Investigation on industrial area soil from Karaikal, Puducherry State using FT-IR, XRD, SEM and Thermal analyses.

R. Selvaraju[a] ,N. Oumabady Alias Cannane[b*], M. Rajendran[c], G. Thiruppathi[d]

[a]Department of Engg. Physics, Annamalai University, Annamalai Nagar, Tamil Nadu, India
[b]Depatrment of Physics, Bharathiyar College of Engg. & Tech., Karaikal, India
[c]Deparment of Mechanical Engg. KGiSL Institute of Technology, Coimbatore, Tamil Nadu, India
[d]Department of Engg. Physics, Bharathiyar Institute of Engineering for Women, Deviyakurichi, Tamil Nadu, India

---***---

Abstract -FT-IR, XRD, SEM and TG–DTA analyticalstudies have been carried out to investigate the chemical compositions of soil samples. Soil samples were collected from an industrial environment at Karaikal, Union Territory of Pondicherry,South India. FT-IR results indicate that soils have variousmineral compositionnamely, kaolinite, quartz, montmorillonite, aragonite, hematite, feldspar, calcite etc. Mineral identification was confirmed by powder X-ray diffraction patterns in association with JCPDS data. SEM gives an insight of morphological analysis. Thermal analysis techniques are employed for the characterization and assessment of endothermic and exothermic behavior of the soil samples and the results are discussed.

Keywords: Soil, FT-IR, XRD, SEM, TG-DTA and Minerals

1. Introduction

Environmental pollution is an undesirable change in physical, chemical or biological characteristics of air, water or land that may be or will be harmful to human and other life, industrial process, living conditions and cultural assets or may cause wastage of raw material resources [1]. Pollution of water, air and soil environment due to industrial and other waste is one of the problems faced by the developed as well as developing countries [2]. Soil contamination also occurs when chemicals are released due tospill or disposal of effluents by industries. The most significant soil contaminants are hydrocarbons, heavy metals, herbicides, pesticides and chlorinated hydrocarbons. Soil salinization, one of the most common land degradation processes, is a severe environmental hazard [3-5].

Fourier Transform Infrared (FT-IR) absorption spectra of soil sediments contain more information about minerals[6]. It is used by mineralogists and sedimentary petrologists in the aspect of mineralogical application. One of the most important and value added applications of the infrared spectroscopic study is the identification of the minerals in the sediment samples. The most widely present clay mineral in soil or sediments is kaolinite which is simplest of all the clay minerals [7, 8].XRD method is the best one for mineral analysis as it is rapid, cheap, time saving and non-destructive. Powder X-ray diffraction pattern gives more information about minerals present in soil or sedimentary samples [6, 9].Major and minor constituent minerals present in sediment samples collected at the coastal area of Tuna, Gujarat were identified by using FT-IR and XRD technique. The presence of quartz, orthoclase, albite, kaolinte, montmorillonite and calcite was reported [10].Among the various analytical techniques used for the elemental analysis, Scanning Electron Microscopy is highly qualified for the identification and the quantification of different elements in various samples of geological, biological and environmental importance [11-13]. SEM analysis is usually used to provide qualitative chemical analyses. It also can be used to provide quantitative elemental analysis [14-16]. With the help of thermal characteristic reactions such as dehydration, decomposition and transformations, minerals can be identified in soil.

FT-IR is a powerful tool to investigate the chemical composition of unknown minerals. Mineralogical investigations were generally performed by using X-ray diffraction (XRD), often in combination with other analytical techniques, like SEM and TG-DTA [17].It is made clear that the FT-IR and XRD analysis of soil samples are usually employed for identification ofmineral composition such as quartz, kaolinite, hematite, calcite, aragonite, feldspar, montmorillonite and organic matter. In the present paper, we have reported the spectroscopic investigation as done with FT-IR, XRD, SEMand TG-DTA methodson soils collected from Karaikal and such investigationprovides good information for the mineral composition and status of soil pollution in the industrial area.

2. Materials and Methods

Thirty six soil samples were collected at 12 different sites using standard procedures from four canals flowing through an industrial area, located near Karaikal Port at Karaikal; Pondicherry State, India.Geographic coordinates: 10.8678° N, 79.8283° E. Each site is separated by a distance of 100 m

approximately. Soil samples were collected during the summer season. In each site, three samples were collected; one at the surface level, second at 15 cm depth from the surface and the third at 30 cm depth. All 36 samples were dried at room temperature in open air for two days, stored in black polythene bags and ground well into a fine powder by using an agate mortar. Out of the 36 samples, nine samples drawn from Second canal (S_{10}, S_{11}.....S_{18})were selected for the present study. FT-IR spectra are recorded using KBr pellet technique in the region of 4000–400 cm^{-1} using NICOLT AVATAR 360 Model FT-IR Spectrometer available at Department of Chemistry, Annamalai University, Tamil Nadu, South India.

The XRD analysis was performed with Model XD-D1 Shimadzu Diffractometer,available at Solid State Structural and Chemistry Unit, Indian Institute of Science, Bengaluru, India and operating at 30 kV and 30 mA with CuKα radiation of λ= 1.54Å. Microphotographs of the samples were recorded with a JEOL JSM 5610 LV SEM. Thermogravimetric analyses were done under nitrogen atmosphere at a heating rate of 8°C min^{-1} in Pt cell under standard gas flow with TA Instruments Model SDT Q600 apparatus, available at Centralised Instrumentation and Service Laboratory, Annamalai University, Chidambaram, India. The temperature range is from 25°C to 800°C in up scan direction.

3. Results and discussion

3.1. FT-IR analysis

FT-IR spectra of soil samples drawn from Second canal (at the surface layer, at 15 cm depth and at 30 cm depth) are qualitatively analyzed[18, 19]. A representative FT-IR data and spectrum of soil at Second canal is shown in Table.1 and Fig. 1. Spectra of soil samples indicated the compositions of quartz, kaolinite, hematite, calcite, aragonite, feldspar, montmorillonite, illite and organic matter. In the Second canal, soil exhibited specific absorption peaks at 3431 cm⁻¹, 2922 cm⁻¹, 1624 cm⁻¹, 1033 cm⁻¹, 779 cm⁻¹, 692 cm⁻¹, 521 cm⁻¹ and 464 cm⁻¹. It is found that soil contained predominant amount for kaolinite and quartz and moderate amount of hematite and montmorillonite.
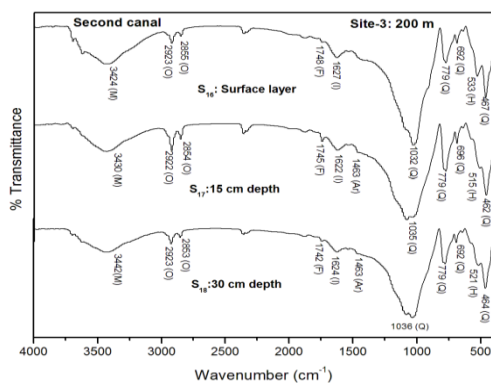

Fig.1.

Table 1Absorption bands and corresponding minerals from FT-IR spectra of soil samples.

S.No.	Absorption bands (cm^{-1})	Mineral name
1.	3627,1033and 915	kaolinite
2.	1879,1084, 779, 692 and 464	quartz
3.	2922	organic matter
4.	521	hematite
5.	3431	montmorillonite
6.	1742 and 641	feldspar
7.	1624	illite
8.	1463	aroganite
9.	1430	calcite

The presence of kaolinite in soil samples of Second canal is supported by O–H stretching of inner hydroxyl group bands between 3700–3600 cm⁻¹ regions. Strong band at 3627 cm⁻¹ indicate the possibility of the hydroxyl linkage. The presence of quartz in the samples can be explained by Si–O–Si asymmetrical bending vibrations in the range   462–467 cm⁻¹[9, 20].

Strong absorption band observed at 533 cm⁻¹ is due to stretching vibration of Si-O–Al (or) $Fe_2O_3$and this supportsthe presence of hematite [6, 20]. The strong absorption bands observed at 692 cm⁻¹ and 779 cm⁻¹are due to Si–O symmetrical stretching vibrations of quartz. The broad absorption band is observed at 1032 cm⁻¹ and it belongs to Si–O stretching of kaolinite (clay mineral) [6, 20, 21]. Very weak absorption band observed at 1463 cm⁻¹ is due toH–O–H stretching and it supportsin the presence of aragonite [6]. Vibration observed at 1624 cm⁻¹ indicates the possibility of the presence of illite [9].

3.2. XRD analysis

X-ray diffraction study is used to bring out the mineralogical composition and to analyze the crystalline nature of the minerals. Select representative XRD data and patterns of soil samples ofSecond canal are shown in Table 2 and Fig. 2.From the XRD analysis and by comparing with JCPDS data, minerals like, quartz (PDF 85-1053), kaolinite (PDF 89-5695), hematite (PDF 89-2810), calcite (PDF 87-1863), aragonite (PDF 76-0606), feldspar (PDF 70-2121) and illite (PDF 29-1496) were identified [22, 23].
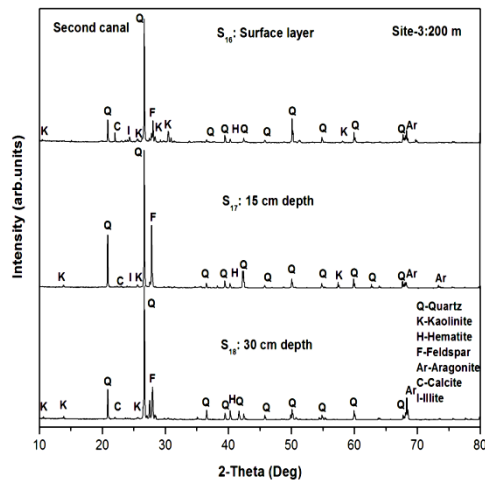
Fig. 2.

Table 2 - X-ray diffraction data of soil samples

Observed value 2θ	Standard value 2θ	Mineral	JCPDS No.
10.551	10.706	kaolinite	02-0105
20.984	20.960	quartz	85.1780
22.156	22.301	calcite	87-1863
24.429	24.318	illite	29-1496
25.657	25.765	kaolinite	02-0105
26.589	26.696	quartz	85-0865
27.845	27.702	feldspar	70-2121
28.057	28.251	kaolinite	83-0971
30.476	30.374	kaolinite	84-0710
36.472	36.551	quartz	85-1053
39.569	39.475	quartz	85-1053
40.482	40.321	hematite	88-2359
42.511	42.575	quartz	85-0865
45.818	45.898	quartz	85-1053
50.26	50.245	quartz	85-0865
55.024	55.327	quartz	85-1054
58.278	58.353	kaolinite	03-0052
59.965	59.958	quartz	85-1054
67.909	67.973	aragonite	76-0606
68.507	68.685	aragonite	76-0606

The observed XRD patterns indicate quartz and kaolinite as the major constituents and other minerals as the minor constituents and they are known to crystallize in hexagonal and anorthic system [9, 19]. Further, the presence of the above minerals in the soil samples is confirmed by FT-IR study [18].

3.3. SEM Morphology

The morphological appearance of soil samples, S_{16}, S_{17} and S_{18} of first site in Second canal is shown in Fig.3 (a-c). The results show that quartz, kaolinite, calcite, illite, hematite and feldspar are present. The morphology gives a sunflower like appearance of globular aggregates (Fig. 3a) and a similar aggregate morphology was reported earlier [24-26]. The observed image reveals isolated over-grown quartz crystals (Fig. 3b). The image displayed rectangular platelets, prismatic and irregularly shaped granular crystalline materials [13, 27, 28]. The agglomeration of finer particles by cementing effect is seen for hematite or amorphous ferrous hydroxides (Fig. 3c).
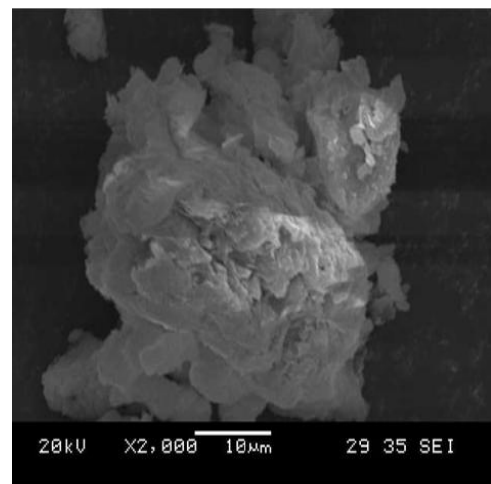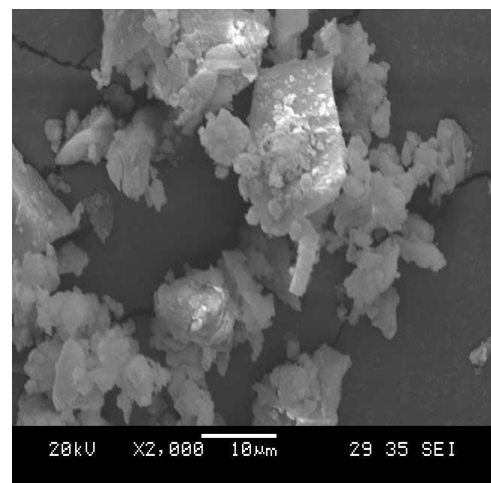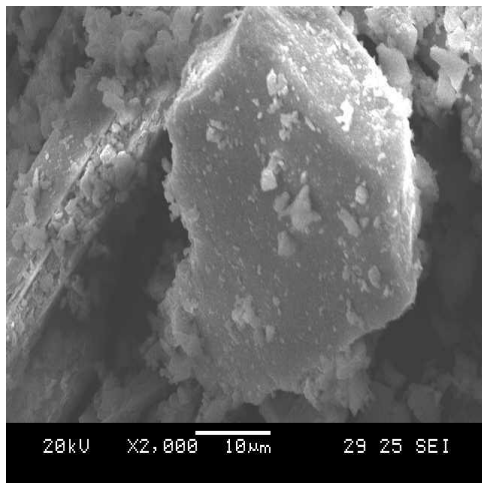

Fig. 3a

Fig. 3b

Fig. 3c

3.4. Thermal analysis

TGA-DTA is very useful, especially in the case of clay group characterization. The TG-DTA curves are shown in Fig. 4 for the samples S_{16} and S_{18}. In TG-DTA curves, weight loss in two stages may be attributed; the decomposition of water at first stage and dehydroxylation of kaolinite in the second stage [20, 29]. Calcite decomposes in the temperature range 700-800°C [30]. The mass losses of first, second and third steps were 0.4%, 0.6% for S_{16} and 1.4%, 1% for S_{18}. These peaks appeared in the range from 180°C to 580°C and are associated with organic matter decomposition and this transformation is partially hidden by the kaolinite dehydroxylation[31]. The DTA curve shows endothermic peaks at 253°C, exothermic peak at 238°C, 500°C for S_{16} and 247°C, 600°C for S_{18} and they are associated with organic matter decomposition and such transformations are partially hidden by the kaolinite dehydroxylation. There is no further weight loss above 850°C. The FT-IR and XRD results are well agreement with TGA and DTA results.
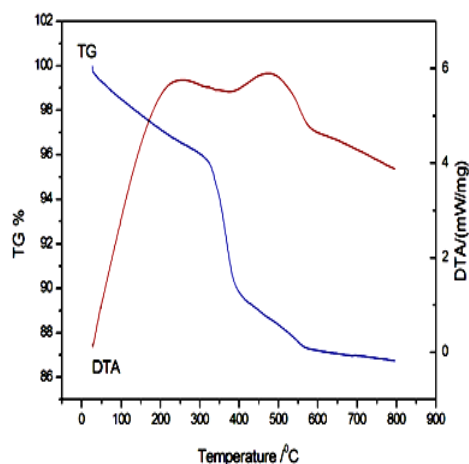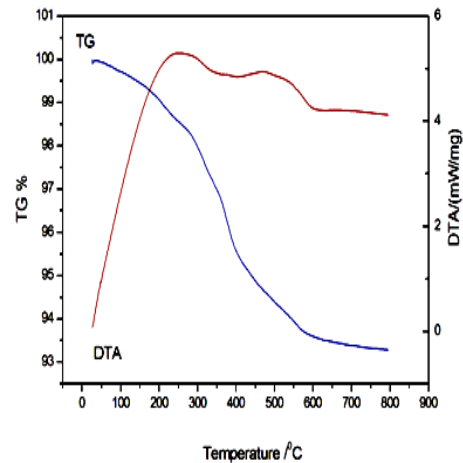

Fig. 4a

Fig. 4b

4. Conclusion

The techniques FT-IR, XRD, SEMand TG–DTA providedetails onmineralogical, morphological characterizations and dehydroxylationof soil samples. The results indicate that soils have different mineral compositions namely, kaolinite, quartz, montmorillonite, aragonite, hematite, feldspar and calcite. The results obtained from different supplementaryanalytical techniques showed good agreement with one another. The microstructure analyses were performed. Thermal analysis results showed the characteristic peaks for dehydration and decomposition of organic material in soil up to 800 °C. The results of spectroscopic studiesreveal that the industrial area soil is asubject of contamination by minerals and metals released from industrial waste. The increase of minerals and heavy metals in canals can make soil quality poorer; reduce crop yield and the quality of agricultural products.

References

[1] D.K. Asthana, M. Asthana, Environment: Problems and Solutions, S. Chand and Company Ltd, Ram Nagar, New Delhi, 2003, 205.

[2] D. Prasanthan, T.V. Nayar, Pollut. Res. 19 (2000) 475–479.

[3] W.Y. Ling, G. Peng, Z.Z. Liang, Pedosphere, 20 (2010) 378–388.

[4] R.L. Dehaan, G.R. Taylor, Remote Sens. Environ. 80 (2002) 406–417.

[5] G.I. Metternichtand, J.A. Zinck, Remote Sens. Environ. 85 (2003) 1–20.

[6] V. Ramasamy, P. Rajkumar, V. Ponnusamy, Bull. Pure Appl. Sci. 25 (2006) 49–55.

[7] S.J. Chapman, C.D. Campbell, A.R. Fraser, G. Puri, Soil Biol. Biochem. 33 (2001) 1193–1200.

[8]   J. Madejova, Anal. Chem. 25 (2003) 1169–1174.

[9]   P.S. Nayak, B.K. Singh, Bull. Mater. Sci. 30 (2007) 235–238.

[10]   R. Ravisankar, G. Senthilkumar, S. Kiruba, A. Chandrasekaran, P.P. Jebakumar, Indian J. Sci. Tech. 3 (2010) 774-780.

[11]   Z.B. Shi, L.Y. Shao, T.P. Jones, A.G. Whittaker, S.L. Lu, K.A. Bérube, R.J. Richards,Atmosphe. Environ. 37 (2003) 4097–4108.

[12]   W. Li, L.Y. Shao, R. Shen, Z. Wang, S. Yang,U. Tang, J. Environ. Sci. 22(2010) 561–569.

[13]   T. Pachauri, V. Singla, A. Satsangi, A. Lakhani,K.M. Kumari, Aerosol and Air Quality Res. 13 (2013) 523–536.

[14]   K. Pye, D. Croft, Forensic Sci. Int. 165 (2006) 52-63.

[15]   S.M. Haley, A.D. Tappin, P.R. Bond, M.F. Fitzsimons, Environ. Chem.Lett. 4 (2006) 235-238.

[16]   D. Beltrami, D. Calestani, M. Maffini, M. Suman, B. Melegari, A. Zappettini, L. Zanotti, U. Casellato, M. Careri, A. Mangia, Analyt. Bioanalyt. Chem. 401 (2011) 1401-1409.]

[17]   R. Ravisankar, G. Raja Annamalai, A. Naseerutheen and A. Chandrasekaran, Int. Res. J. Pure & Appl. Chem. 3 (2013) 210-219.

[18]   N. Oumabady, M. Rajendran, R. Selvaraju, SpectrochimicaActa Part A, 110 (2013) 46-54.

[19]   N. Oumabady, M. Rajendran, R. Selvaraju, J. Environ. Nanotechnol. 3 (2014) 23-29.

[20]   C. Manoharan, P. Sutharsan, S. Dhanapandian, R. Venkatachalapathy, J. Mol. Struct. 1027 (2012) 99–103.

[21]   K. Ramaswamy, R. Venkatachalapathy, Indian J. Pure Appl. Phys. 30 (1992) 171–175.

[22]   JCPDS, 2002, Joint Committee on Powder Diffraction Standards.

[23]   ICDD 2003, Powder Diffraction File, International Centre for Diffraction Data, Newton Square, PA.

[24]   W.D. Keller, Clays and Clay Minerals, 26 (1978) 1-20.

[25]   C.S. Manju, N.V. Narayanan, M. Lalithaambika, Clay and Clay Minerals, 49 (2001) 355-369.

[26]   K. Rajkumar, A.L. Ramanathan, P.N. Behera, J.Geologi. Soc. India,80 (2012) 429-434.

[27]   L.R.R. Gutierrez, E.T.R. Guzman, A.C. Prieto, R.R. Castillo, J. Min&Mater.Charact.&Engg. 7 (2007) 59-70.

[28]   P. Sengupta, P.C. Saikia, P.C. Borthakur, Clay J. Scint. Indust.Res. 67 (2008) 812-818.

[29]   J. Kaloustian, A.M. Pauli, P. Lecheme de la Porte, H. Lafont, H. Portugal, J.Therm.Analys&Calorim. 71 (2003) 341-351.

[30]   V.A. Drebushchak, L.N. Mylnikova, T.N. Drebushchak, V. Boldyrev, J. Therm. Analys&Calorim. 82 (2005) 617-626.

[31]   R. Palanivel,U. Rajesh Kumar, Rom. J. Phys. 56 (2011) 195–208.