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Gunavathi P

Department of Soil Science and Agricultural Chemistry, Anbil Dharmalingam Agricultural College and Research Institute, Trichy, Tamil Nadu, India

Janaki D

Department of Soil Science and Agricultural Chemistry, Anbil Dharmalingam Agricultural College and Research Institute, Trichy, Tamil Nadu, India

Balasubramaniam P

Department of Soil Science and Agricultural Chemistry, Anbil Dharmalingam Agricultural College and Research Institute, Trichy, Tamil Nadu, India

Alagesan A

Department of Soil Science and Agricultural Chemistry, Anbil Dharmalingam Agricultural College and Research Institute, Trichy, Tamil Nadu, India

Geethanjali S

Department of Soil Science and Agricultural Chemistry, Anbil Dharmalingam Agricultural College and Research Institute, Trichy, Tamil Nadu, India

Corresponding Author:

Gunavathi P

Department of Soil Science and Agricultural Chemistry, Anbil Dharmalingam Agricultural College and Research Institute, Trichy, Tamil Nadu, India

Characterization and identification of elemental sulphur, iron pyrite, mineral gypsum, Phospho gypsum and marine gypsum by using ATR-FTIR

Gunavathi P, Janaki D, Balasubramaniam P, Alagesan A and Geethanjali S

Abstract

The Amendments generally used for sodic soil reclamation should be source of sulphates viz., Elemental sulphur, Iron pyrite, Mineral gypsum, Phospho gypsum and Marine gypsum. Characterization of sources by ATR-FTIR is rapid and elementary. The peaks of IR spectra obtained from FTIR is compared with Bio-Rad (Know it all) software, to interpret and qualitative analysis of functional groups in mentioned materials. The active peaks of spectra denote the presence of principle compounds of sulphur as well as gypsum. ATR-FTIR is most promising and non destructive method to precisely provide the result without tiresome conventional chemical analysis of characterization. The strong spectra of gypsum held at 668cm^{-1} , 1130cm^{-1} , 1630cm^{-1} and 2200cm^{-1} range. The OH stretch at 3522cm^{-1} and 3400cm^{-1} confirmed the presence of gypsum and sulphate compounds. The S-O bending of gypsum observed at 669cm^{-1} and 597cm^{-1} . The S-O stretching and S-O bending of sulphates peaks appeared at $1140-1080\text{cm}^{-1}$ and $680-610\text{cm}^{-1}$. The alkyl thioketones (-C=S) of sulphur compounds vibrations found at the range of $1240-1050\text{cm}^{-1}$. This helps to confirm that the sources are suitable for sodic soil reclamation.

Keywords: ATR-FTIR, Sulphur, Mineral gypsum, Phospho gypsum, Marine gypsum

Introduction

The available materials which are used for sodic soil reclamation is source of calcium and sulphur compounds. The characterization and analysis of such materials by chemical methods are tedious and destructive. The FTIR instrumental analysis is rapid, error free and non destructive. The chemicals using for conventional analysis will invade and sometimes produce invalid results. Even with micro quantities of sample, it provides highly precise and reliable data. The IR spectroscopy draws attention due to identification and analysis of multi-components as well as minor and traces in systematic manner (Wei, *et al.*, 2016) (La Russa, *et al.*, 2009) [17, 9]. Sulfate mode frequencies such as ν_1 , ν_2 , ν_3 , and ν_4 are similar for all Ca-Sulfates spectra. And a broad peak is observed in ν_2 vibration for gypsum (Bishop *et al.*, 2014) [3]. Identification and pinpointing of functional groups in sodic soil reclamation sources will provide information about chemistry and nature of those materials. The objective of the study is to present and discuss spectra of sodic soil reclamation sources such as Elemental sulphur, Iron pyrite, Mineral gypsum, Phospho gypsum and Marine gypsum.

Materials and Methods

Fourier Transformer Infra Red Spectroscopy (FTIR) of Thermo Scientific nicoleet IS10 accompanied with omnic software is used to identify the spectrum of materials used for sodic soil reclamation such as Elemental sulphur, Iron pyrite, Mineral Gypsum, Phospho gypsum and Marine gypsum. Pinch of fine powdered samples were placed on diamond platform of attenuated total reflectance (ATR-FTIR). ATR-FTIR is ease and promising non destructive method of characterizing samples. It is an alternative way for transmission spectroscopy. The Infra red beam of high optical density passed through samples by critical angle, absorbed waves are reflected and recorded by detector (Blum MM and John H, 2011). Within 30-40 seconds of contact, the spectral data is generated. The spectra obtained from omnic software is processed by Bio-Rad (Know it all) software, which comprises various spectral library (Asan Mohamed and Janaki, 2021) [2].

Results and Discussion

Elemental Sulphur

The functional groups identified from Elemental Sulphur are Triazines, Azo and Silicon compounds. Coupling or overlapping of Triazines and Azo compounds found at the region of 1550-1400 cm^{-1} . Hence it forms weak vibration stretching. Under the silicon compounds, strong and sharp Si-H stretching is obtained at 2160-2120 cm^{-1} . Likewise, two sharp and strong bands of Ar-Si aromatic silanes obtained at 1430-1410 cm^{-1} and 1120-1100 cm^{-1} . Medium intensity of Si-CH₃ asymmetric deformation vibration held at range of 1420-1390 cm^{-1} . Symmetrically, strong and sharp deformation vibration of Si-CH₃ group found near 1260-1230 cm^{-1} . Strong

and broad stretch of Si-C is located at 900-700 cm^{-1} in Spectral peak (Fig.1). Sulfate minerals may be distinguished using thermal infrared (mid-infrared) spectroscopy. The infra red spectra of aqueous sulfate anion shows symmetrical stretch (ν_1) at peak 983 cm^{-1} . These vibrations are modified when the sulfate anion is present within a solid-state medium, such as a mineral with a repeating molecular order, resulting in the potential appearance of sulfate vibration modes in the spectrum (Lane M, 2007) [10]. The weak to medium absorbance symmetrical stretching of sulfone (SO₂-C) peak found at 1100-1126 cm^{-1} . The peak of Thiophene shows weak ring stretching at 1395-1412 cm^{-1} (Tang *et al.*, 2020) [16].

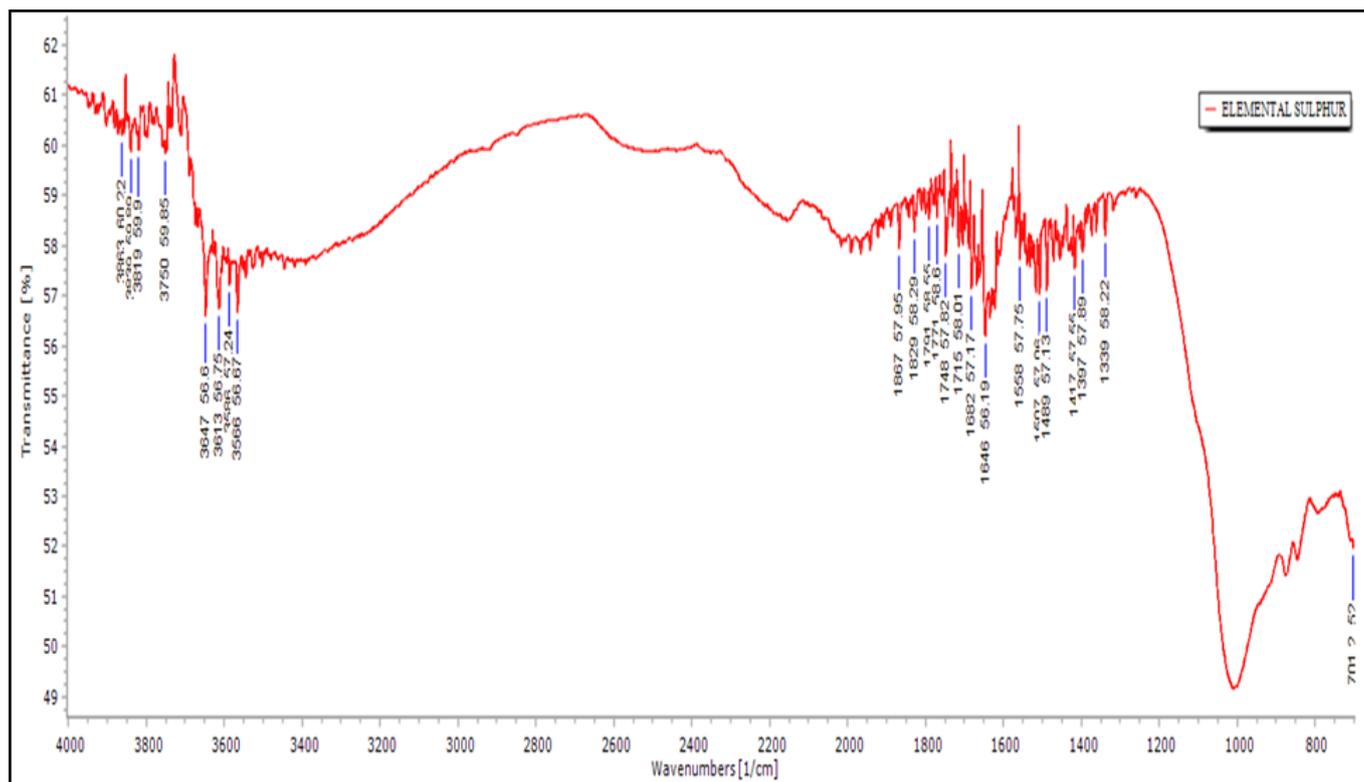


Fig 1: IR Spectra of Elemental sulphur

Iron Pyrite

The spectral band of Iron Pyrite shows the functional groups such as Alkanes, Triazines and Azo compounds. The C-H stretching vibration of normal alkanes has CH₃ asymmetric and symmetric stretching at 2972-2952 cm^{-1} and 2882-2862 cm^{-1} respectively. Asymmetrical and symmetrical stretch of CH₂ at ranges of 2936-2916 cm^{-1} and 2863-2843 cm^{-1} . The overlapped asymmetrical bending of CH₃ and CH₂ IN C-H bending vibrations located at 1470-1430 cm^{-1} and 1485-1445 cm^{-1} . The carbon attached CH₃ symmetrical bending of C-H bending vibrations located at 1380-1365 cm^{-1} . C-H weak wagging vibration held at 1307-1303 cm^{-1} and rocking

vibration of CH₂ at 750-722 cm^{-1} . Alkanes of Mono, Di, Tri, Tetra and Penta substituted benzene compounds held at range of 3100-675 cm^{-1} . The triazines of weak N=N stretching vibrations (aromatic azo) is obtained at 1550-1400 cm^{-1} . The azo compounds also arising from the aromatic ring vibrations give weak vibration due to coupling or overlapping (Fig.2). The symmetric stretching of sulfate appears at near 1011 cm^{-1} and 996 cm^{-1} . The maximum bands of SO₄ mode observed in the region of 1000-1300 cm^{-1} (Rouchon *et al.*, 2012) [15]. The peaks of pyrite (Fe=S), stretching of S-S and Fe-S arising in the range around 1120-1156 cm^{-1} and 607-622 cm^{-1} (Khabbaz and Entezari, 2016) [8].

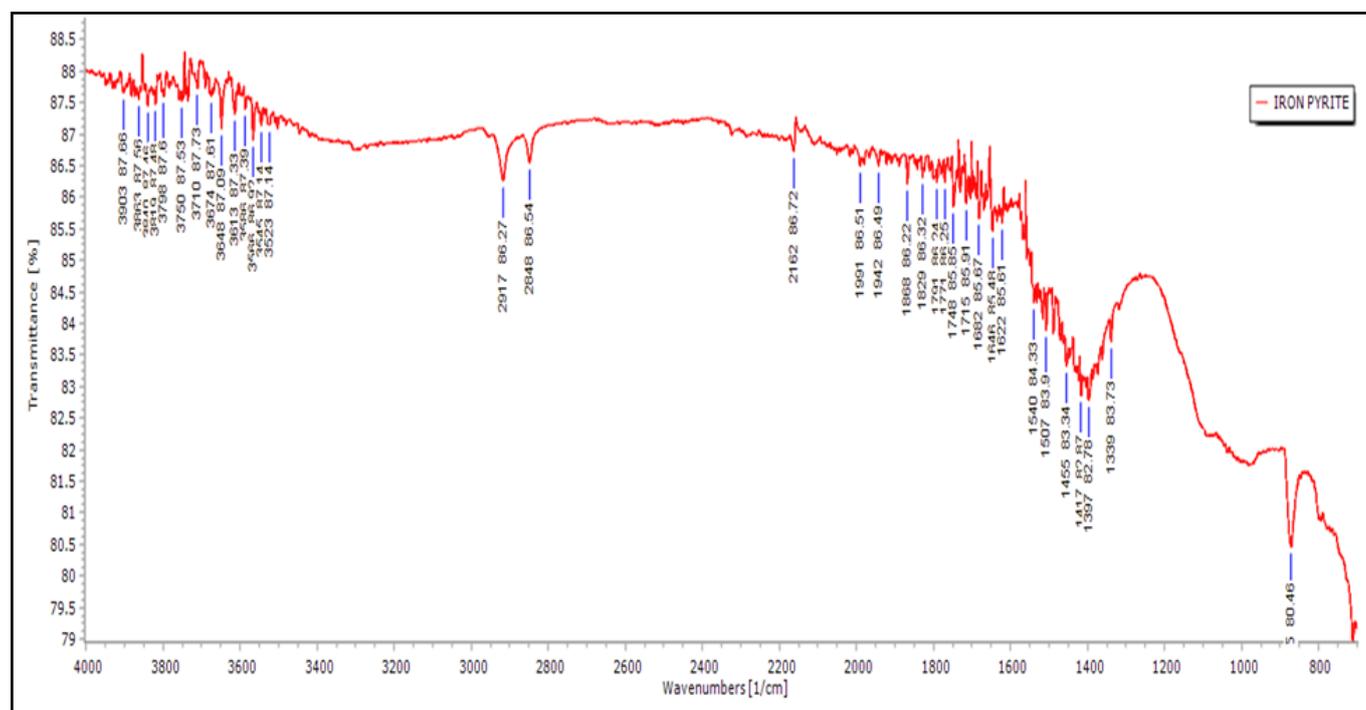


Fig 2: IR Spectra of Iron pyrite

Mineral gypsum

The alcohols, nitriles, alkynes, ethers, halogens, phosphorous, silicon and sulphur compounds are identified in mineral gypsum spectral peaks. The primary, secondary and tertiary alcohols of strong intense O-H stretching, C-OH stretching and O-H deformation vibrations held at range of 3650-3450 cm^{-1} , 1215-970 cm^{-1} and near 1400 cm^{-1} respectively. The sharp, weak to strong nitriles (C=N) stretching vibration found at 2260-2240 cm^{-1} which is conjugated with olefinic C=C and aromatic C=C resulting lowered frequency in absorption band and intensity of C=N absorption band. The mono substituted alkynes (RC=CH) vibrations held at range of 3300-615 cm^{-1} and di substituted alkynes (RC=CR') of non-conjugated stretching found at 2260-2190 cm^{-1} . The strong multiple absorption bands of aliphatic ethers and aromatic ethers with side chained oxygen to C atom found at 1225-1060 cm^{-1} and the aromatic C-O-C of ethers stretching in vibration gives strong and medium absorption band at 1270-1230 cm^{-1} and 1050-1010 cm^{-1} and its heterocyclic bands obtained at 1250-830 cm^{-1} . In halogens, fluorinated aliphatic hydrocarbons and fluorinated aromatic hydrocarbons are found in the range of 1400-1000 cm^{-1} and 1300-1200 cm^{-1} respectively. The P-H, alkyl phosphines, aryl phosphines, cyclic and acyclic P=N compounds shows weak to medium intensity spectra at 2500-965 cm^{-1} , 2285-910 cm^{-1} , 2285-1085 cm^{-1} and 1500-1170 cm^{-1}

respectively. The aliphatic ethers and aromatic ethers of silicon compounds gives strong multiple absorption band at 1225-1060 cm^{-1} and the aromatic C-O-C of ethers stretching in vibration gives strong and medium absorption band at 1270-1230 cm^{-1} and 1050-1010 cm^{-1} and its heterocyclic bands obtained at 1100-900 cm^{-1} . The alkyl thioketones (-C=S) of sulphur compounds vibrations found at the range of 1240-1050 cm^{-1} (Fig.3). The alcohol and hydroxyl compounds of dimeric, internally bonded, non bonded, primary alcohol, secondary alcohol, tertiary alcohol and phenols are observed in peaks of 3550-3450 cm^{-1} , 3570-3540 cm^{-1} , 3645-3600 cm^{-1} , 3645-3630 cm^{-1} , 3635-3620 cm^{-1} , 3620-3540 cm^{-1} and 3640-3530 cm^{-1} respectively (Nandiyanto *et al.*, 2019) (Coates J, 2000) [12, 6]. The C-F stretching is observed at 1340 cm^{-1} in ATR-FTIR (Petit T and Ljiljana Puskar, 2018) [14]. The strong spectra of gypsum held at 668 cm^{-1} , 1130 cm^{-1} , 1630 cm^{-1} and 2200 cm^{-1} range. And the weak bands are arising at 1010 cm^{-1} and 1670 cm^{-1} . Sulfate mode frequencies such as ν_1 , ν_2 , ν_3 , and ν_4 are similar to calcium sulfates data obtained from transmission, Raman and emission spectra (Bishop *et al.*, 2014) [3]. The spectrum of pure gypsum which shows centered strong bands of sulfate at 1140 cm^{-1} and 1128 cm^{-1} and the strong peaks of sulfate shown in ranges of 669 cm^{-1} and 602 cm^{-1} (AL Dabbas *et al.*, 2014) [1].

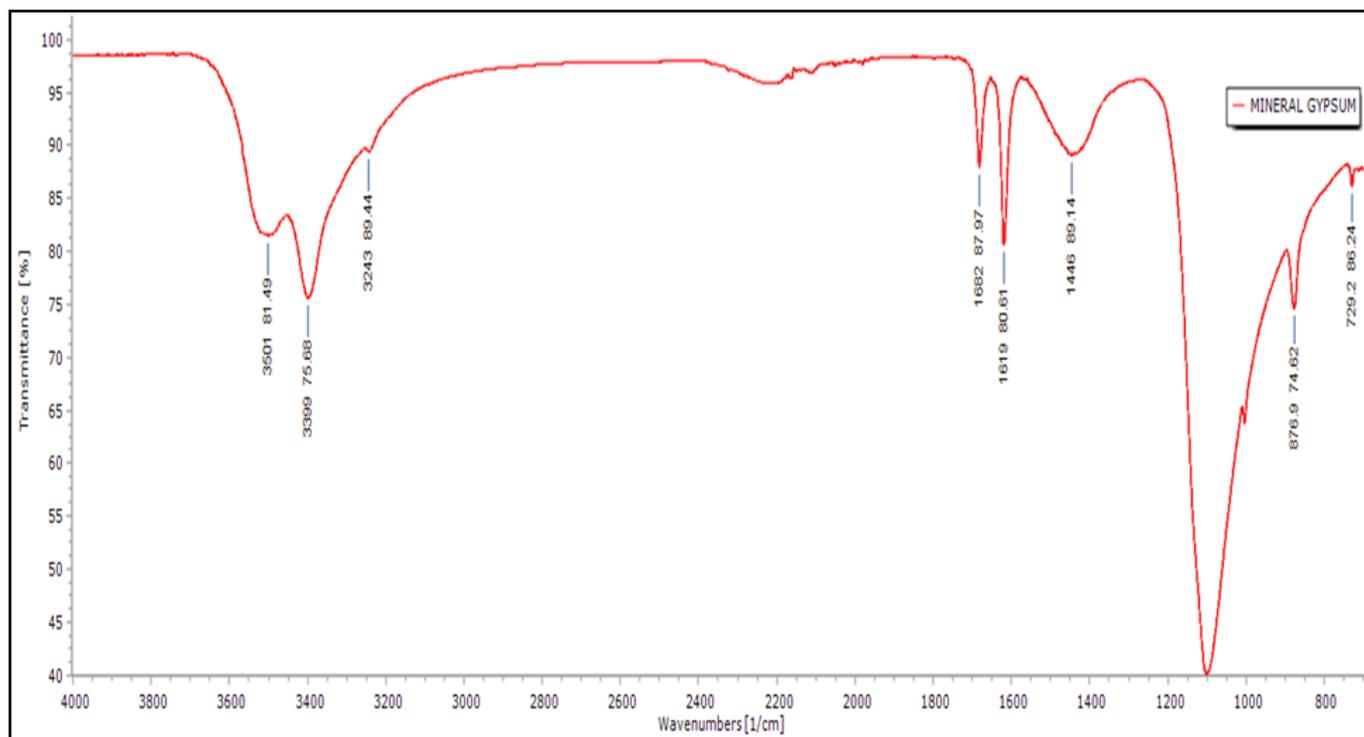


Fig 3: IR Spectra of Mineral Gypsum

Phospho gypsum:

The alcohols, nitriles, alkynes, ethers, halogens, phosphorous, silicon and sulphur compounds are identified in mineral gypsum spectral peaks. The strong intense O-H stretching of primary, secondary and tertiary alcohols arising at 3650-3320 cm^{-1} , The C-OH stretching of primary, secondary and tertiary alcohols held at range of 1075-1000 cm^{-1} , 1125-970 cm^{-1} and 1210-1100 cm^{-1} . The O-H deformation vibrations found at near 1400 cm^{-1} . The sharp, weak to strong nitriles(C=N) stretching vibration found at 2260-2240 cm^{-1} which is conjugated with olefinic C=C and aromatic C=C resulting lowered frequency in absorption band and intensity of C=N absorption band. The mono substituted alkynes (RC=CH) vibrations held at range of 3300-615 cm^{-1} and di substituted alkynes (RC=CR') of non-conjugated stretching found at 2260-2190 cm^{-1} . The strong multiple absorption bands of aliphatic ethers and aromatic ethers with side chained oxygen to C atom found at 1225-1060 cm^{-1} and the aromatic C-O-C of ethers stretching in vibration gives strong and medium absorption band at 1270-1230 cm^{-1} and 1050-1010 cm^{-1} and its heterocyclic bands obtained at 1250-830 cm^{-1} . In halogens, fluorinated aliphatic hydrocarbons and fluorinated aromatic hydrocarbons are found in the range of

1400-1000 cm^{-1} and 1300-1200 cm^{-1} respectively. The P-H, alkyl phosphines, aryl phosphines, cyclic and acyclic P=N compounds shows weak to medium intensity spectra at 2500-965 cm^{-1} , 2285-910 cm^{-1} , 2285-1085 cm^{-1} and 1500-1170 cm^{-1} respectively. The aliphatic ethers and aromatic ethers of silicon compounds gives strong multiple absorption band at 1225-1060 cm^{-1} and the aromatic C-O-C of ethers stretching in vibration gives strong and medium absorption band at 1270-1230 cm^{-1} and 1050-1010 cm^{-1} and its heterocyclic bands obtained at 1100-900 cm^{-1} . The alkyl thioketones (-C=S) of sulphur compounds vibrations found at the range of 1240-1050 cm^{-1} (Fig.4). The OH stretch at 3522 cm^{-1} and 3400 cm^{-1} confirmed the presence of gypsum and sulphate compounds. The S-O bending of gypsum observed at 669 cm^{-1} and 597 cm^{-1} . The S-O stretching and S-O bending of sulphates peaks appeared at 1140- 1080 cm^{-1} and 680-610 cm^{-1} . The P-O stretching of phosphates and Si-O stretching of Silicates spectra held at 1100-1000 cm^{-1} and 1100-950 cm^{-1} respectively (Palacio S *et al.*, 2014) [13]. The occurrence of HPO_4^{2-} in sulfate matrix is confirmed by the peaks of bands at 836 cm^{-1} and 1015 cm^{-1} (Hammas *et al.*, 2013) [7]. The sulfate group of calcium sulfate is attributed by the S-O stretching vibration at 1125 cm^{-1} (Chouaya *et al.*, 2019) [5].

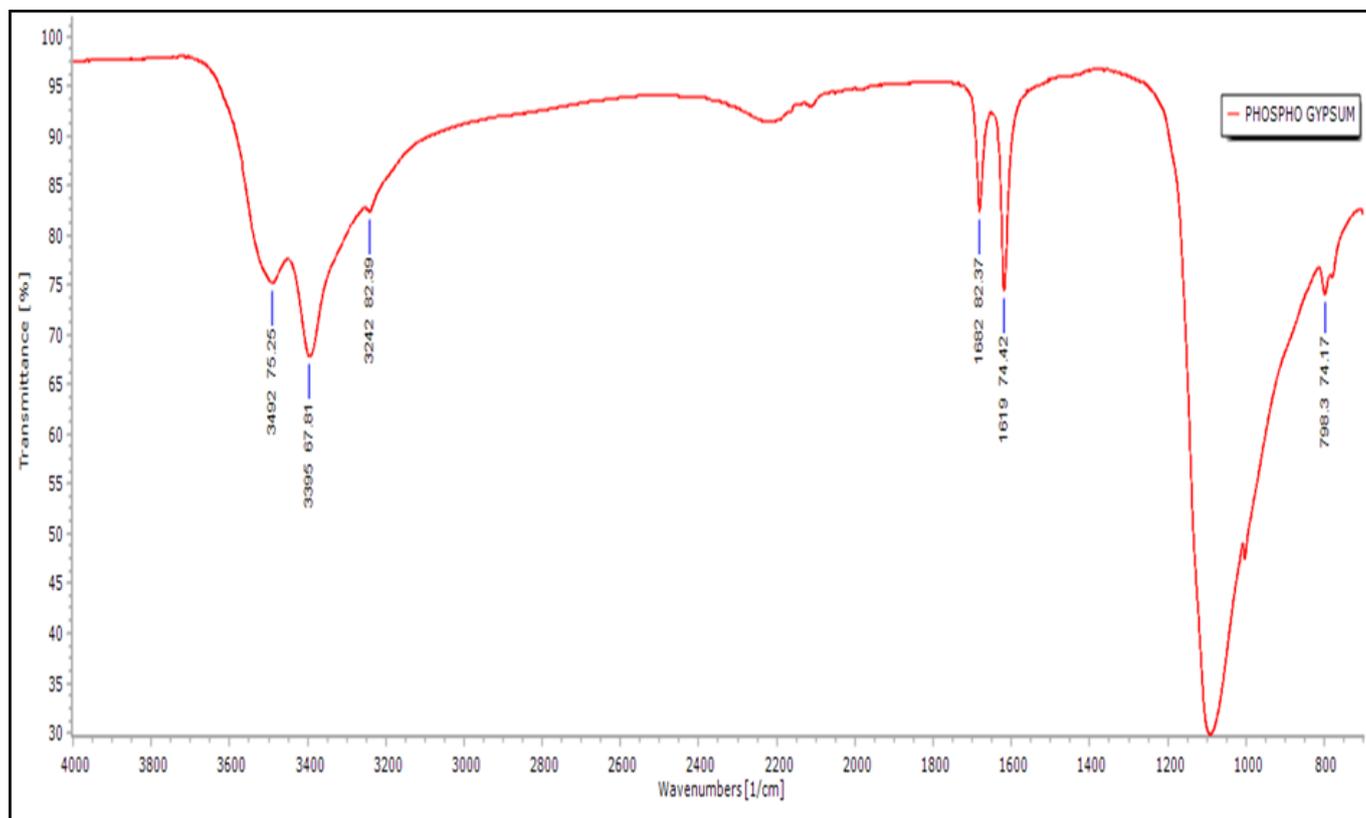


Fig 4: IR Spectra of Phospho Gypsum

Marine gypsum

The alcohols, nitriles, alkynes, ethers, halogens, phosphorous, silicon and sulphur compounds are identified in mineral gypsum spectral peaks. The strong intense O-H stretching of secondary and tertiary alcohols arising at $3650-3320\text{cm}^{-1}$, The C-OH stretching of secondary and tertiary alcohols held at range of $1075-1000\text{cm}^{-1}$, $1125-970\text{cm}^{-1}$ and $1210-1100\text{cm}^{-1}$. The O-H deformation vibrations found at near 1400cm^{-1} . The sharp, weak to strong nitriles(C=N) stretching vibration found at $2260-2240\text{cm}^{-1}$ which is conjugated with olefinic C=C and aromatic C=C resulting lowered frequency in absorption band and intensity of C=N absorption band. The mono substituted alkynes (RC=CH) vibrations held at range of $3300-615\text{cm}^{-1}$ and di substituted alkynes (RC=CR') of non-conjugated stretching found at $2260-2190\text{cm}^{-1}$. The strong multiple absorption bands of aliphatic ethers and aromatic ethers with side chained oxygen to C atom found at $1225-1060\text{cm}^{-1}$ and the aromatic C-O-C of ethers stretching in vibration gives strong and medium absorption band at $1270-1230\text{cm}^{-1}$ and

$1050-1010\text{cm}^{-1}$ and its heterocyclic bands obtained at $1250-830\text{cm}^{-1}$. In halogens, fluorinated aliphatic hydrocarbons and fluorinated aromatic hydrocarbons are found in the range of $1400-1000\text{cm}^{-1}$ and $1300-1200\text{cm}^{-1}$ respectively. The P-H, alkyl phosphines, aryl phosphines, cyclic and acyclic P=N compounds shows weak to medium intensity spectra at $2500-965\text{cm}^{-1}$, $2285-910\text{cm}^{-1}$, $2285-1085\text{cm}^{-1}$ and $1500-1170\text{cm}^{-1}$ respectively. The aliphatic ethers and aromatic ethers of silicon compounds gives strong multiple absorption band at $1225-1060\text{cm}^{-1}$ and the aromatic C-O-C of ethers stretching in vibration gives strong and medium absorption band at $1270-1230\text{cm}^{-1}$ and $1050-1010\text{cm}^{-1}$ and its heterocyclic bands obtained at $1100-900\text{cm}^{-1}$. The alkyl thioketones(-C=S) of sulphur compounds vibrations found at the range of $1240-1050\text{cm}^{-1}$ (Fig.5). The peaks of 3532cm^{-1} and 3403cm^{-1} confirmed the presence of gypsum. The band assigned at 1105cm^{-1} and 668cm^{-1} is related to gypsum. The ranges related to sulfate stretch of gypsum observed at $1620 - 1660\text{cm}^{-1}$ (Morillas *et al.*, 2015) ^[11].

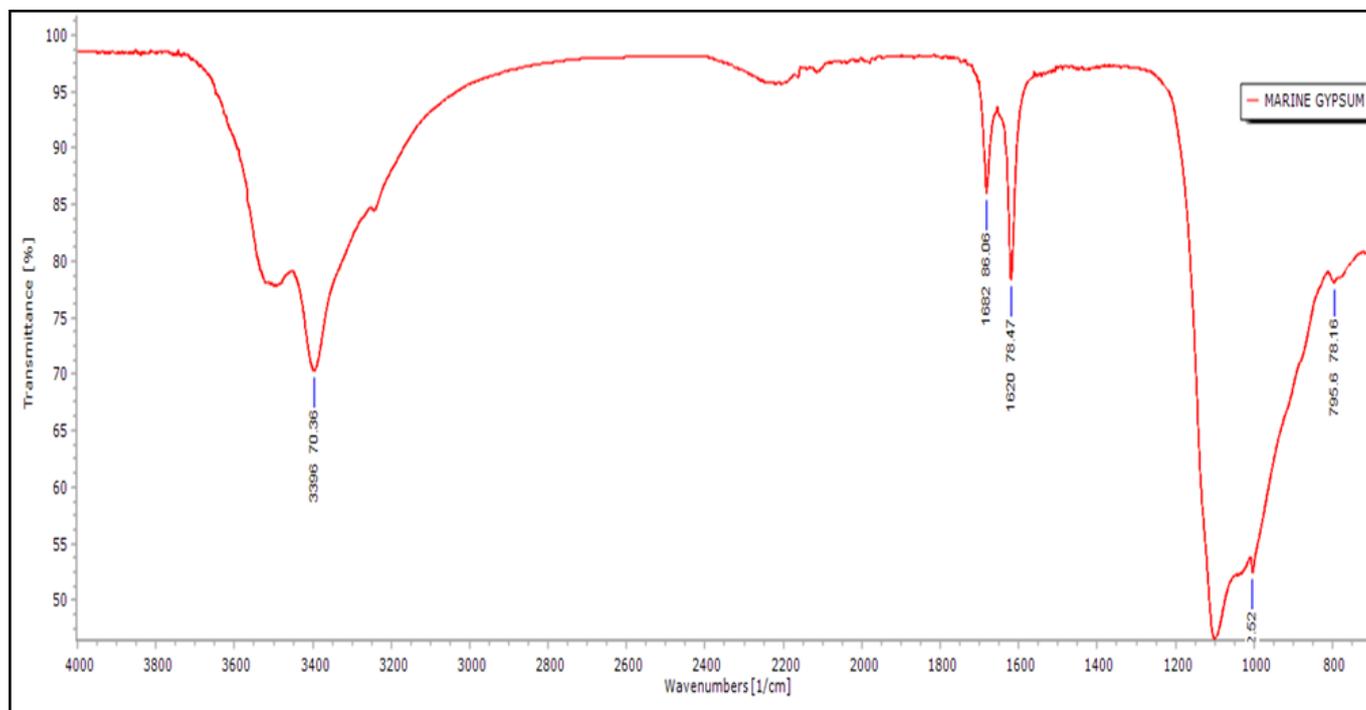


Fig 5: IR Spectra of Marine Gypsum

Conclusion

In conclusion, the various functional groups such as Triazines, Azos, Silicons, Nitriles, alcohols, alkynes, Ethers, Halogens, Phosphorous and Sulfurs are identified in the sodic soil reclamation sources spectra. The peaks and bands of spectrum confirm the proportion of such compounds in individual material. The gypsum spectra found at 668cm^{-1} , 1130cm^{-1} , 1630cm^{-1} and 2200cm^{-1} range. The 3522cm^{-1} and 3400cm^{-1} ranges indicates the gypsum and sulfur compounds in sources. The S-O bending of gypsum arises at 669cm^{-1} and 597cm^{-1} . The peaks at $1140\text{--}1080\text{cm}^{-1}$ and $680\text{--}610\text{cm}^{-1}$ shows that the S-O stretching and S-O bending of sulphates. Alkyl thioketones (-C=S) of sulphur vibrations found at the range of $1240\text{--}1050\text{cm}^{-1}$. This helps to confirm that the sources are suitable for sodic soil reclamation. The ranges of spectra systematically showed the presence of principle compounds such as Sulphur and gypsum materials in mentioned sodic soil reclamation sources.

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