geographical and weather conditions of the granite materials. From AAS analytical study, a perceptible variation in the metal concentration of samples for all four different soils was measured including agricultural land soils.

From the acid digestion process, the liquid extracts are collected and diluted with deionised distilled water for estimating the HMs concentration. The diluted liquid extracts were subjected to identify the concentration of heavy metals by means of Atomic Absorption Spectrometry (AAS) with known concentrations of HMs solutions prepared earlier. From Table 3, The Cr concentration ranged from 157 to 192 mg/kg, the Co from 128 to 175 mg/kg, the Ni from 166 to 204 mg/kg, the Cu from 288 to 363 mg/kg, the Zn from 433 to 548 mg/kg, and the Mn from 714 to 769 mg/kg for three locations of granite mining areas such as mineral bench, dump yard and stock yard. It is observed that the HMs concentration in granite mining soil samples was exceeded the maximum permissible levels set by standard organizations (WHO and FAO) except manganese metal. But the agricultural soils showed the concentrations of heavy metals are at an acceptable level and less than the limits set by WHO/FAO. The maximum allowable limits of heavy metals in soils, water and vegetation have been set and amended by WHO, FAO and other standard guidelines of Europe [42].

Statistical analysis

We calculated the mean, standard deviation, and standard error mean of the *i*th HM concentration values for each group of soil samples using Equations 1-3.

Simple statistical analysis was applied to examine the significant concentrations of HMs in the four groups (mineral bench, stock yard, dump yard, and agricultural soils). All the data were taken as mean \pm standard error mean (SEM) for five replicates from each group. The Cr concentrations 157 ± 0.04 , 192 ± 0.02 and 177 ± 0.04 mg/kg, the Co 149 ± 0.01 , 175 ± 0.01 and 128 ± 0.027 mg/kg, the Ni 166 ± 0.016 , 204 ± 0.011 and 183 ± 0.01 mg/kg, the Cu 287.9 ± 0.02 , 363 ± 0.03 and 315 ± 0.03 mg/kg, the Zn 432.8 ± 0.01 , 507.6 ± 0.026 and 548 ± 0.01 mg/kg, the Mn 714 ± 0.06 , 734 ± 0.052 and 769 ± 0.05 mg/kg for three groups of mining soils. The concentration values of metals would be more significant with less than 0.05 standard error mean value for five replicate. In case of agricultural soils the metal concentrations for the Cr 17.6 ± 0.004 , the Co 10.7 ± 0.01 , the Ni 25.5 ± 0.01 , the Cu 30.4 ± 0.007 , the Zn 33.4 ± 0.01 and the Mn 212 ± 0.02 mg/kg respectively. In addition, six HMs concentrations were found in the order of Mn>Zn>Cu>Ni>Co>Cr for mining and agricultural soils. The statistical data reported in Table 3.

CONCLUSIONS

The granite mining waste soils have caused a long-term impact on the natural ecosystem. Although the range of mining soil texture, pH, redox potential, electrical conductivity, TDS and zeta potential of mining soils have been found more than agricultural soils. Moisture, organic content has been found low and inorganic content has been more as compared to the agricultural soil, which indicated that the deterioration of soil quality. In this study, we identified the twenty two important minerals in granite mining waste including agricultural soils using XRD pattern data analysis. The presence of the main six HMs (Cr, Co, Ni, Cu Zn, and Mn) were identified and their concentrations were measured using EDX and AAS analysis. The statistical analysis was applied to examine the significant concentrations of HMs within the groups (mineral bench, stock yard, dump yard, and agricultural soils) and comparisons were made with WHO/FAO limits. The concentrations of HMs in three groups of mining soils were in the range of Cr: 149-177 mg/kg (>100), for Co: 128-175 mg/kg (>50), for Ni: 166-204 mg/kg (>50), for Cu: 288-363 mg/kg (>100), for Zn: 433-548 mg/kg (>200) and for Mn: 714-769 mg/kg (<2000). The results demonstrated that the HMs

Table 3: Statistical analysis and comparisons with WHO/FAO limits for HM concentrations in four groups of soils.

Element	Mineral bench (mg/kg)	Dump yard (mg/kg)	Stock yard (mg/kg)	AGRI soils (mg/kg)	WHO Limits in soil (mg/kg)	Remarks
Chromium	157±0.04	192±0.02	177±0.04	17.6±0.004	<100	High
Cobalt	149±0.01	175±0.01	128±0.027	10.7±0.01	<50	High
Nickel	166±0.016	204±0.011	183±0.01	25.5±0.01	<50	High
Copper	287.9±0.02	363±0.03	315±0.03	30.4±0.007	<100	High
Zinc	432.8±0.01	507.6±0.026	548±0.01	33.4±0.01	<300	High
Manganese	714±0.06	734±0.052	769±0.05	212±0.02	<2000	Acceptable

concentrations in mining soils were exceeded the maximum permissible levels set by standard organizations (WHO/FAO) except for Mn, and an acceptable level in case of agricultural soils. The order of the heavy metals Mn>Zn>Cu>Ni>Cr>Co found for mining soils on the basis of their relative concentrations.

The knowledge of the physicochemical properties of mining soils are important to optimize its exploitation and useful for assessing appropriate damage to the environment due to excessive deposition of mineral waste and associated heavy metal content. The study is also useful for the assessment of the quality of investigated granites based on their mineralogical aspect, particularly in the production of granite stones.

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