Application of spectroscopy in pollution monitoring

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ABSTRACT

The motivation for the present review study is to highlight the various applications of spectroscopy in pollution monitoring and environmental hazards happening in our day to day life across the globe. Environmental pollution is rising significantly due to several anthropogenic activities such as excessive use of harmful chemicals and emission of toxic gases causing severe environmental degradation through various pollution, such as, Air Pollution, Water Pollution, Land Pollution, Sound Pollution etc. Pollutions possess harmful threats on the environment as well as on the whole biosphere. Different spectroscopic techniques like FT-IR, Fluorescence Spectroscopy, Soil Reflectance Spectroscopy, Laser Spectroscopy, Nuclear Magnetic Resonance (NMR) Spectroscopy, Mass Spectroscopy, Raman Scattering, etc have been found to be very effective and potentially helpful analytical tools to analyze spectral signatures that are omitted by or reflected from targets of interest, such as polluted air, water, or land and thus inspire environmentalists to explore possible and suitable ways to minimize the effects of harmful pollutants. These spectroscopic techniques also enable to identify and monitor the harmful pollutants in the environment and minimize their effects using the knowledge of Spectroscopy.

Keywords: Pollutant, Environmental management, FT-IR spectroscopy, Fluorescence spectroscopy, Soil Reflectance spectroscopy, Laser Spectroscopy, NMR Spectroscopy, Raman Scattering, Mass Spectroscopy

INTRODUCTION

Spectroscopy is the study of light-matter interaction that mostly involves the absorption and emission of radiation by matter, where the light energy plays an important role. The basic principle of any spectroscopic technique is to irradiate the sample with a suitable light, and observe how the sample responses to that excitation. Spectroscopy has been explored to be an effective and potential multidisciplinary analytical tool for investigating the remote atmosphere of the earth [**1**]. The spectral analysis often provides accurate data to create unique reflectance of minerals and compounds found in nature that enables to determine the geological elements and provides accurate information on the possible contamination in rivers, oceans, lakes, and streams [**2**]. Concentration of Green House Gases, such as, as carbon dioxide (CO_2) and methane (CH_4) that are typically released from the automobile and industrial exhausts as well as from the natural sources like volcanic eruptions and causes marked changes on the atmosphere which can also be monitored through detection techniques based on the principles of spectroscopy [**3**]. Moreover, Spectroscopic tools also can be used for the analysis of processes at surfaces like surface modification, surface degradation and study of enzymatic degradation of a substrate film attached to a solid surface, study of sunscreens on human skin, research of cereal, food and wood systems, detection of microbial metabolic products on carbonate mineral surfaces, self-assembled thin films, grafted polymer layers, adsorption processes of biological and synthetic materials [**4**]. Thus several naturally as well as anthropogenic ally occurring pollution aspects can be monitored using techniques based on the principles of spectroscopy to avoid adverse health hazards, which in turn, maintain the biodiversity and conserve natural resources useful for a sustainable future.

APPLICATIONS OF SPECTROSCOPY IN POLLUTION MONITORING

Fourier Transform Infrared (FT-IR) Spectroscopy: Applications

Fourier Transform Infrared (FTIR) Spectroscopy is considered to be a very fast, sensitive and useful spectroscopic tool that mostly measures the vibrational signature of a sample under study in the exposure of Infrared lights. Different characteristic frequencies with different intensities are analyzed to predict information on the qualitative and quantitative aspect of the sample. In the field of environmental studies, FTIR spectroscopy is routinely used to probe a large number of volatile organic compounds (VOC) emitted from industrial and biogenic sources and the gas concentrations across the stratosphere and troposphere [**5**]. The analysis of the FTIR spectra not only provides information on the nature, structure and composition of environmental samples [**6**] but also describes the bonding mechanism through which pollutants are occasionally removed by sorption process. Beside this, FT-IR spectroscopy is also coupled with other techniques like AAS (Atomic Absorption Spectroscopy) to assess air quality parameters [**7, 8**]. Recent FTIR studies are performed widely in different modes such as, transmission, reflectance, Attenuated Total Reflection (ATR-FTIR) and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) in various fields like environmental, agricultural, pharmaceuticals and food studies, where the choice basically depends on sort of information required (surface vs bulk analysis), nature of the samples and the sample preparation time etc [**9**]. The oldest and most common FTIR analysis is conventionally performed in transmission mode where both inorganic and organic samples in all possible forms are analyzed using the resulting interferogram and accordingly the molecular structure, chemical bonding and molecular environment are predicted [**10**]. FTIR studies find special environmental applications in the fields of power plants, petrochemical and natural gas plants, waste disposal, agricultural and industrial sites and detection of gases originating from flames, in biomass burning and in flares [**11- 14**], where direct detection and measurement of both the criteria and toxic pollutants, organic and inorganic volatile compounds in the ambient air is performed to characterize and analyze microorganisms and monitor biotechnological processes at a given location. Based on the unique fingerprint signatures, gases like Ammonia (NH_3), Nitrous oxide (N_2O), Methane (CH_4) and volatile organic compounds (VOC) that are potential sources of air pollution are estimated at commercial animal farms [**15**] and manure management sites. Remote FT-IR spectral radiometers provide sensitive concentration measurements of abundant ambient gases like water vapor (H_2O), Carbon dioxide (CO_2), sulfur dioxide (SO_2), hydrogen sulfide (H_2S), carbon monoxide (CO), hydrochloric acid (HCl), hydrofluoric acid (HF), hydrogen (H_2), helium (He), silicon tetrafluoride (SiF_4), carbon oxysulfide (COS) etc that originate from volcanic eruptions [**16-19**].

IR Spectroscopy provides fast, accurate and very sensitive analytical detection technique that enables to analyze inorganic and organic arsenic acid adsorbed by major minerals such as ferrihydrite (FH), hematite, goethite, and titanium dioxide both qualitatively and quantitatively. This particular process has also found to be very useful to study arsenic contaminants in water bodies [**20**].

Adsorptive removal of heavy metals from aqueous effluents has been explored using ATR-FTIR technique [**21**] that essentially leads to the development of new useful transport models of toxic species in natural waters and remediation of liquid wastes in the water bodies [**22-24**]. ATR-FTIR technique also provides detailed information on the composition of PM (particulate matter) samples [**25**]. On the other hand, accurate estimation of soil composition such as monitoring of several nutrients [**26**] and Nitrate ion concentration in soil to maintain soil fertility and detection of soil pollution issues have been successfully probed using ATR-FTIR detection tools. Thus ATR-FTIR appears to be a potentially useful analytical tool for direct and close to real-time determination of nitrate concentration in soils, with minimal treatment of the soil samples [**27-29**].

Diffuse Reflectance Infrared Fourier Transform (DRIFTS) spectroscopy has been explored as an excellent in-situ nondestructive surface sensitive technique, that mainly operates in transmission mode and studies very tiny amount of (even upto sub-micrograms) nitrate ions in environmental samples like soil, dry deposit samples, and coarse and fine aerosol particles [**30**]. Beside these, characterization of soil organic matter (SOM) to determine the overall soil quality, quantifying the lignite contribution to the total organic carbon (TOC) content of soil samples [**31**], identification and estimation of ambient nitrogen dioxide in terms of nitrite at sub-microgram level **[32**], presence of inorganic salts, such as, sulfate, nitrate, and ammonium in atmospheric aerosols [**33**], characterization of gas sensors to detect toxic pollutants such as CO, H_2S, NO_x, SO_2, and inflammable gases such as hydrocarbons, H_2, CH_4 etc [**34**] are also found to be potentially useful and important applications of DRIFTS technique.

Fluorescence Spectroscopy: Applications

Fluorescence spectroscopy (also known as fluorimetry or spectrofluorometry) offers useful optical detection schemes that have been continuously used to assess environmental quality through pollution monitoring for last few decades. The usual excitation wavelength and the detector to analyze samples under fluorescence detection schemes depend mainly on the nature of the sample under study. The identification and recognition of fluorophores are understood from the fluorescence life time and quantum yield that in turn depends on factors like solvent polarity, temperature, pH and ionic strength of the medium, inter- and intra-molecular interactions etc.

Due to high sensitivity and high selectivity issues, fluorescence based detection techniques have been extensively implemented to explore pollution monitoring through environmental samples especially in the fields of real-time wastewater quality assessment. Based on the fact that wastewater exhibits higher fluorescence intensity compared to natural waters for the components associated with peak T (living and dead cellular material and their exudates) and peak C (microbially reprocessed organic matter), useful correlations between water quality parameters like biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC) and the fluorescence intensity have been successfully explored [**35, 36**] to probe microbiological activity of the water sample [**37**].

Studies using excitation-emission matrix (EEM) based Fluorescence Spectroscopy reveals how to characterize marine and terrestrial dissolved organic matter (DOM) in seawater [**38, 39**], analyze the components in aerobically treated waste water samples collected from municipal waste water plant [**40**], identify fluorophores like humic-like C, tyrosine-like B and tryptophan-like T in rain water samples [**41**]. Laser Induced Fluorescence (LIF) is another useful analytical tool that offers in-situ detection of water pollutants and predict their possible interactions with phytoplankton and break-down products (yellow substances) [**42**], that enables to detect trace amount of heavy metals like lead [**43**], cadmium [**44**], chromium [**45, 46**] in water samples and effectively uses for in situ sea water analysis for deep sea [**47-49**]. LIF also finds application in the classification of viruses and markedly reduces the time and operational cost of virus analysis [**50**].

Fluorescence detection schemes also play important roles in the monitoring of soil quality estimating the pollutant like the concentration of Poly-cyclic aromatic hydrocarbons (PAH) [**51**] and also evaluate the humidification degree of soil organic matter (SOM) [**52**].

Soil Reflectance Spectroscopy: Applications

Soil reflectance spectroscopy is an emerging technique to assess soil properties rapidly from efficient detection and monitoring of soil contaminants such as petroleum hydrocarbons, heavy metals like Ni, Cr, Cu, Cd, Hg, Pb, Zn and As, acid mine drainage and pesticides. The fact that soil moisture is highly correlated with soil spectra enables near IR based reflectance spectroscopy (NIRS) to be utilized across several disciplines such as food science, pharmacology, textile, tobacco, and oil industries [**53**]. Sensitive and accurate predictions of pesticide sorption to soil became possible from NIRS studies [**54**]. Few heavy metals such as Cu and Zn can also often serve the role of essential micronutrients for vegetation species and thus exhibit positive effects in the reflectance spectra like a red-shift of the red edge and decreased reflection indicating enhanced photosynthetic activity [**55**]. The detection technique also finds useful and have potential applications in planetary surface remote sensing studies [**56, 57**] and land resource utilization studies [**58, 59**].

Laser Spectroscopy: Applications

Laser based spectroscopic tools started developing soon after the laser was discovered in 1960 and found potential applications in atmospheric studies [**60**]. A large number of linear as well as nonlinear detection schemes based on the principles of laser action are routinely used to detect environmental pollutants, where particularly the interaction of the trace species with laser light (absorption, emission, scattering) is monitored. A couple of suitable features of the laser, such as, high selectivity and sensitivity, wide dynamic monitoring range, wide tunability, fast response, good temporal resolution, noninvasiveness and non-destructiveness, make the laser based analysis and detection more robust and widely applicable in the vast field of environmental studies. Absorption based laser detections find useful applications, such as, detection of specific molecules in gas sensors. Remote sensing techniques like Light Detection and Ranging (LIDAR) and Differential Optical Absorption LIDAR (DIAL) mainly involves the detection and measurement of radiation of different wavelengths reflected or scattered from distant samples and enables to understand how particles mix vertically in the atmosphere over time.

LIDAR is operated from ground, trucks, aircraft platforms and spacecraft [**61, 62**] where a laser source is used to measure distance by illuminating an atmospheric target like particles or water vapor and the backscattered light that reflects back to its sensor is analyzed. LIDAR is found to be a very popular detection scheme that studies trace constituents, aerosols, atmospheric structure and dynamics, clouds, and important meteorological parameters, such as temperature, humidity and wind velocity and thus enables to predict accurate information on the air quality. On the other hand, DIAL explores the concentration of molecules like O_3, CO_2, CO, CH_4, H_2O in the space using two different wavelengths [**62**]. Fluorescence LIDAR has been found to be a potential detection scheme that monitors water and vegetation [**63**] to identify environmental stress [**64**] where spectral signatures from enclosed trace elements are analyzed to determine their geographical origin that assists in restoration activities [**65**].

A multi-photon process that involves simultaneous absorption of two or more laser photons via virtual states [**66**] gives rise to Multi-Photon Excited Fluorescence (MPEF) detection that investigates the aerosol composition [**67, 68**] in ambient air and thus plays an important role in the field of pollution monitoring. Resonant Enhanced Multi-Photon Ionization (REMPI) offers another important analytical detection scheme that detects and identifies a wide variety of compounds in the environment such as polychlorinated dioxin and furan below parts per trillion (ppt) concentrations directly in the ambient gases [**69**].

Laser-Induced Breakdown Spectroscopy (LIBS) (also known as Laser-Induced Plasma Spectroscopy, LIPS) leads to the generation of a dielectric breakdown through optical absorption using high intensity laser light that enables to analytical detection (detection limit is in the order of ppm or even better) of trace elements in solid materials [**70 - 72**] with high spatial and temporal resolution.

Other spectroscopic applications

In order to monitor environmental pollution, many other detection schemes based on the principles of well known spectroscopic techniques, such as, Nuclear Magnetic Resonance (NMR) Spectroscopy, Mass Spectroscopy, Raman Spectroscopy are also quite popular and have been reported in the literature. NMR is one of the premiere techniques for studying intermolecular interactions and thus it has been extensively used to explore potential detection tools to characterize humic substances, to investigate the environmental chemistry of humic substances through their interactions with organic contaminants and toxic metals in nature and to study sorption by humic substance and soil [**73**]. On the other hand, few popular detection schemes based on Mass Spectroscopy like ambient ionization mass spectrometry (AIMS) [**74**] are reported as playing very important role in aiding our understanding of environmental pollution and processes. Analysis of air quality parameters, particularly the identification and estimation of aerosols /particulate matter, industrial and biogenic emissions like flue gas, studies on Drinking Water, Surface Water, Wastewater and soil quality parameters are efficiently performed by Mass Spectroscopic Techniques [**75**]. Surface enhanced Raman spectroscopy (SERS) has emerged as one of the most promising and versatile analytical tools in the field on Environmental pollution monitoring schemes. This technique offers sensitive tools for the determination of organic pollutants like pesticides, PAHs and PCBs, explosives, heavy metal ions, and pathogens. SERS also offers on-site sensitive detection agricultural pollutants like biological pollutants including bacteria and viruses, chemical pollutants that include pesticides, antibiotics, and additives, microplastics and also nanoparticles from the environment [**76, 77**].

CONCLUSION

The present study aims to highlight how environmental pollution monitoring can be effectively done using the detection techniques based on the principles of spectroscopy. Few important and popular applications of FT-IR, Fluorescence Spectroscopy, Soil Reflectance Spectroscopy and Laser Spectroscopy are given emphasis in the present article to describe how qualities of different environmental samples are assessed to predict the pollution aspects related mostly to air, water and land. All the schemes highlighted in the discussion part above have been found to offer common advantages, such as, real time and rapid data collection and reporting, excellent sample-to-sample reproducibility, enhanced frequency accuracy, high signal-to noise ratios, very good sensitivity and analytical performance compared to the other known detection methods and thus enable to explore the spectroscopic tools as very useful in predicting and correct diagnosis of environmental hazards. Additionally such studies also assess the impact of pollution on health and environment and determine the level of decontamination processes as well.

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