Spectral characteristics of organic soil matter: A comprehensive review

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ABSTRACT

The information about the chemical composition of the soil is essential for agricultural, environmental, geological as well as in forensic science. The chemical constituents of soil could be revealed either by elemental methods or by spectroscopic techniques. The present review highlights the potential application of spectroscopic techniques, i.e., Fourier Transform Infrared spectroscopy (FTIR), Raman, UV–Vis-NIR, and laser-induced breakdown spectroscopy (LIBS) for the examination of spectral properties of soil samples which ultimately reveal its chemical makeup. This review explains various spectroscopic methods that are used for characterization and discrimination of soil based on organic matters; study on soil pollution, carbonates, etc.; and the principal finding of the studies are emphasized. Some lacunae in soil studies are still present in the literature. These lacunae are highlighted in the future challenges section in the hope to escalate the interest of researchers/ readers of soil science.

1. Introduction

Soil is a natural active body that occurs on the upper surface of the earth. It is a multi-component biogeochemical system that contains solids, liquids, and gases [1]. Chemically, soil contains organic/inorganic compounds, i.e. humic acids, fulvic acids, iron oxides, carbonates, etc. The humic acid in the soil gets decomposed because of the biological activity of microorganisms and hence, affects the soil structure, fertility, and water holding capacity considerably [2]. The chemical composition of soil reveals various features such as fertility, water retention capacity and nutrient present in the soil that directly affects the production of crops [3]. The analysis of soil samples solely depends on estimating the presence of total soil carbon. Presently, many soil scientists and researchers are taking interest in the study of SOC because various

chemical, physical, ecological, and biological functions depend on the SOC constituents, and thus, it is more an indicator of soil quality [4].

1.1. Agricultural perspective

Generally, soil carbon consists of organic and inorganic carbon. In the chemical composition of soil organic carbon (SOC), the animal tissues and plant fibers play a vital role as they get decompose through various stages. During the soil formation, various minerals, organic matter, oxides, carbonates, microorganisms have been formed [5]. This ultimately affects the chemical makeup of the soil. The fertile agricultural soil contains almost 3–6 % of soil organic matter which depends on the type of soil, land management, etc. Knowledge about the chemical composition of the soil is essential for agricultural as well as

environmental preservations. For example, in agriculture, organic/inorganic components ascertain soil fertility [6], water retention capacity [7], and nutrients value of the soil [8] which ultimately helps in enhancing the crop's nutrition value as well as its productions.

From an environmental perspective, soil provides the support for the survival of algae, bacteria, microorganisms, etc. which facilitates balancing the environment/ecology by scavenging the chemical waste and biodegradable toxic materials [9]. Besides, the toxic heavy metals in the soil cause potential health risk not only to human beings but also to other living organisms/plants via ingestion, drinking polluted water, food chains, contact with polluted soil, etc. The soil provides an important environment filtering medium that decomposes most of the toxic metals (the major part of soil/water pollutions) by natural anthropogenic activities [10]. Hence, it is essential to characterize the soil to reduce such exposure. Further, the concentration of heavy metals should be monitored to minimize the various health hazards.

1.2. Forensic perspective

Soil forensic is the use of soil sciences in a criminal investigation, thereby allowing linkage of crime with the criminals. Soil can be used as important physical trace evidence due to its transferrable properties from one place to another. It can be collected from clothes and shoes of the suspect supposed to step into the crime scene; shovel used for attacking the victim; any burying materials; the vehicle of the suspect in a hit and run cases; and wildlife trafficking cases because the majority of these cases involve footmarks/tire marks impression left at the crime scene. The forensic expert examines whether the soil collected from suspected materials/persons is matched with the soil collected from a crime scene or not [11]. This methodology can also reveal the geographical areas of the cases related to wood, wildlife, and human trafficking.

Soil forensic has not gained much popularity worldwide. The elemental analysis of soil samples from a forensic perspective has been done by utilizing SEM-EDS, XRD, ICP-MS, ICP-AES, and XRF analytical approaches by different research groups. The elemental analysis of soil provides better results in comparison to spectroscopic methods. However, these techniques require lengthy sample preparation setups and hence are time-consuming, destructive as well as expensive in nature. Moreover, these techniques are rarely available in forensic science laboratories. Therefore, in the present review, we have emphasized the applications of advanced spectroscopic methods for the examination of soil samples.

Soil can acts like fingerprints because of its unique characteristics. G. Popp from Frankfurt, Germany, was the first forensic scientist who examined the soil evidence forensically and solved the murder case in 1904 [12]. Thus, the soil is evidence that can link the persons to the crime scenes and provide useful information about crime and the criminal. The identification of soil fingerprints is particularly useful in a hit and run cases, wildlife and animal trafficking, wood trafficking, etc. The importance of soil analysis has been recognized only in agricultural and environmental perspectives; but, soil as forensic evidence has not gained much importance. The major problem associated with soil as evidence is its chemical complexity.

Many articles have been published on applications of spectroscopic methods for the investigation of the chemical composition of the soil. Still, an amalgamate review on the applications of spectroscopic methods in agriculture, organic carbon contents, soil contamination, and forensic science has not been published as per the knowledge of the authors. In this review, the authors have to figure out the agricultural, environmental as well as forensic importance of the soil analysis and its investigation by utilizing spectroscopic methods. The spectroscopic techniques especially FTIR and Raman spectroscopy have proved their potential and feasibility in physical, chemical, and biological sciences. In recent times, the advancement of these techniques helps in on-spot soil monitoring and investigation that ultimately provides fast, cost-effective, and reliable outcomes. These emerging techniques are now combined with multivariate methods to gain more robustness and accurate results than the conventional techniques.

2. Chemical composition of soil

Soil is a complex mixture of organic as well as inorganic particles, but its concise definition is still elusive as being a heterogeneous component. In other words, soil can be defined as a layer of loose particles which are formed on the earth's surface through the combination of various biological processes, sediment accumulation, weathering, etc. There are huge spatial variations in soil properties due to the interaction of the soil with flora/fauna, microbes, climatic conditions, and past time. The physical characteristics like the size and density of soil particles yield more complexity to the soil.

In addition to this, human activities such as urbanization and the inclusion of fertilizers and pesticides also alter the properties of soil. In general, half of the soil volume contains inorganic and organic minerals [13]. Organic matter includes various living/dead animals and plants called humus. In humus, the humic substance is the major organic component of soil, and is based on solubility in water at different pH; it is further divided into three groups [14].

a) Humins: large molecules which are not soluble in water at any pH
b) Humic acid (HAs): Soluble in water in alkali condition
c) Fulvic acid (FAs): Soluble at all pH

In inorganic minerals, the soil consists of aluminum, silicon, calcium, magnesium, iron, potassium, and sodium as major elements, and boron, magnesium, copper, molybdenum, fluorine, iodine, cobalt as minor elements [15]. Thus, the evidential value of soil generally depends on chemical/physical properties.

3. Soil examination

Soil can be analyzed for different purposes, i.e., identification of organic, inorganic, and elemental components in the soil; differentiation and mapping of soils collected various geographical regions worldwide; and the effects of climatic changes on chemical/physical properties of agricultural soil that ultimately explore about the soil fertility. Climatic changes like temperature and rainfall variations affect soil fertility significantly [16]. Thus, it is necessary to analyze the soil samples at regular intervals for better crop production. Similarly, the elemental analysis reveals the level of heavy metal pollutants in the soil and their effects on human health [17]. From a forensic standpoint, the characterization and discrimination of soil studies are helpful in the linkage of criminals with the crime and hence, the crime scene [18]. Conventionally, it was assumed that the soil having different colors belongs to the different geographic areas [19]; however, it is not necessary in each forensic case because some physical modification might be done by the suspect to manipulate the results.

3.1. Conventional methods

In the past, the soil is conventionally examined through organic matter detection. Several methods were used to detect organic matter such as Walkley–Black dichromate oxidation, Loss-on-ignition (LOI) method, chemical reagents, ignition test, color comparison, weight loss, particle size distribution, etc. are still used in many laboratories (see Supplementary Materials). However, these conventional methods have some limitations including inaccurateness, require an ample amount of soil sample, tedious digestion methods, and might provide biased results in the estimation of the concentration of chemical compounds. Because of these limitations, the last two decades have witnessed the development of various analytical techniques for the examination of soil.

3.2. Analytical techniques

Recently, many analytical techniques are utilized for the estimation of chemical components in the soil. These techniques include; microscopic methods like scanning electron microscope (SEM), transmission electron microscope (TEM), atomic force microscope (AFM); X-Ray based methods like X-ray diffraction (XRD) and X-ray fluorescence (XRF); thermal methods including thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTA); chromatographic methods like high-performance thin-layer chromatography (HPLC), thin-layer chromatography (TLC); ion chromatography (IC); atomic absorption spectroscopy (AAS) and some miscellaneous methods like inductive coupled plasma-optical emission spectroscopy (OES), mass spectrometry (MS), absorbance emission spectroscopy and neutron activation analysis (NAA), etc. for the detection of morphological, thermal and fluorescent properties of soil along with its elemental compositions.

The aforementioned techniques provide accurate and objective outputs even for a small number of soil samples. However, these techniques require lengthy sample preprocessing steps resulted in lengthy, costly, and destructive examination. Some specific limitations include; X-ray based methods, e.g., XRF is inappropriate for detection of all elements in the periodic table [20]; thermal methods reveal about the reaction mechanism, but not able to quantify organic materials [21]; chromatographic methods, e.g., in IC, other ions elute at the same timeframe in which the ion of interest should elute and the trace ions estimation is very difficult in case of high levels of other ionic species [22]; microscopic method i.e. SEM-EDS can detect the elements but cannot distinguish between ionic and non-ionic species and vacuum is required for the analysis [23].

Some of these shortcomings like destructiveness, time-consuming, etc. can be eliminated by utilizing spectroscopic methods, i.e., diffuse reflectance UV–Vis-NIR spectroscopy, ATR-FTIR spectroscopy, Raman spectroscopy, and LIBS especially in the detection of organic/inorganic components and elements in the soil [24–27]. The advantages of these techniques include cost-effectiveness, non-destructive, rapid, and required minimal to no sample preparation. Again, these techniques are frequently available in most laboratories [28].

Some review articles have been published on soil examination [29–32] by employing spectroscopic methods. These reviews highlight the Pb (lead), Cd, and Microplastics along with other heavy metal pollutants detection in the soil and hence, explain the environmental and health risk of contaminated soils. Soodan et al. described various analytical techniques used for the elemental analysis of soil samples. They have reviewed organic/inorganic matters in the soil which play an essential role in crop production [30].

In the year 2011, Maurel and McBratney published a review on the application of NIR and MIR spectroscopy for the detection of carbon contents in the soil. They have concluded that the MIR spectroscopy is better than the NIR spectroscopy for the detection of carbon contents because MIR provides 10–40 % fewer prediction errors. However, the in-field sensors facilitate promising prediction accuracy for C-contents with a cost-effective methodology than that of MIR spectroscopy [29]. In the year 2014, Armenta et al. published a review of vibrational spectroscopy in soil and sediment analysis. They have explained various spectroscopic methods for the detection of organic/inorganic constituents present in the soil. They have also explained the importance of chemometric methods in soil analysis with various prerequisites and preprocessing methodologies [33]. However, the forensic perspective of soil was remained obscured. Senesi and Senesi, 2016 have published a review article on the application of LIBS on quantitative measurement of soil carbon, especially organic carbon. They have found that the accuracy, sensitivity, precision, and selectivity of the LIBS technique are comparable with the conventional/elemental methods. This technique is cost-effective, robust, and can analyze many samples simultaneously [34]. However, LIBS possesses some limitations like the interaction of

radiation with the surrounding environment, difficulty controlling the plasma/ablation formation, and more importantly, the elimination of self-absorbance effects [35]. More recently, E.S. Mohammad et al. have published a review article on the application of NIR reflectance spectroscopy for the quantitative estimation of soil properties. They concluded that VIS-NIR could be a good tool for the mapping of soil properties because it reduces the time and cost. They have recommended different models such as PLSR, SMLR, ANN, PCR, etc. as a calibration model for soil assessment [32].

However, none of the above-mentioned reviews explain the utilization of these analytical techniques in both agricultural and forensic perspectives simultaneously. The critical limitations of spectroscopic methods should also be incorporated into a review for better understanding. The future statistical trends, spectral properties of soil, and principal findings have not been discussed in these reviews. Thus, a comprehensive review is required that explains every aspect of spectroscopic methods, their utilization in agriculture as well as in legal investigation, advantages, and disadvantages, spectral peak positions on soil constituents, etc. The present review explains all these aspects and thus, facilitates a complete platform for the analytical, agricultural, environmental and forensic experts for solving their future challenges. Further, the recent advancement in these methodologies resulted in portable devices which help in on-spot detections of organic/inorganic constituents and minerals. Over the last two decades, the quantification of soil organic matters (SOM) has been emerged significantly by using spectroscopic methods [36]. Thus, historical knowledge about spectroscopic methods is necessary before the recent advancements.

4. Brief history of spectroscopy

The history of spectroscopy began in the 17th century with Isaac Newton's invention. Newton discovered the nature of light and the basic color of light. At that time, he also described the colors of the rainbow and introduced the word "spectrum". In the year 1859, G.R. Kirchhoff who was a professor of physics at Heidelberg stated that "A solid, liquid or dense gas excited to emit light will radiate at all wavelengths and thus produce a continuous spectrum." Thereafter, G.R. Kirchhoff and R. Bunsen developed the first practical spectroscope in the year 1859. They showed that the spectrum for each element or matter is unique and a little amount is needed to get the spectra. Kirchhoff and Bunsen were also known as the father of modern spectroscopy [37–40]. After this, the different spectroscopic instrument has been developed till date. Currently, four spectroscopic methods i.e. UV–Vis-NIR, FTIR, Raman, and LIBS spectroscopy have extensively been used for the analysis of chemical properties of the soil.

5. Applications of spectroscopic methods

The spectroscopic techniques are comparatively robust, cost-effective, and less time-consuming for quantitative estimation as well as monitoring SOC on-spot, and in laboratories. Conventionally, the application of these techniques was confined to the laboratory only; however, some of these methods are subsequently used for in-situ measurements [41] and air-borne monitoring [42]. Some applications of these spectroscopic methods for soil investigation are presented below.

5.1. UV–Vis-NIR spectroscopy

Vis-NIR (VNIR), shortwave IR (SWIR), mid-IR (MIR) diffuse reflectance spectroscopic techniques have been utilized to reveal SOC contents. The differences among these techniques are mainly due to the spectral wavelength regions, e.g., VNIR (400–1100 nm), SWIR (1100–2500 nm), and MIR (2500–25,000 nm) respectively. The spectra through these techniques can be taken either in the laboratory or in the field [6]. Being one of the main chromophores of the soil, SOC content

can be estimated by using VNIR-SWIR laboratory spectroscopy [43–44]. UV–Vis-NIR spectroscopy is widely used in the characterization of soil. The minerals of soil absorb radiation in the UV–Vis-NIR region. The absorption in this region is caused by the electronic transition of the atom which is frequency-dependent. This dependency on frequency helps us to predict information about the minerals. We have compiled some of the work done on the soil by using UV–Vis and NIR spectroscopy as represented in Supplementary Table S1. The characteristic UV–Vis-NIR peaks for the soil components are reported in Table 1.

5.1.1. Agricultural applications

Accurate assessment of total carbon is essential for fertility and nutrients determination of soil. For the same purpose, McDowell et al. used Vis-NIR-MIR diffuse reflectance to estimate total carbon contents in soil collected from different horizons of the Islands of Hawaii, USA. The authors have used PLSR and random forests (RF) for the estimation of total carbon content. The paper reports the study of 307 samples from 10 different places, i.e. 30 samples per place, and these 307 samples are divided into 215 calibration and 92 validation samples respectively. In this study, the PLSR model resulted $R^2 = 0.95 / 0.94$, RMSE = 2.80 % / 3.08 %, RPD = 4.25 / 3.91, and RPIQ = 3.66 / 3.38 for Vis-NIR and MIR respectively gives high quality in the prediction of carbon content than other conventional methods. Similar types of results are obtained from the RF model. It is further concluded that the DRS spectroscopy could be utilized as an alternative tool for the analysis of total carbon contents [48].

Critical Assessment: Both of these methods have their advantages and disadvantages based on the dataset and circumstances. For example, PLRS is an extensively used parametric regression model for the prediction of soil properties content. However, the output of this model is adversely affected if the data has non-normal distribution. On contrary, RF is a nonparametric method that is not affected by non-normal distribution but, the structure of the RF model is very complex and difficult to operate by an individual who is not an expert in this field. Thus, it is advisable to explore and compare the statistical results by different models to conclude.

However, R^2 should not consider as an indicator for evaluating the linearity of calibration curves for a wide range of a dataset and heteroscedasticity should not be neglected in the calibration process. Thus, weighted least squares (WLS) should be considered as the best fitting technique option to regression curves. Normally, the choice of the fitting depends on the range of concentrations of interest e.g. when a narrow range is considered, an ordinary or unweighted linear model is usually adapted, while a larger range may require a more complex or weighted model.

The numbers of samples used in this study are adequate to perform multivariate analysis. Obviously, the higher the number of samples/experiments, the better will be the predictions, but it takes time, effort, and expenses. The ability to determine how well the data fit a linear model depends on the number of degrees of freedom which is given, in this case, by $D = N - P$, where D is the degree of freedom, N is the number of experiments and P is the number of coefficients in the model. Through this, one can obtain a value that relates to how well the experiment obeys a linear model, often referred to as an error or variance. These errors can be overcome by replication of experiments. It is useful to repeat the experiment a few times under identical conditions. In such instances, the degrees of freedom are calculated by $D = N - P - R$ where R equals the number of replicates. A good rule of thumb is that the number of replicates (R) should be similar to the number of degrees of freedom for the lack-of-fit (D). Thus, the greater is the degree of freedom, the more accurate will be the prediction but the more effort and works are required [49].

Thus, DRS can be used as an alternative tool for the prediction of total carbon contents in the soil when compared with traditional methods for quantification of total carbon i.e. chromate oxidation and combustion method respectively. However, more advanced methods such as ATR-FTIR and Raman spectroscopy should be preferred over DRS methods as these methods are more reliable and accurate.

Vasques et al., 2014, have proposed a method based on diffuse reflectance Vis-NIR spectroscopy for the classification of soil collected at different depths (0–20 cm, 40–60 cm, and 80–100 cm) of southeastern Brazil. The multivariate PCA and Multinomial logistic regression are used to classify soil at the level of order (highest), suborder (second highest), and suborder plus textural classification (STC). The validation mode provides 67 %, 48 % and 24 % correct classification for order, suborder and STC level respectively [50].

Critical Assessment: In this research, the validation phase is not successful when compared with the calibration phase because success rates are lower in the validation phase than in the calibration phase. The soil samples collected from the same geographical locations show similar chemical, physical and morphological characteristics and suffer only minor changes in spectral curves. Thus, the spectral curves of such soils show remarkable similarities in the overall shape and position of absorbance features which relate to major soil constituents, including minerals (mostly kaolinite, and aluminum and iron hydroxides), organic matter, and water. This might have resulted in poor classification rates of the validation phase. Again, the overfitting of PCs values might be resulted in the validation phase and resulted in poor validation. It should be worth mentioning that the use of a small number of samples, with low representatively of the different classes or groups, might also lead to unreliable results.

The mapping of soil can be done by using plant materials such as a leaf. In this direction, Pascoa et al. 2016 have used Vis-NIR diffuse reflectance spectroscopy coupled with multivariate methods on vineyard leaves with the purpose of mapping soil taxonomic types. For the same purpose, two vineyard properties were selected for the collection of soils (center and south Portugal). A total of 14 and 15 spots are selected from each vineyard for examining the leaves spectra variability

Table 1
UV–Vis–NIR band assignment of soil components reported in the literature [45–47]

Sr. No.	Range (nm)	Band assignment
1	180 nm	Pi – Pi*Allowed transitions
2	205 nm	Benzenoid and e^- transfer band
3	240 nm	Aromatic or unsaturated compounds (conjugation of quinone and ketone)
4	254 nm	Dissolved organic carbon
5	260–280 nm	lignin and quinone moieties, Humic acid (double bonds of humic acid)
6	265 nm	Protein like structure related to biological productivity
7	280	Total aromaticity, humification of peat
8	270–280 nm	$e-$ transitions between $\pi-\pi^*$
9	290 nm	Aromatic or unsaturated compounds (conjugation of quinone and ketone)
10	300–310 nm	Glutamic acid
11	312, 355 and 395 nm	Fulvic acid
12	430 nm	Fe^{3+} in oxy/hydroxide in visible region (electronic transition)
13	460 nm	Lead, Fe oxide mineral including hematite and goethite
14	500–530 nm, 650 nm	Fe^{3+} in oxy/hydroxide in visible region (electronic transition)
15	510, 530 nm	Clay minerals, hematite
16	600 nm	Zinc content
17	600–670 nm	Indicate strongly humified material with a high degree of aromatic and condensed group
18	700 nm	Fe^{3+} presence
19	880–900 nm	Iron oxide minerals (hematite and goethite)
20	1400–1450 nm, 1910–1930 nm	H_2O and OH^-
21	1725 nm	C–H bonds, goethite
22	2060 nm	Amine group
23	2200 nm	Al–OH bonding

within the same grape variety planted on different soil taxonomic types. The spectral measurement of each leaf was performed in triplicate and average reflectance was used for further processing. Savitzky-Golay (15-points filter size, second-order polynomial, and second-order derivative) filter was used as preprocessing method. PCA was used to detect the presence of outliers in the dataset. PLS-DA was used as a discrimination model for soil taxonomic type. The developed PLS-DA model achieved a correct classification of 95 % which is in the agreement with the existing soil maps. [45].

Critical Assessment: The selected numbers of spots are adequate for discrimination purposes. The preprocessing method reduces the noise in the dataset and the second-order derivative increases the resolution among the adjacent peaks. However, a 15 point filter size might result in loss of information and therefore, a filter that results in minimum loss of spectral information should be used, i.e. 9 point filter. Again, baselines of spectra are not corrected in this research otherwise will be an add-on advantage to reduce the true spectroscopic singles from interference effects and also remove background effects of stains, or traces of compound. PCA was used to detect the outliers. For PLS-DA, the data was divided into 70:30 ratios for calibration and testing of dataset respectively. This division was used to avoid overfitting problems. Mean centering pre-processing is used on spectral data before the multivariate analysis.

The main unsupervised pattern recognition method is principal component analysis (PCA). It is the 1st step of data analysis to detect the patterns in the dataset. PCA primarily reduces the dimension of the dataset without losing any information from the original data. The newly generated few principal components explain most of the information from the dataset. The linear coefficients of the inverse relation of linear combinations are called the component loadings. The values that represent the samples in the space defined by the principal components are the component scores. The scores can be used as input to other multivariate techniques, instead of the original measured variables.

In general, there are two types of approaches for using supervised pattern recognition: 1st based on discrimination among the classes, i.e., partial least squares discriminant analysis (PLS-DA), linear discriminant analysis (LDA), k-nearest neighbor (kNN), and artificial neural networks (ANN) and 2nd based on modeling the individual classes, i.e., soft independent modeling class analog (SIMCA). The main drawback of LDA is that the matrix inversion is required by the software for the calculation of the matrix. So, this technique is practicable only when the numbers of variables are smaller than the number of samples. Similarly, kNN has a similar disadvantage that of LDA and it does not give good results when the distances among the samples are large. Similarly, SIMCA provides the best result when the difference between the classes is much larger than within-class differences [51]. The problem of the smaller number of variables, the distance among the variables, etc. can be overcome by using the PLS-DA model.

Dotto et al. 2018 have used Vis-NIR spectroscopy to predict the SOC in the south region of Brazil. They have used seven statistical pre-processing methods and nine statistical models were tested for estimation of SOC. The weighted average partial least-square (WAPLS) chemometric method with normalization by range (NBR) preprocessing gives the highest model accuracy for SOC prediction with $R^2 = 0.82$, RMSE = 0.48 %, and RPIQ = 3.18 [47].

Critical Assessment: The statistical preprocessing used in this study are: Savitzky-Golay first derivative with a first-order polynomial and a window size of 9 nm (SGD), normalization by range (NBR), standard normal variates (SNV), multiplicative scatter-correction (MSC), continuum removed reflectance (CRR), the transformation to absorbance and application of a Savitzky-Golay first derivative with a first-order polynomial and a window size of 5 nm (ASG). Among the preprocessing techniques, CRR showed improved prediction capability. The improved performance of CRR can be attributed to effective noise removal and the reduction of the physical variability between samples, providing a more consistent definition of band depth. Continuum removal can also be used

to analyze the absorption features and correct the band minimum to the true band center. This technique can be used to normalize absorption features and emphasize the reflectance features of spectrum curves. CRR proved to be a great preprocessing for SOC content prediction regardless of the multivariate method applied.

Nine statistical models used are PLSR, PCR (principal components regression), MLR (multiple linear regression), SVM (support vector machine), RF (random forest), BMA (Bayesian model averaging), WAPLS (weighted average partial least-square), GPR (Gaussian process regression), and ANN (artificial neural network). Except for random forest (RF), all the multivariate methods presented robust predictions. The best fit and highest model accuracy for SOC models in validation mode were achieved when applying the weighted average partial least-squares (WAPLS) method and normalization by range (NBR) pre-processing (R2 = 0.82, root mean square error = 0.48%, and the ratio of the performance to the interquartile range = 3.18). Findings from this systematic methodology study identified the reliability of SOC determinations by examining how preprocessing techniques and multivariate methods affect spectral analyses.

5.1.2. Forensic applications

From a forensic perspective, only one paper has been published that utilizes UV–Vis spectroscopy and chemometrics [52]. In this paper, the authors have discriminated 44 soil samples on the basic quantity of acid fraction of humus in the soil collected from Epirus, Greece. They have extracted the humic and fulvic acids from the humus and their absorbance values are subjected to multivariate analysis after the appropriate preprocessing method. For the reduction of the dataset, they have employed cluster analysis and principal component analysis. Thereafter, the reduced numbers of variables are subjected to linear discriminant analysis. They have 85 % correctly classified the soil samples with a Wilks' lambda value of 0.042.

Critical Assessment: The authors have used UV–Vis spectroscopy which is a destructive method and should be avoided in forensic cases as the amount of sample collected in forensic cases are nominal and destructive technique results in no further testing of samples if required in the future. Moreover, the sample size is very limited in this study, resulted in no preprocessing of the dataset which is essential to obtain an unbiased outcome.

5.1.3. Principal findings

- The ATR-FTIR and Raman spectroscopes are more suitable than VIS and NIR for soil analysis because of vibrational and rotation transitions respectively that require less energy and also, these techniques are non-destructive.
- The combined preprocessing method gives better results in comparison to single preprocessing methods.
- Advanced prediction methods such as PLS-DA, SVM, etc. provide better results than linear regression methods.

5.2. Infrared spectroscopy

IR is a very effective tool for the study of organic and inorganic constituents of soil samples. IR spectroscopy has been utilized in soil science for decades. There are varieties of sampling methods used in IR spectroscopy nowadays. The most common methods are transmission, DRIFT (diffuse reflectance infrared Fourier transform spectroscopy), and the ATR method. Transmission is the oldest mode of collecting IR data. Later on, the DRIFT methodology comes into existence. In this, the penetration of radiations to a depth depends on the reflective as well as absorptive properties of the sample [53]. DRIFT is appropriate for soil examination because of its minimal sample preparation requirements. The coarser soil traps more light than finer soil which resulted in higher absorbance [54]. The physical morphology of soil can cause variations in specular reflection. ATR-FTIR spectra provide information about the

functional groups present in the sample. It works on the principle of total internal reflection [55–56]. The advantage of ATR-FTIR over other sampling methods is the collection of spectra in the presence of moisture contents. Water molecule absorbs the radiations strongly in the MIR range [57].

Recently, I. Barra et al., 2021 reviews the recent developments in mid and near-infrared techniques coupled with chemometrics and machine learning tools in addition to the preprocessing transformations and variable selection strategies to diagnose soil physical and chemical properties [58].

5.2.1. Spectral peaks Assignments

The major problem in the soil comparison is the variation in the soil samples occurs both within a particular site and between sites, and the extent of this is as yet unknown. IR spectroscopy of soil samples shows its characteristic peaks associated with inorganic minerals (quartz, clay, feldspar, mica, etc.) and organic matter. Many research articles revealed characteristic peaks in soil and sediment samples such as broadband around 3430 cm^{-1} is due to the OH stretching of water molecules. The peak at 3699 and 3620 cm^{-1} is attributed to the presence of stretching of the OH bond in Kaolinite. The peak at 2940 cm^{-1} shows the presence of CH stretching in the methyl (–CH$_3$) and methylene (–CH$_2$-) groups. The peaks at the range of 2800–3000 cm^{-1} correspond to aliphatic CH vibrations. The peak at 1879 shows the presence of quartz. The presence of metal carboxylate appears at around 1643 cm^{-1}. The peak at 1630 cm^{-1} is due to the presence of C $=$ O vibrations of carboxylate [59–64] and OH bending in water molecules [153]. A detailed FTIR band assignment for all the organic, inorganic and mineral constituents has been summarized in Table 2.

Kaiser et al. have noted that carbonate peak appears between 1620 and 1630 cm^{-1} and this shift is due to the interaction between organic matter and Al and Fe mineral components. The peak at 1050 cm^{-1} shows the presence of polysaccharides and vibration of Si-O in clay content. This peak shows the interaction between the carboxyl group of organic matter and metal. Stretching of Si-O in Kaolinite shows the band at 999 cm^{-1}. The bands at 2506 cm^{-1} 1430 cm^{-1} and 875 cm^{-1} correspond to carbonate content [65]. The presence of calcite shows the peaks at 1433, 873, and 712 cm^{-1}. The peaks at 797 and 693 cm^{-1} represent the presence of carbonate content in soil [158]. These characteristic peaks can be useful in the detection of SOM (Soil organic matter), SOC (Soil organic carbon), Carbonates examination, physical, chemical, and mechanical properties examination of soil, and forensic examination of soil, etc.

5.2.2. Agricultural perspectives

The difference in the soil characteristics is represented by soil fertility. Soil fertility is the function of different properties of soil, including nutrients, moisture, minerals content, and organic matter of soil [66]. The fertility of soil differs from area to area, such as in tropical area, moisture and acidity is the main factor of fertility [67]. Fertile soil helps in the development of root, provide nutrients and air to the plants, water supply and do not have disease and pest that directly affects the plants' growth [68]. The soil used for agriculture is known as arable soil. Soil is the main source of nutrients due to its complex chemical nature, i. e., mineral particles, liquids, gas, and living organism, etc. that play an important role in food production [69].

Soil organic matter is one of the most important portions of soil composition that directly influence soil fertility and quality. It is an important constituent for nutrient cycling, water retention, and aggregates formations [70]. Hence, SOM contents are required for sustainable agriculture. With the development of precision agriculture, the need for the efficient determination and identification of organic matter is increasing [71]. From an agriculture perspective, most of the studies are based on the determination of carbonate contents, total organic matters, and contaminants in the soil. As FTIR is sensitive to organic/inorganic materials, most of the studies characterize the soil sample from an

Table 2
FTIR band assignment of soil samples reported in the literature [61–64]

Sr. No.	Peak (cm^{-1})	Regions (cm^{-1})	Band assignment	
			Inorganic Components	Organic Components
1				
2	3622 cm^{-1}	3625–3615 cm^{-1}	Si–O–H vibrations of clays, gibbsite, Fe oxides, kaolinite	Moisture and the oxygen-containing organic matter
3		3600–3000 cm^{-1}		O–H, N–H stretching (phenol, alcohol, and water)
4		2930–2853 cm^{-1}		Symmetric, asymmetric vibrations of aliphatic C–H bonds (=CH$_2$ and –CH$_3$)
5	1743 cm^{-1}	2700–1800 cm^{-1}		C $=$ O carboxylic acid
6	1755 cm^{-1}			C $=$ O carboxylic acid
7	1953 cm^{-1}		Quartz overtone	
8	1641 cm^{-1}	1640–1650 cm^{-1}		C $=$ O stretching vibrations of amides, H–bonding in conjugated ketones, quinones, lignin, and carboxyls, C $=$ N stretching
9	1640–1633 cm^{-1}		Oxygen and nitrogen-containing a polar functional group	Hydrophilic materials of SOM
10	1431 cm^{-1}	1440–1430 cm^{-1}		C–O stretching, C–H deformation in phenolic groups, bendings in C–H of aliphatic CH$_2$, CH$_3$ group
11	1423 cm^{-1}	1420–1425 cm^{-1}	Inorganic Carbonates	
12		1403–1354 cm^{-1}		C–O of phenolic OH, COO$^-$ and O–H, CH$_3$ bend, COCH$_3$
13	1370 cm^{-1}			C–H absorption in aliphatics, CO–CH$_3$ vibrations in lignin-derived phenols
14		1185–1144 cm^{-1}		Carbohydrate groups C–OH
15		1060–1010 cm^{-1}	Al–OH deformation of kaolinite	C–O stretching of polysaccharide groups
16		995–1005 cm^{-1}		Aromatic CH out–of–plane bending
17		945–870 cm^{-1}		Benzoic acid, pyranose ring cellulose, RHC $=$ CH$_2$, R$_2$C $=$ CH$_2$
18	872 cm^{-1}	870–890 cm^{-1}	Carbonate	Lignin C–H out of the plane
19	794 cm^{-1}	820–752 cm^{-1}	Inorganic materials (clay and quartz minerals), carbonate, kaolinite	R$_2$C $=$ CHR phenyl groups
20		797, 693 cm^{-1}	Carbonates	
	720 cm^{-1}		Calcite	Long chain alkanes (CH$_2$)
21	650 cm^{-1}		Bentonite, Silicates	
22	520 cm^{-1}		Si–O–Al bending	
23	464 cm^{-1}	470–460 cm^{-1}	Si–O–Si bending in kaolinite, illite, smectite	

agriculture perspective only. Since the year 2009, many research articles have been published on FTIR study of soil as represented in Supplementary Table S2 and some of the findings are critically reviewed.

In general, the carbonate content is a basic soil component that affects the soil properties. The carbonate content affects the pH of soil considerably [72], e.g., the higher concentration of carbonates denotes alkaline soil, a widely used parameter during soil mapping by soil reviewers. These carbonates are also used to detect soil erosion status. Therefore, it is necessary to determine carbonate contents in the soil by cost-effective methods. Many articles are reported in the literature on carbonate detection by using IR spectroscopy [73–74], FT-IR spectroscopy, on the other hand, has proven to have the potential for accurate quantitative estimations [59].

Changwen et al., 2013 observed the intense absorption band of carbonate at 1410 cm^{-1} by using FTIR-PAS spectroscopy. A significant correlation is observed between carbonate content and FTIR-PAS spectral components in 1000–2000 cm^{-1} wavenumber regions. Several absorption peaks are observed in the spectra of calcium carbonate in the MIR region of 500–2900 cm^{-1}. These peaks are divided into three sub-regions, i.e., fingerprint, C-O, and CO_3^{2-} vibrations respectively. These researchers have also utilized the partial least squares regression model for the prediction of carbonate contents. They have compared two multivariate models, i.e., PLSR and GRNN, and concluded that the GRNN approach provides the best results with a root mean square error (RMSEP) of 1.21 % along with a ratio of the standard deviation to prediction error (RPD) of 3.83 for predicting the soil carbonate contents [75].

Critical Assessment: The FTIR-PAS has several advantages over conventional chemical methods as well as infrared spectroscopy techniques e.g. soil particle size and high infrared radiation absorption by soil samples, better repeatability, improved accuracy/precision, and soil carbonate content can be directly measured using CO laser photoacoustic spectroscopy (PAS). The selected numbers of samples in this study are adequate to perform multivariate analysis and preprocessing methods results in smoothing of the dataset that avoids inferential dataset from the final data set. For data reduction, PCA is used that allows a minimum to no information/data loss in the final dataset. The lower RMSEP and RPD in the GRNN method is because the PLSR method is based on linear transformation failing to identify some non-linear relationships between IR spectra and soil carbonate content whereas a GRNN model falls into the category of probabilistic neural networks. Using a probabilistic neural network is especially advantageous due to its ability to converge to an underlying function of the spectral data with relatively few training samples, subsequently; this makes GRNN a very useful tool for predicting soil properties from soil spectra. However, a lower R^2 in the 500–1000 cm^{-1} and 2000–3500 cm^{-1} has not been discussed which might be resulted due to the absence of organic/inorganic components characteristics peaks in these spectral regions or strong interference caused by other soil components in these regions.

Similar to carbonate, SOM is considered an important factor for a healthy soil system because it plays a vital role in many processes like water retention capacity, nutrient cycling in soil, etc. It helps modify the biological, physical, and chemical properties of the soil such as increasing nitrogen content, carbon storage that directly affect plant growth. Also, the effects of various climatic conditions on SOM have been studied by various groups. Thus, an accurate measurement of SOM is helpful in the detection of soil fertility.

Arachchi et al. have utilized NIR and MIR spectroscopic techniques for the quantification of the carbon content and its aggregate fractions contained in soil samples. 45 surface soil samples are taken from three bioregions of New South Wales. All soil samples are analyzed in the NIR (800–2500 nm) region as well as MIR (2500–25,000 nm) spectral region. They have recovered an average of 98.25% carbon after the wet sieving of the soil. Further, the authors have validated their results by the Cubist regression model selecting the absorbance values of aromatic, polysaccharides, and inorganic materials observed in the spectra. The

cross-validation results revealed that MIR spectra established a good correlation between the measured and predicted total carbon content of the aggregate fractions and observed by a high R^2 value and smaller RMSE for MIR ($R^2 = 0.88$; RMSE = 2.257 g kg^{-1}) compared to NIR ($R^2 = 0.90$; RMSE = 3.11 g kg^{-1}) [2].

Critical Assessment: MIR spectroscopy predicted the total organic carbon better than the NIR spectroscopy because MIR spectroscopy resulted in a lower RMSE. The prediction error of total organic carbon is 10–40 % lower in MIR spectroscopy compared with NIR spectroscopy and attributed due to more resolved peaks, more absorbance, and hence, more chemical information about the soil samples. However, 'high R^2 in NIR region depicts high RMSE and low R^2 value depicts low RMSE' has been not discussed in this research. A thumb rule is that high R^2 should depict low RMSE because maximum data points will fit on the linear line accurately. In some cases, e.g. in this study, the high RMSE might be due to overfitting of the dataset.

Besides the prediction of carbonates and SOM, the rapid and cost-effective screening tests for the determination of soil contaminants are booming around the world and are very challenging. Concerning this, Bray et al. worked on diffuse reflectance Vis-NIR and MIR for the diagnostic screening of heavy metal and polycyclic aromatic hydrocarbon in urban soil contaminants [76]. They have analyzed Cadmium, Copper, Lead, and Zinc as total polycyclic aromatic hydrocarbons (PAH) and benzopyrene. The results are further validated by using the ordinal logistic regression technique. The authors can predict Zinc with an accuracy of about 89%, copper predictions with 75% accuracy; Cadmium and lead are the least predicted heavy metal (67% and 70% respectively). Thus, the average PAH prediction is 78.9%. The average prediction accuracy for MIR is 79.9% which is slightly more accurate than Vis-NIR (77.1%) spectroscopy. Oudghiri et al. have utilized TGA-FTIR for the prediction of pollution degree of marine sediment from Cadiz port and Pristine Zone, China. Soil samples were thermally heated with a heating rate of 10 °C/min. It is observed that the pollution in Cadiz port is mainly caused by anthropogenic origin. The authors have concluded that the sample from the Cadiz port shows a high degree of pollution at four stages of decomposition as represented in Fig. 1 while from the pristine zone, no pollution has been observed and shows decomposition in two stages only [77].

Ng et al. worked on the determination of petroleum contamination in the soil collected from Australia by using IR spectroscopy. The detection of petroleum contamination is affected by various soil factors such as texture, amount of organic matter, degree of contamination, etc. The hydrocarbon contamination has been detected in 2990–2810 cm^{-1} in MIR regions and 2300–2340 nm in NIR regions. It is also found that the hydrocarbons contents decrease with time due to the volatilization process. Three statistical methods were used to predict total recoverable hydrocarbon, i.e., linear regression for 1 IR region which gives poor
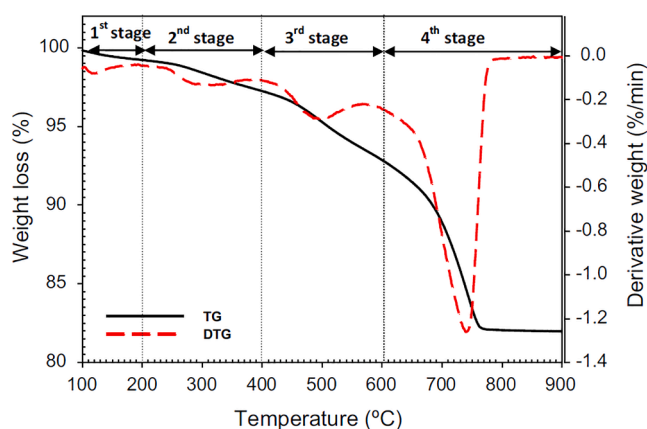

Fig. 1. DTG and TGA curve of sediment S1 showing highest degradation of pollutants at stage 4 (with permission from ref.77).

results, MLR for 4 IR regions that gave the coefficient of determination $R^2 = 0.71$ and 0.53 for portable MIR and lab MIR respectively, and PLSR model for whole spectra gives $R^2 = 0.75$. The PLSR model provides better accuracy than the linear and MLR models [78].

Critical Assessment: The spectra were transformed from reflectance (R) to absorbance by log (1/R), smoothed using the Savitzky-Golay (SG) algorithm with a window size of 21 and polynomial of order 2, and followed by Standard Normal Variate (SNV) transformations. The window size used is very large that resulted in the loss of important information about the chemical constituents and amount of soil samples. SNV is used to normalize the spectra, scaling it to zero mean and unit standard deviation and resulted in an unbiased outcome. The better accuracy of PLRS model is resulted due to larger number of parameters has been studied in this model in comparison to the linear and MLR model respectively.

5.2.3. Forensic applications

In the year 2000, Cox et al. first utilized FTIR spectroscopy for the discrimination of soil samples from a forensic perspective [79]. The FTIR provides conclusive results contrary to the color measurements which gives inconclusive results. However, the sample size is very low, and multivariate analysis was not performed to establish the soil type clustering. Later on, B.A. Weinger et al. analyzed and differentiated ninety-six samples by ATR- FTIR and IR microprobe method [80]. They revealed the application of IR microprobe in soil mineral identification, the study showed that IR microprobe can be a fast and reliable method in forensic soil identification. L.A. Dawson has utilized different techniques along with analytical methods such as XRD, and FTIR for characterization and discrimination of soil samples. From this study, it was concluded that each technique has different scales of resolution depending on the nature of the criminal case. Further, each method has its pros and cons [81].

Baron et al. have published research with the soil collected from 12 different sites in Lincoln (UK). A total of 60 soil samples were collected from different sites. They have incorporated NIPALS-LDA and PLS-DA statistical methods for the discrimination of soil. It is concluded that the NIPALS-LDA provides better classification results than PLS-DA [63].

Critical Assessment: The numbers of sites used in this research are very limited i.e. 12 sites with 4 sites per land type. For a better statistical prediction, including more sites in this study is highly recommended. Again, the statement about 'PLS-DA has problems with multiclass modeling' is not accurate. PLS-DA can provide better results for multiclass modeling also and it depends on the number of samples and preprocessing methods. If a large number of samples with adequate preprocessing methods are used in the study, PLS-DA can provide better results.

More recently, X. Xu et al., 2020, investigated LIBS and FTIR techniques and their practical feasibility were tested by applying these techniques to forensic soil samples in two criminal cases. The PCA of a typical soil sample indicated that five typical soil types were clearly distinguished by LIBS and FTIR-ATR spectra. It was concluded that the variations in the soil elements (i.e., Si, Mg, Al, Ca, K, O, and N) and functional groups (i.e., O—H/N—H, C=C/C=O, Si—O, CO_3^{2-}, Al—OH, and NH_2) are crucial indicators for soil identification [82].

5.2.4. Principal findings

- FTIR technique can be used as a substitution for the conventional Scheibler method.
- The advanced statistical method, i.e., Cubist and GRNN provides better results than the linear regression models for total organic contents/carbonates prediction.
- The soil water repellency is directly affected by degradation in the aliphatic structure of SOM. The presence of oxygen increases the volatilization rate of organic matter considerably.

- Humic acid is the carrier for moving inorganic pollutants from the surface to groundwater.
- The detection of petroleum contamination is affected by various soil factors such as texture, amount of organic matter, degree of contamination, etc.

5.3. Raman spectroscopy

In the year 1928, Raman spectroscopy was first experimentally observed by CV Raman and Krishnan [83]. Raman spectroscopy is a widely used spectroscopic technique in the field of environmental science, agriculture, and geosciences because it gives information about the mineral composition of soil and sediments. There are many advantages of Raman spectroscopy such as less time to prepare the sample, being non-destructive, and provides information about the inorganic minerals also which is not possible with IR. Raman spectroscopy is used to detect mineral composition in soil and sediment samples. The novel methods such as SERS (surface-enhanced RS) and confocal Raman micro-spectroscopy have augmented the utilization of Raman spectroscopy for soil analysis [84–85].

In the year 1974, Fleischmann et al. have observed SERS [86]. In the year 1977, it was further explicated by Jeanmaire and V. Duyne [87] and Albrecht and Creighton [88]. The exact mechanism of the enhancement effect of SERS is still ambiguous. According to electromagnetic theory, the intensity of analysts is enhanced by using nanostructure metallic surfaces as the substrate. The surface plasmons are generated from the oscillation of the electron density laterally to the metal surface. Because of high intensity, SERS can be used for low-intensity samples. With the high sensitivity and ability to suppress the fluorescence, SERS Raman has gained importance in the soil sciences, e. g., the technique is used for characterization of carbon in soil [89]; investigation of humic binding mechanisms [84–85,90–92], etc.

5.3.1. Soil characterization

Ling and his team worked on 4 lunar soils collected from different stations of Apollo by using laser Raman spectroscopy. They have calculated the compositional distribution of feldspar, pyroxene, and olivine minerals in each lunar soil. In this, the peaks of olivine and pyroxene are major whereas feldspar gives minor peaks in Raman spectra. The minerals modes obtained for lunar soil are consistent with studies based on optical petrography, electron microprobe, and X-ray imaging methods [93].

Vogel et al. 2017 have utilized ultraviolet Raman Microspectroscopy for the analysis of the chemical state of phosphorus compounds in soil collected from Australia. The ultraviolet has the advantage to avoid interference with strong fluorescence. Raman's study shows characteristic peaks of phosphate compounds in all soil samples as mentioned in Table 3. The effect of cooling has shown that some phosphate i.e. β-glycerophosphate and aminomethylphosphonic acid degraded less when cooled at –100 °C. However, phytic acid and adenosine monophosphate degraded even with cooling. Therefore, the study has some drawbacks as SOM can be degraded with ultraviolet rays and cooling conditions. The cooling effect can be reduced by using liquid helium [84].

5.3.2. Agricultural applications

Some reviews and texts discussing the technique and its application have been written in recent years [94–97]. In the present review, we have combined the researches done in the last decade on soil samples by Raman spectroscopy and is listed in Supplementary Table S3.

Roldan et al. have studied the interaction between paraquat and humic acid of soil collected from Cadriano, Italy by using SERS and SEF. They have used Ag nanoparticles for Raman analysis. The interaction of herbicide on humic acid has been studied at varying pH and laser excitation wavelengths. The different excitations i.e. 514.5 nm and 1064 nm provide selective information about SOM and pesticide. The

Table 3

Characteristics peaks of soil components reported in the literature via Raman spectroscopy [84,99]

Sr. No.	Peaks Ranges (cm^{-1})	Band Assignments
1	1650 cm^{-1}	C = O vibrations of esters and amides
2	1600–1610 cm^{-1}	Aromatic C = C vibrations
	1600–1800 cm^{-1}	C = O stretching vibrations
3	1600–1620 cm^{-1}	Aromatic C = C vibrations
4	1500–1530 cm^{-1}	Graphite C = C (G bond)
5	1560 cm^{-1}	Asymmetric stretching vibrations of COO−
6	1420 cm^{-1}	Skeletal vibrations of the aromatic ring
7	1380 cm^{-1}	Symmetric COO − vibrations in aromatic rings/CH$_3$ deformation (Fulvo–aquic soil)
8	1330–1320 cm^{-1}	C = C vibrations of amorphous carbon (diamond)
9	1308 and 1611 cm^{-1}	Aromatic part of HS
10	1200–1300 cm^{-1}	C–H bending in aromatic ring and C–O stretching vibration in phenols
11	1000–1200 cm^{-1}	C–C, C–O stretching vibration
12	1000–1100 cm^{-1}	Symmetric stretching of iron and aluminum phosphates
13	900–1000 cm^{-1}	Symmetric stretching of phosphate, Si–O symmetric stretching vibration
14	963 cm^{-1}	Calcium phosphate
15	960 cm^{-1}	Stretching vibrational modes of PO$_4$ (phosphate)
16	700–800 cm^{-1}	Si–O stretching mode
17	463, 198 cm^{-1}	Quartz
18	410, 228 cm^{-1}	Cristobalite
19	350–500 cm^{-1}	O–Si–O bending modes

aggregation and adsorption on metallic surfaces affect the emission considerably. The strongest changes were detected for the C–N–C side of paraquat, indicating the importance of the ionic interaction of the positive of the pesticide with the anionic group of humic acid. These interactions are more intense at high pH [98].

For soil characterization, the 1st paper was published by Xing et al. have proposed a method for the identification of soil and quantification of SOM of soil collected from farmland in China by using Raman spectroscopy combined with multivariate statistics. They have correctly identified 200 soils sample with 96 % accuracy by using the probabilistic neural network (PNN) and PCA. For quantity estimation, they have developed a PLSR model. The developed model facilitates accurate prediction with RPD = 1.92, R^2 = 0.74, and RMSEP = 8.16 g kg^{-1} [99]. The characteristics of Raman signals of soil components are highlighted in Table 3.

5.3.3. Forensic application

In the year 2011, Edwards et al. have utilized Raman spectroscopy to discriminate soil samples. They collected samples from both rural and urban areas of England. They utilized a step-wise oxidative treatment method on the soil by using hydrogen peroxide to eliminate the issue of fluorescence. The peak at around 1000–2000 cm^{-1} shows the presence of organic components in soil [100].

Kammrath et al. have utilized the potential of Raman spectroscopy for the investigation of soil samples from a forensic perspective. The authors have illustrates the potential of morphologically-directed Raman spectroscopy (MDRS) in two real-life cases. In the first case, soil samples from different geographical areas, i.e., UK, USA, and Japan were collected while in the second case, the samples were collected from four different sites with an interval of 300 m along a single road from the USA. They have studied the particle size distribution, mineral identification, and morphological characteristics of the soil. In the first case, the result shows that the sample from the USA and UK resembles in terms of size distribution are contrary to Japanese soil. UK and USA contain a high proportion of quartz whereas Japan contains a higher proportion of orthoclase. The pyrophyllite was found only in the USA soil whereas calcite and haematite were completely absent [101].

In the second case study, discrimination has been done based on

minerals such as rutile, labradorite, albite, microcline, epidote, quartz, almandine, diopside, and muscovite. The results showed that soil 'C' had the largest amounts of quartz and diopside, which are the two minerals important for its discrimination, while rutile was important for the distinction of soil 'B'. Rutile, almandine, and epidote are important for the discrimination of soils A and D. The multivariate PCA analysis revealed 87.7 % variation in the soil data as shown in Fig. 2.

Critical Assessment: In the second case study, the authors have employed PCA analysis without preprocessing the dataset which might be resulted in a biased outcome. The preprocessing methods are generally employed in a study to overcome the errors caused by instrument, sample handling, and processing, etc. One should include detailed methodology in the research, e.g. number of samples, spectral regions, preprocessing methods, normalization, etc. so that repeatability and reproducibility of the developed method can be studied. Again, the number of samples studied in this case study is very less and the study lacks the cross-validation steps that are generally used to predict the origin of unknown soil samples.

5.3.4. Principal findings

- At higher pH, the SEF gives better results than SERS and vice-versa.
- The quantity estimation of soil constituents can be done by PLSR modeling.
- The compositional distribution of feldspar, pyroxene, and olivine minerals has been done on the lunar soil.
- The SOM contents can be degraded with ultraviolet rays and cooling conditions.
- SERS Raman spectroscopy has some advantages over conventional Raman spectroscopy.

5.4. Laser-Induced breakdown spectroscopy

LIBS is a robust chemical analysis technique that uses a short laser pulse to create a micro-plasma on the sample surface. This technique offers many advantages over other elemental techniques, e.g., no sample preparation, rapid, detects low atomic weight elements, thin films can be analyzed without the interference of substrate properties, etc. A potential lower detection limit of LIBS for heavy metallic elements (-ppm range) makes this technique ideal for agriculture, environmental and forensic purposes. The main advantage of the LIBS technique is the possibility of real-time analysis. Because of this advantage, LIBS allows
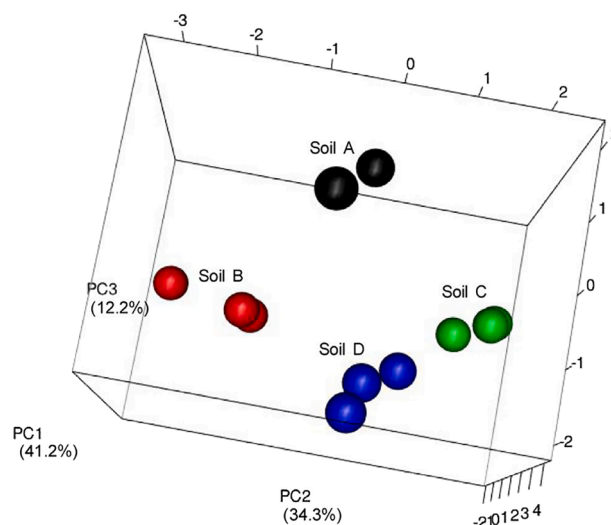
Fig. 2. LIBS spectra of SW 1, CRM 143 and WT-H soil samples (with permission from ref.101).

us to reveal the presence of several atomic species, in a particular spectral region by using a single laser shot. By using this real-time data a suitable algorithm can be developed to obtain qualitative and quantitative information about the sample [102]. LIBS can be utilized for some sample matrices including metals, glasses, plastics, biological tissues, soils, plants, and thin-paint coating, etc. Recently, a review on advanced and future trends in LIBS applications to agricultural materials and their food derivatives has been published that reveals the developments of LIBS techniques in the last decade (2010–2019) [103]. D.A. Goncalves et al., 2021 describe LIBS techniques in context to the environmental systems and their potential contaminants [104]. Similarly, R.S. Harmon et al., have reviewed LIBS as a geochemical tool for the 21st century [105]. K. Yu et al., 2020 highlight the importance of LIBS techniques from an agricultural perspective [106].

Some available portable devices can be used as an alternative approach for in-situ SOC estimation. Several researchers have reported a very good correlation between LIBS and conventional dry combustion that determined total SOC [107–108]. The researches done on the soil samples by using LIBS spectroscopy is listed in Supplementary Table S4.

The emission lines and corresponding spectral regions of major elements of soils are summarized in Table 4.

5.4.1. Agricultural applications

In the last two decades, the concentration of heavy metals in soil samples has been increased considerably. In the year 1994, Richard Wisbrun and his team utilized laser plasma spectroscopy to detect the heavy elements in different environmental solid samples that include soil, sludge, and other materials [111]. They studied different factors that affect the analysis such as particle size effect, the energy of the laser, sample humidity, etc. In the year 1996, A. Ciucci et al. analyzed trace elemental pollutants in soil by using the time-resolved LIBS technique [102]. They concluded that the LIBS spectrum is observed in the UV–Vis range. A dangerous pollutant can be easily identified. Similarly, R. Barbini et al. have also utilized LIBS to detect the heavy metals in soil samples [112].

Kim et al. have utilized LIBS for the detection and discrimination of soil contaminated with heavy metal or oils and clean soil samples. The effect of grain size and water contents on LIBS emission was also studied. The results revealed that the effect of water content on LIBS emission lines is more pronounced than the grain size effect. LIBS emission lines were decreased by 59–75 % with the increment of water content from 1.2 to 7.8%. For validation purposes, PCA and PLS-DA model was used. The results showed that based on PCA analysis, three soil samples were discriminated and a blind test on the PLS-DA model provides a correct prediction of 100 % for the soil contaminated with heavy metals and oils whereas a 95 % correct prediction rate is achieved for non-contaminated

Table 4
LIBS assignment of some major elements present in the soil and reported in the literature [109,110]

Sr. No.	Elements	Wavelengths (nm)
1	Aluminum	I 308.22, I 309.2, II 394.40, II 396.15
2	Barium	II 455.40, II 493.41, I 553.54
3	Calcium	II 315.89, II 317.93, II 373,69, II 393.37, II 396.85, I 422.67, I 443.50, I 445.48, I 588.88, I 610.28, I 612.22, I 616.22, I 643.91, I 646.26, I 649.38
4	Chromium	I 420.45 , I 420.60 , I 420.84
5	Iron	I 356.54, I 357.02, I 404.58, I 407.17,I 425.07, I 427.15, I 432.57, I 438.35, I 440.47, I 441.48, I 522.71, I 523.29
6	Lithium	I 670.78
7	Magnesium	I 382.94, I 383.83,I 516.73, I 517.27, I 518.36
8	Potassium	I 766.48, I 769.89
9	Silicon	I 263.15, I 288.21, I 390.55, I413.09
10	Sodium	I 588.99, I 589.63, I 589.59
11	Titanium	I 453.32, I 453.47,II 454.95, I 521.02 I 522.45

soils [113].

Critical Assessment: Only C-lines are not significant for chemometric methods and hence, all emission lines were used as input variables in the chemometric method. Approx 80 spectral data points were analyzed for each class to develop the PLS-DA model which is very much adequate. In the blind test of the contaminated soil samples, no misclassification was found or soil samples contaminated with heavy metals and oil residues with 100% correction rates. However, one clean soil sample was misclassified as oil-contaminated soil, three clean soil samples were not categorized into any class, and 76 clean soil samples were correctly identified. No preprocessing methods have been utilized in this study that might result in the overfitting of data.

X. Xuebin et al., 2019 have applied data fusion strategies for laser-induced breakdown spectroscopy (LIBS) and attenuated total reflectance Fourier-transform mid-infrared spectroscopy (FTIR-ATR), as well as a combination of multivariate calibration methods to investigate for prediction of soil organic matter (SOM) content. The root means square error (RMSE) and residual prediction deviation (RPD) of the calibration and validation sets, systematic error, and residual assessment, were applied to evaluate the robustness and accuracy of these predictions [114].

Critical Assessment: The calibration set contained 228 soil samples and the validation set contained 76 soil samples respectively. The root means square error (RMSE) and residual prediction deviation (RPD) of the calibration and validation sets, systematic error, and residual assessment were applied to evaluate the robustness and accuracy of these predictions. The results of a principal component analysis (PCA) indicated that baseline wander present in the spectral data could be effectively removed using morphological weighted penalized least squares (MPLS) and wavelet transform (WT) algorithms. The quantitative prediction ability of SOM content by a partial least squares regression (PLSR) model could be improved using principal component weighted mean (PCWM) and Euclidean distance weighted mean (EDWM) algorithms applied to parallel LIBS spectra.

The characteristic LIBS spectra obtained using the PCWM, and EDWM algorithms presented lower errors and higher quantitative prediction ability of SOM in the PLSR model than using the AM and PCA algorithms. The quantitative prediction ability of SOM could be dramatically improved by using mid-level data fusion based on feature extraction of the PLSR model (MLDF-LV). Moreover, the SVR (support vector regression) and ANN models also showed excellent prediction accuracy and robustness for SOM prediction according to systematic error and residual assessment.

5.4.2. Forensic applications

Jantzi et al., 2011 have utilized LIBS for the elemental analysis of soil. It is the first article that has utilized a laser beam of 266 nm for the analysis of soil in forensic science. The results obtained from LIBS were further compared with the LA-ICP-MS technique. Precision for both methods was < 10% for most of the elements. The LIBS detection limits were < 33 ppm and bias < 40% for most of the elements. LIBS method discriminated two different sites of soil samples successfully. Analysis of variance (ANOVA), Tukey's post hoc and Student's *t*-test provides 100 % discrimination of two soil samples with no type I and type II errors. The PCA analysis resulted in a clear clustering of two soils. LDA with leave-one-out cross-validation provides a 99.4 % correct classification of soil samples. LIBS and LA-ICP-MS provide similar information about the soil samples [115].

Woods et al., 2014 examined 29 soil samples from different areas of Australia by using SEM-EDX, XRF, and LIBS. They have compared these techniques in the examination of soil. All the soil samples were discriminated against by these techniques. SEM-EDX provides 99.5 %, LIBS provides 92.4% discrimination and XRF provides 98.5% discrimination. It is suggested by the authors that any of the aforementioned techniques could be used for the differentiation of soil specimens [116].

5.4.3. Principal findings

- The obtained emission spectral lines are unique for an individual element.
- LIBS can be used as an alternative tool for the detection of heavy metals in the soil.
- LS-SVM provides better results than SIMCA.
- Multivariate approaches provide better results than univariate approaches.
- The external magnetic field improves the detection limits of heavy metals.

6. Discussions and statistical trends

The present review discussed the applications of spectroscopic methods for soil analysis. The soil quality assessment has been changed through time, in terms of objective, methodology, qualitative analysis, and overall approach. In the last decade, the applications of spectroscopic methods have considerably increased. The reported studies have successfully utilized UV–Vis-NIR, FTIR, Raman, and LIBS spectroscopy for various purposes including agriculture, environmental, and forensic perspectives. Moreover, the combination of these analytical techniques with statistical approaches like PCA, PLSR, Regression analysis, Cubist model, ANN, and SVM has been proved their potential in the prediction of different soil components.

Nowadays, these methods are generally used for quantitative as well as qualitative analysis. Again, these methods are available to support interpretations of soil data, both in the field and in the laboratory. In agricultural research, new methods have been developed for the estimation of organic/inorganic contents; forecasting of landslides, effects of pollutants on human health, etc. Agriculture is a major part of the world economy, which is affected by climatic changes such as temperature and rainfall. Insufficient water, agriculture practices, and nutrient deficiencies also affect agriculture. Adequate soil parameters and suitable application of fertilizers and pesticides might facilitate attenuating these issues. In this regard, soil organic carbon proves to be a major component of soil that does not only regulate the climate but also affects other soil properties. The study of SOC storage at different spatial scales, i.e. from local to regional scales is the most challenging objective for researchers worldwide. Another vital area that attracts researchers is to reduce the effect of soil erosion/degradation on agriculture/crop production. In forensic science, the soil database has been generated by geologists of the United Kingdom and the USA. Still, much work has to be done especially from forensic perspectives worldwide.

6.1. Statistical considerations

The majority of analytical techniques provide good results for the soil analysis along with statistical confidence. The principal findings and critical assessment of the research have been highlighted to encourage the use of spectroscopic methods which provide fast, non-destructive, and accurate results in the determination of carbon contents, soil organic matters, and phosphates, etc. in the soil samples. The characterization and discrimination studies have been also explored to achieve unbiased results in a forensic setting.

Despite the ample application of spectroscopic methods in chemical, biological, and physical sciences, the utilization of these methods is deprived of soil analysis. According to the Web of Science search with 'Soil', there are around 591,923 publications are reported on soil analysis since 1989 worldwide which includes research articles, book chapters, reviews, etc. Among them, approx. 94.226 % are research articles that explain the exponential level of research on the soil and its constituents across the world. More interestingly, 57.21 % of publications have been published during the last decade. Among these, only 0.54 % of publications have utilized spectroscopic methods for the analysis of soil samples in the last decade.

Soil is a multidisciplinary material having vast applications in core as well as allied fields i.e. in agriculture (crop production), environmental (pollutions), plant sciences (food and household purposes), chemistry (drugs/medicines), forestry (ecological balancing and animal habitat), toxicology (poison and fertilizers), forensic science (criminal identification), etc. The majority of researches have been published on environmental soils because soil contamination affects the environment considerably which ultimately influences human health. The research on agricultural studies on soil samples has gained much importance as it leads to developing the strategies for enhancing the crop productions as well as eliminates those parameters which adversely affect the productions. The Web of Science data is presented in Fig. 3 along with some major/minor research areas.'

The major research areas include environmental, soil science, chemistry analytical, geosciences, plant science, agronomy, ecology, etc. while minor research disciplines include remote sensing, toxicology, spectroscopy, statistical probability, and forensic science. It is clear from the data that there is a need for boosting the spectroscopic methods for the examination of soil samples. In spectroscopic methods, FTIR is the most used spectroscopic technique for the investigation of soil organic/inorganic constituents. Although Raman is more sensitive and accurate than FTIR spectroscopy; yet, the use of Raman spectroscopy is very limited for soil investigation. Unexpectedly, in the era of multivariate modeling, the spectroscopic methods combined with statistical modeling are utilized in only 780 research papers. Moreover, the field of forensic science in soil analysis is not explored much.

Moreover, most of the work on soil has been done in the USA, China, Germany, Brazil, and Australia according to the published literature. India is ranked at 6th position in soil examination as shown in Fig. 4.

The ongoing researches in India can support the Government to form some regulations which may improve the quality of soil and crop production. Some major research areas that are in limelight in India are; a study of insecticides and their effect on agriculture; spatial variability of soil properties that are important for agriculture productivity; a bacterial study on agriculture soil; digital soil mapping, etc. Though plenty of works on agricultural soil has been reported by authors yet there is a wide gap vis-à-vis forensic investigation.

6.2. Strengths and limitations of spectroscopic methods

UV–Vis spectroscopy works on electronic transitions of the molecule which is specific for every material and mostly used in diffuse reflectance mode for soil analysis. Similarly, NIR spectroscopy in diffuse reflectance sampling mode is a widely used technique nowadays to predict the chemical properties of the soil because of its non-destructiveness, fast, accurate, and reproducible results. In this mode, many soil properties can be estimated from a single measurement.

IR spectroscopy is a powerful tool for qualitative and quantitative identification of particular functional groups in organic matter. IR is used in three modes; transmission, diffuse reflectance, and ATR mode. The major advantage of ATR-FTIR is that it works on aqueous samples also while transmittance and diffuse reflectance work on desiccated samples only. However, zero dipole moment compounds do not give IR spectra. This limitation is overcome by Raman spectroscopy. It can also detect IR inactive molecules precisely. Among all spectroscopic methods, Raman spectroscopy is the most sensitive technique because it works on the light of the laser. In this, the laser is absorbed by the sample and then reemitted with a different frequency known as Raman Effect. These frequencies give information about the sample. Similarly, LIBS spectroscopy analyzed the soil samples by generating the plasma with the help of pulsed lasers. For ideal matrixes, the spectral lines do not get overlapped and their intensities provide the concentration of the elements. However, the ideal matrix is not possible for complex samples such as soils and thus influences the accuracy in quantitative analysis.

More recently, portable NIR, FTIR, Raman, and LIBS spectroscopy has evolved as advanced analytical methods for the on-spot analysis of
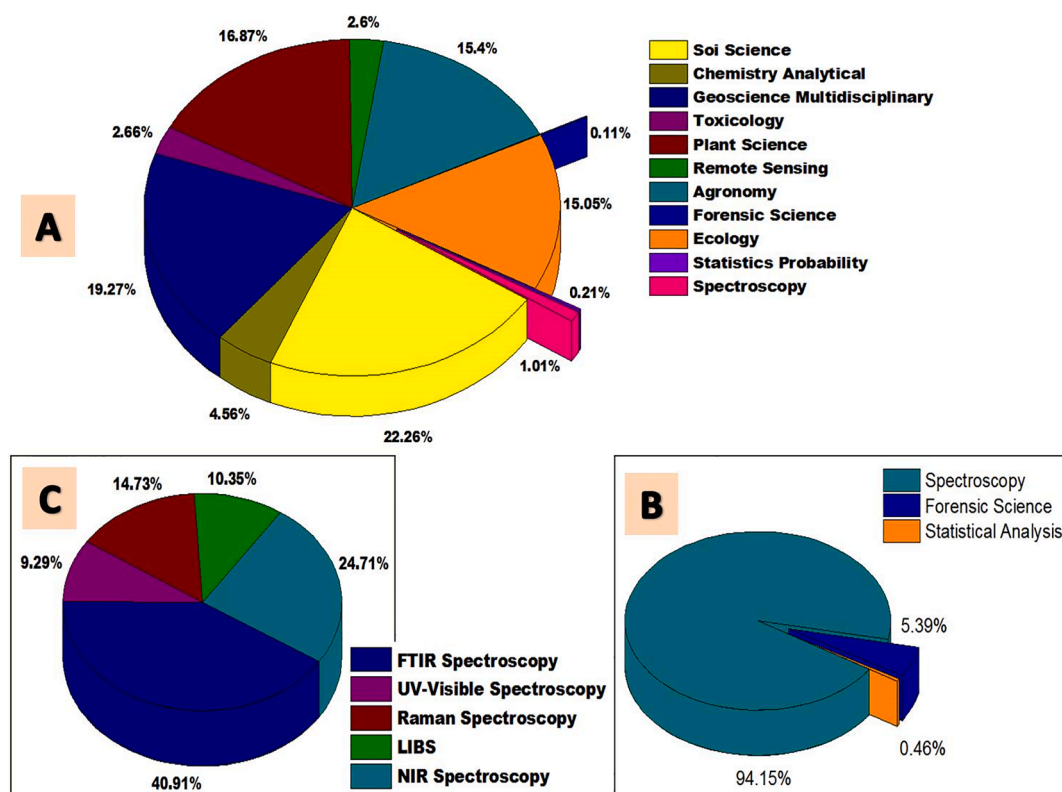
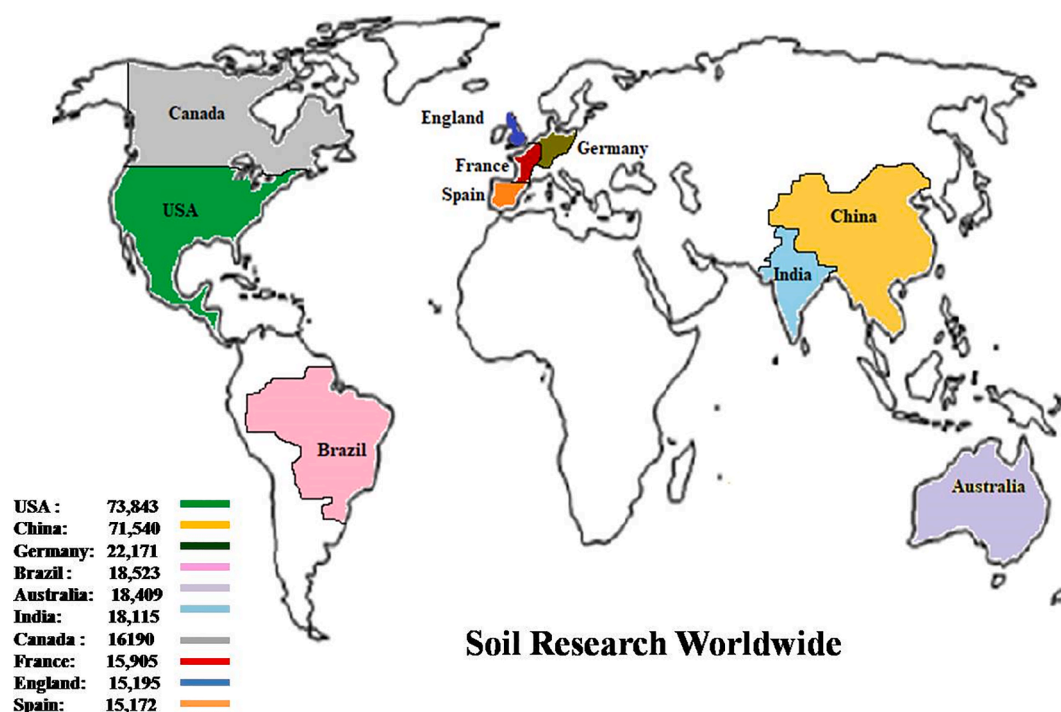**Fig. 3.** Major and minor research areas of the soil science.

Fig. 4. Main geographical regions having maximum soil research across the world.

the soils. Previously, FTIR was used in transmittance mode which requires sample preparation, also known as the KBr pellet technique. This methodology is time taking and tedious to handle. However, nowadays, ATR mode is the most used method in FTIR spectroscopy which is fast, requires no sample preparations, and facilitates accurate results. FTIR generally provides information about the functional group present in a

compound. Despite the various advantages of spectroscopic methods, some limitations cannot be avoided. These limitations are;

- Diffuse reflectance spectroscopy can be affected by different physical properties such as color, particle size, surface texture, etc.

• The change in dipole moment is necessary for IR active molecules. Hence, all compounds are not IR active.
• Raman spectroscopy is very expensive; having fluorescence problems and sometimes, the required light source is not available for spectra acquisitions.
• In LIBS, the ideal matrix is not possible for the complex samples.
• For the data analysis by multivariate methods, one should strictly follow the mathematical assumptions should strictly follow before the data analysis.

6.3. Future challenges

Increased human impacts, i.e., industrialization on fertile soils often result in soil degradation and extensive bare land. In the last 2–3 decades, the climate has been changed drastically because of human interference which leads to an increase in greenhouse gases. Most of the present-day problems like soil degradation, natural disasters, heavy or low rainfall, etc. are just because of harsh climate changes. Many studies have been summarized in this review article that helps in the determination of SOM, SOC, and phosphate contents, factor influencing soil contaminations, etc. which ultimately facilitates in increasing the soil fertility and hence, crop productions. Yet, more researches are required to tackle future problems regarding soil science. Moreover, soil research is not explored in forensic science where it can play an important role as physical evidence in the cases like wildlife crime, hit and run cases (soil on vehicle), murder in indoor and outdoor, assault cases, etc. The examination of soil can help in linking the suspect to the crime. Therefore, it is very important to determine the origin of the soil. Some of the future challenges or gaps regarding soil investigations are;

i. New materials can be developed for increasing the water retention capacity of the soil.
ii. More research should be focused on enriching the soil with SOM, especially in eroded and depleted geographical areas.
iii. The mixture of soil should also be examined as no literature is available for the determination of mixing of soil with the analytical methods as per the best knowledge of authors.
iv. The effect of environmental factors such as climate, weather, humidity, etc. on soil should be studied in more depth.
v. The incorporation of statistical methods provides more subjectivity in the results. In this review, most of the research papers utilized only one or two statistical models in their studies. It is suggested to include more methods to get more accurate and significant results.
vi. The mapping of soil has not been in most of the country which is very crucial for agriculture as well as forensic point of view.
vii. The effect of prolonged heating on soil has been not studied which can be helpful in fire and arson cases.
viii. Extensive research has been done on soil, yet the country-wise computer database is not available to date.

7. Conclusions

This review mainly focuses on the spectroscopic application of the soil. Although, a lot of research has been done on soil science; yet, some gaps have to be filled. The spectroscopic techniques have advantages over conventional methods. Recently, spectroscopic methods particularly LIBS, Raman spectroscopy, and ATR-FTIR are gaining more popularity in soil investigation due to their fast, automated, non-destructive, environmentally friendly character; provide accurate, repeatable, and significant results. However, their drawbacks and instrument specifications such as scans, wavelength range, and stability must be considered before the spectral measurements. Similarly, sample preparation in UV–Visible and FTIR can also affect the results. The advanced chemometric methods provide objectivity to the results. However, basic prerequisites and assumptions should be followed before

applying such methods otherwise false positive/negatives results might be obtained. Still, the scope of soil identification is wide open particularly in agriculture and forensic scenario by employing advanced analytical and chemometric methods altogether. In the coming years, more research would need to be done to improve the prediction ability, i.e., organic/inorganic constituents in the soil, soil forensics, geographical areas of soil, soil forecasting, etc. by using multivariate methods.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.microc.2021.106836.

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