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RESEARCH ARTICLE

Identification and characterization of functional groups in epiphytic lichen *Pyxine cocoes* (Sw.) Nyl. in proximity to coal based Thermal Power Plants in Uttar Pradesh, India

Namita Gupta[1], Vartika Gupta[2*], S. K. Dwivedi[1], D. K. Upreti[3]

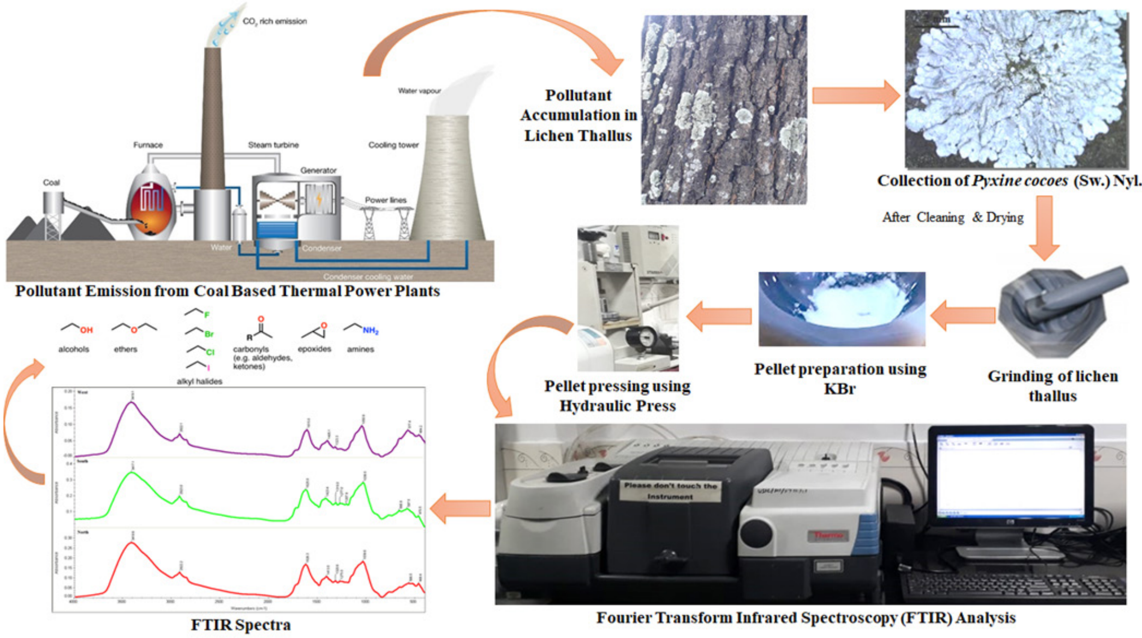
Abstract

Thermal power plants rely on fossil fuels such as coal, oil, or natural gas to produce heat, but they are significant contributors to environmental pollution, emitting metals and other harmful substances. However, the utilization of Fourier Transform Infrared Spectroscopy (FTIR) methods to assess atmospheric pollution in disturbed tropical environments using the spectral properties of lichens has been underexplored. In this study, toxitolerant foliose lichen, *Pyxine cocoes* (Sw.) Nyl. was collected from various disturbed sites around Panki and Feroze Gandhi Unchahar National Thermal Power Plants (TPPs) in Uttar Pradesh, India and subjected to FTIR analysis. The objective was to investigate and compare the functional groups associated with metal accumulation in lichen thalli.

Results of the FTIR analysis revealed similar absorption bands in appearance but varying in intensity, indicating that both TPPs produce comparable chemical components with varying metabolite quantities. The identified specific functional groups responsible for distinct characteristics within the chemical composition of phytochemical compounds in lichens. The presence of metabolites in *P. cocoes* spectra enhanced the detection probability of IR bands in various regions, including 3500-3300 cm^{-1} (N-H and O-H groups), 3300-2500 cm^{-1} (O-H stretching; carboxylic acid), 1450-1400 cm^{-1} (C=O symmetric stretching –COO-). FTIR offers a faster and more reliable approach, particularly with the cost-effectiveness and wide distribution of lichens. This study highlights the valuable information obtained through FTIR analysis, which enhances understanding of chemical involvement in polluted environments.

Keywords: Bioaccumulation**,** FTIR Spectroscopy, Lichens, Metabolites, Pollution, Thermal Power Plants

Graphical Abstract



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Introduction

Coal is widely recognized as one of the foremost energy sources globally, widely utilized for electricity generation and remains the most abundant availability among fossil fuels. However, the emissions arising from coal-fired power plants worldwide contribute significantly to a host of illnesses and premature deaths. Despite its significant impact on human health and its role as a major source of toxic pollutants, coal has remained a staple in global energy production for decades. The United States (US) reportedly possesses a quarter of the world's total fossil fuel reserves, with significant reserves also found in countries like Russia, China, Australia, South Africa and India (Vig *et al.* 2023). In India particularly, atmospheric emissions from coal-fired power plants pose a significant threat to human health. In the period of 2010-2011, 111 plants with a collective generation capacity of 121 gigawatt consumed 503 million tons of coal. This consumption led to emissions of approximately 580 kilotons of particulates with a diameter less than 2.5 µm ($PM_{2.5}$), 2100 kilotons of sulfur dioxide (SO_2), 2000 kilotons of nitrogen oxides, 1100 kilotons of carbon monoxide (CO), 100 kilotons of volatile organic compounds and 665 million tons of carbon dioxide (CO_2). These emissions were linked to an estimated 80,000 to 115,000 premature deaths and 20 million asthma cases due to $PM_{2.5}$ pollution exposure. The resultant healthcare costs, borne by both the public and the government, were estimated at Rs. 16,000 to 23,000 crores (USD 3.2 to 4.6 billion) (Guttikunda and Jawahar 2014).

The environmental impact of TPPs, particularly concerning the emission of heavy metals, raises significant concerns. Metals such as arsenic (As), cadmium (Ca), lead (Pb) and mercury (Hg) emitted into the atmosphere, pose threats to both ecosystems and human health (Zhang *et al.* 2020). It is imperative to monitor the presence and concentration of these metals to assess environmental damage and implement remedial measures. Biological indicators such as lichens, offer an effective, cheap and reliable method for monitoring heavy metal pollution.

Lichens are regarded as promising biomonitors and sensitive indicators of air pollution, capable of assessing changes at various levels to determine the impact of air pollutants (Malaspina *et al.* 2018). Lichens are particularly susceptible to SO_2 due to their ability to absorb it, resulting in fast sulphur accumulation when exposed to high levels of SO_2 pollution (Satya and Upreti 2015). Due to their high sensitivity to acidic gases and enormous ability to accumulate both organic and inorganic chemicals beyond their physiological needs, lichens serve as effective tools for quantifying pollution in specific environments (Sujetovienė 2015). Lichens are studied worldwide for assessing physiological parameters, metals and polyaromatic hydrocarbons (Protano *et al.* 2014, Chetia *et al.* 2021, Thakur *et al.* 2023). The changes in lichen concentration are often linked to the proximity to pollution sources i.e., TPPs (Conti and Cecchetti 2001, Wolterbeek 2002, Adamo *et al.* 2003, Sczapaniak and Bizuk 2003, Giardano *et al.* 2005, Bermudez *et al.* 2009). In India, several studies on pollution monitoring employing lichens as bioindicators have been conducted in various regions. These studies aimed to monitor diverse pollution sources , as reported by (Dubey *et al.* 1999, Upreti and Pandey 2000, Pandey *et al.* 2002, Mishra *et al.* 2003, Saxena *et al.* 2007, Shukla and Upreti 2007, 2008, Bajpai *et al.* 2004, 2010a, b, 2013 a, b, Gupta *et al.* 2017a, b, 2020, 2014, 2015, 2021, 2023, 2024).

FTIR Spectroscopy is the most adaptable analytical technique for determining the kinds of chemical bonds (functional groups) within lichens, offering information about the molecular structure of both organic and inorganic compounds (D' Angelo and Zodrow 2011, Von *et al.* 2014). This technique relies on the transition between quantized vibrational energy states (Coxon *et al.* 2020). Through FTIR spectroscopy analysis, a diverse array of functional chemicals in lichens reveal distinct characteristic peak values. In the spectrum's IR regions, excited states prompt the vibration of molecular bonds, encompassing stretching, bending, rocking, twisting, wagging and deformation. Molecular bonds that have an electric dipole moment susceptible to alteration due to natural vibrations are classified as IR active. IR spectroscopy quantifies these vibrational modes, offering a unique, label-free approach to examining molecular composition and dynamics without disrupting the sample (Chen *et al.* 2015).

Lichens have traditionally served as valuable indicators for studying contaminant distribution and monitoring air quality in urban and industrial environments (Lucadamo *et al.* 2021). However, combined signals can be affected by seasonal atmospheric circulation patterns, leading to

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[1]Department of Environmental Science, Babasaheb Bhimrao Ambedkar University, Raebareli Road, Lucknow (U.P.), India-226025

[2]Department of Botany (Environmental Sciences), University of Lucknow, (NBRI), Lucknow (U.P.), India -226007

[3]Lichenology Laboratory, CSIR- National Botanical Research Institute, Rana Pratap Marg, Lucknow (U.P.), India -226001

***Corresponding Author:** Vartika Gupta, Department of Botany (Environmental Sciences), University of Lucknow, Lucknow (U.P.), India -226007, E-Mail: vartika1292@gmail.com

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a reduction in combined signals (Vigouroux *et al.* 2015). In India, research on the impact of TPPs on vegetation and air quality deterioration has been limited (Rao *et al.* 1990, Singh *et al.* 1994). Nonetheless, studies have explored the effect of TPPs emissions on bioaccumulation of metals, spatial distribution, and lichen physiology in Feroze Gandhi Unchahar Thermal Power Plant, Raebareli, Uttar Pradesh as reported by (Bajpai *et al.* 2010a,b); from Tanda Thermal Power Plant, Ambedkar Nagar, Uttar Pradesh by (Gupta *et al.* 2017a); from Panki Thermal Power Plant, Kanpur, Uttar Pradesh by (Gupta *et al.* 2017b). Other studies have focused on physiological responses using two growth forms of lichens around coal-based Tanda Thermal Power Plant, Ambedkar Nagar, Uttar Pradesh, India (Gupta *et al.* 2020) and phytochemical screening by FTIR spectroscopic analysis of lichen *Rinodina sophodes* commonly growing around Panki and Feroze Gandhi Unchahar Thermal Power Plants of Uttar Pradesh, India as reported by (Gupta *et al.* 2021). Despite these research, only few research have utilized FTIR analysis with lichens assummarized in Table 1. Hence,

Table 1: Utilization of lichen for FTIR analysis in the World

S. No.	*Countries*	*State/Region*	*Locations*	*Species involved*	*Technique Used*	*References*
1	Malaysia	Pahang	Gohtong Jaya, Genting Highlands,	*Parmotrema tinctorum*	FTIR Analysis	Fam *et al.* 2014
			Genting Highlands, Golf Course area, Taman Awana (non-polluted); JalamAwana, Semi polluted area, JalanGohtong (polluted area)	*Usnea baileyi*	FTIR Analysis	Abu *et al.* 2014
2	Southeast Asia	Thailand	KhaoYai National Park in NakornRachasrima Province and Queen Sirikit Botanic Garden in Chiang Mai Province	*Parmotrema tinctorum*	ATR-FTIR Analysis	Srivibbon *et al.* 2014
3	India	Andhra Pradesh	Goolapalli, Ramakuppammandalam, Chittoor district	*Parmeliopsis ambigua, Punctelia subrudecta, Evernia mesomorpha, Xanthoparmelia plitti*	Biosynthesis of SNPs, Production of Mycelia Mat, Synthesis SNPs by Mycelia Mat, Chracterization of SNPs, UV-VIS Spectra Analysis, FTIR Analysis, Antimicrobial Activity of SNPs, Determination of Biological Activities of the SNPs	Dasari *et al.* 2013
		Uttar Pradesh	Ambedkar Nagar, Tanda TPP	*Pyxine cocoes* and *Bacidia incongruens*	Metals analysis, SEM and FTIR	Gupta *et al.* 2017a
			Panki Thermal Power Plant, Kanpur and Feroze Gandhi Unchahr Thermal Power Plant, Raebareli	*Rinodina sophodes*	FTIR Analysis	Gupta *et al.* 2021
			Pharmacy Unit, Aligarh Muslim University, Aligarh	*Usnea longissima*	UV-VIS, FTIR, TEM and SEM Analysis, Evaluation of antibacterial activity	Siddqi *et al.* 2018
			Bahraich	*Bacidia convexula* and *B. submedialis*	Metals analysis, SEM and FTIR	Gupta *et al.* 2024
		Maharastra	Kohlapur	*Parmelia perlata* (Decolourization and biodegradable of Solvent Red 24 (SR24)	HPTLC, FTIR and GC-HRMS; Phytotoxicity and genotoxicity analysis	Kulkarni *et al.* 2014
		Tamil Nadu	Local Herbal Market	*Parmelia sulcata*	Estimation of free radicals, total phenols, total flavonoids; GC-MS, FTIR and NMR Analysis	Gandhi *et al.* 2022
4	Asia & Europe	Turkey	Middle Anatolian Region	*Cetraria isladica*	Synthesis and Characterization (by TEM, EDX, UV-VIS, FTIR Analysis) of Ag nanoparticles	Yildiz *et al.* 2014
			Textile Factory [Acid Red P-2BX (ARP-2BX) dye was supplied]	*Cladonia convolute* and *Evernia prunastri*	Dye biosorption analysis, FTIR Analysis	Bayazit *et al.* 2019

the present study aims to: (i) measure the identified wave numbers corresponding to functional groups, (ii) reveal the functional groups present in lichen thalli of *P. cocoes* using FTIR analysis, (iii) compare the identified FTIR spectra observed from both TPPs.

Materials and Methods

Study Area

Kanpur, the second largest and most populated industrial city in Uttar Pradesh, India, accommodates over 3 million residents, , situated within the Gangetic plain, its coordinates ranges from 26º57’11.86” N to 25º55’25.12” N and 80º00’53.79” E to 80º14’08.95” E. The Panki Thermal Power Plant, Kanpur is located at 26°28’31.41” N and 80°14’25.39” E within the Gangetic Plain of Uttar Pradesh (Figure 1a, b, c). During the investigation, the area surveyed lichen species from 34 different locations in all four directions (i.e., east, west, north, and south). It has an installed capacity of 210 MW (2 x 105 MW), with all units being supplied with coal via railways from BCCL and ECL coal mines. The study area has a humid subtropical climate characterized by three distinct seasons: the Cold season (November to February), the Hot season (March to June) and the Monsoon season (July to October). The monsoon typically brings heavy rainfall (usually 70-80% of the total rainfall) occurs. Despite this, the district has few dispersed, open-canopy deciduous forests due to the fast pace of industrialization, urbanization, and forest degradation.

Raebareli, the district’s population is 3,405,559 (as per the census 2011), making it the 27th largest in the state, situated within the coordinates of 26º35’39.76” N to 25º48’36.00” N and 81º09’59.41” E to 81º20’18.00” E. The Feroze Gandhi Unchahar National Thermal Power Corporation (FGUNTPC) is located in Unchahar, Raebareli, Uttar Pradesh, India, between 25°54’58.18” N and 81°19’45.15” E at an elevation of 120.4 m (Figure 1a, b, c) and situated along on the banks of the Sai River. It is surrounded by agricultural fields and mango orchards. This power plant sources its coal from the North Karnpura Coal Fields and its water from the Sarda Sahayak Canal. It has a stack height of 130 m with an installed capacity of 1050 MW (5 x 210 MW) of installed energy output. The climate of the region is tropical, with eight months of dry weather and four months of rainfall ranging from 110 to 485 mm from June to September. The temperature ranging from 13.2°C in winter to 45.2°C in summer.

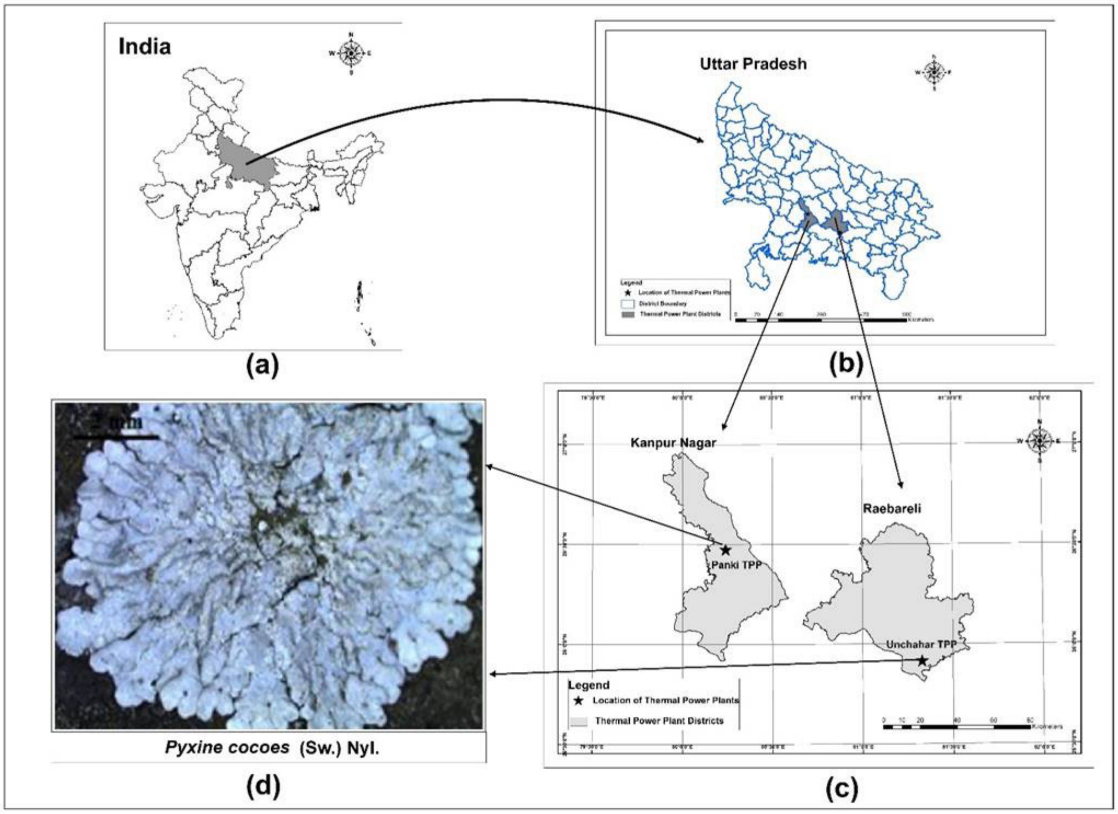


Figure 1: Sampling Locations: (a) Map of India showing Uttar Pradesh; (b) Uttar Pradesh Region showing Kanpur and Raebareli districts; (c) Panki TPP, Kanpur and Feroze Gandhi Unchahar NTPC, Raebareli; (d) Lichen species *Pyxine cocoes* (Sw.) Nyl. collected from the locations around TPPs

Sample Collection

The area around both TPPs was randomly surveyed for lichen sample collection from 114 locations around the thermal power plants. The lichen *P. cocoes* exhibited abundantly growth on the trunks, barks, and branches of *Mangifera indica* (Mango), *Acacia nilotica* (Babool) and *Azadirachta indica* (Neem) trees around both the thermal power plants and further taken for FTIR analysis (Figure 2).

Collected samples were dried and stored in the paper packet. The voucher specimens were preserved in the Lichen Herbarium (LWG) of CSIR- National Botanical Research Institute, Lucknow, India. The morphological, anatomical and chemical characteristics of the lichen samples were evaluated using a LABOMED dissecting microscope for external morphology and LEICA ATC 2000 compound microscope for microscopic anatomical features of the samples. The macro lichen key outlined by (Awasthi 2007) was utilized as the main literature reference for the identification process. TLC in solvent system A (Toluene: 1-4 Dioxane and Acetic acid; 180:60:4) was used to identify the chemical component contained in the lichen thallus (Orange *et al.* 2001).

Fourier Transform Infrared (FTIR) Analysis

The FTIR analysis was done by an FTIR spectroscope (Thermo-Nicolet 6700). To eliminate moisture content, the pellets of lichen samples were dried in an oven at 40-50°C for 4 to 5 hrs. Dried powders of lichen samples were utilized for FTIR analysis. The sample (5 mg) was mixed with KBr pulverized and formed into a disk-shaped pellet. The dried biomass of lichens was ground into powders (blended with dry spectroscopic grade powders) and then hydraulic pressure (CAP-15T) was used to compress the KBr-based pellet into a thin disc under ten tons of pressure. Samples were scanned at the frequency region of 400- 4000 cm^{-1} against the KBr background.

Results and Discussion

Morphological, anatomical and chemical analysis

Pyxine cocoes (Sw.) Nyl.

Thallus corticolous, foliose, whitish grey, orbicular, 1.8-6.0 cm across, UV+ yellow, maculate, sorediata; lobes rotund, pruinose, 0.4-1.3 mm wide; medulla white to off-white; lower surface pale yellow to brown, rhizines brownish. Ascomata apothecia, rare, 0.3-1.2 mm diam.; margin con colours with the thallus, gradually darkening and becoming lecidine; disc black, plane to concave, epruinose of slightly white pruinose. Exciple hyaline, with algal cell when young, brownish at maturity; epihymenium brown, K+ purple; hymenium hyaline to slightly yellowish; hypothecium brown; paraphyses simple to branching, apical cell swollen and brown pigmented. Ascus 8 spored, clavate; ascospores brown, transversely 1 septate, mischoblastiomorphic, oblong, 15.3-22.1 x 7.6-9.1 µm (2.5x). Chemistry: Thallus K+ yellow, C-, KC-, P-. TLC: Triterpenes between Rf 4-5, a yellow spot of lichenoxanthane between Rf 6-7 were detected.

Fourier Transform Infrared (FTIR) Analysis

FTIR analysis was employed to find specific spectroscopic biomarkers in *P. cocoes,* facilitating rapid and reliable identification and discrimination of functional groups around both thermal power plants in Uttar Pradesh.

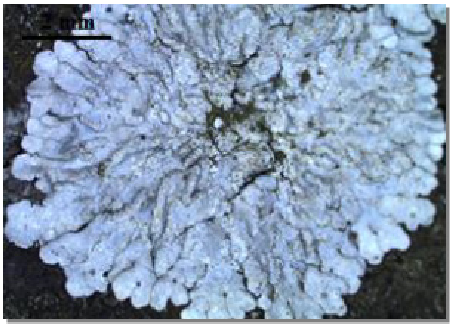
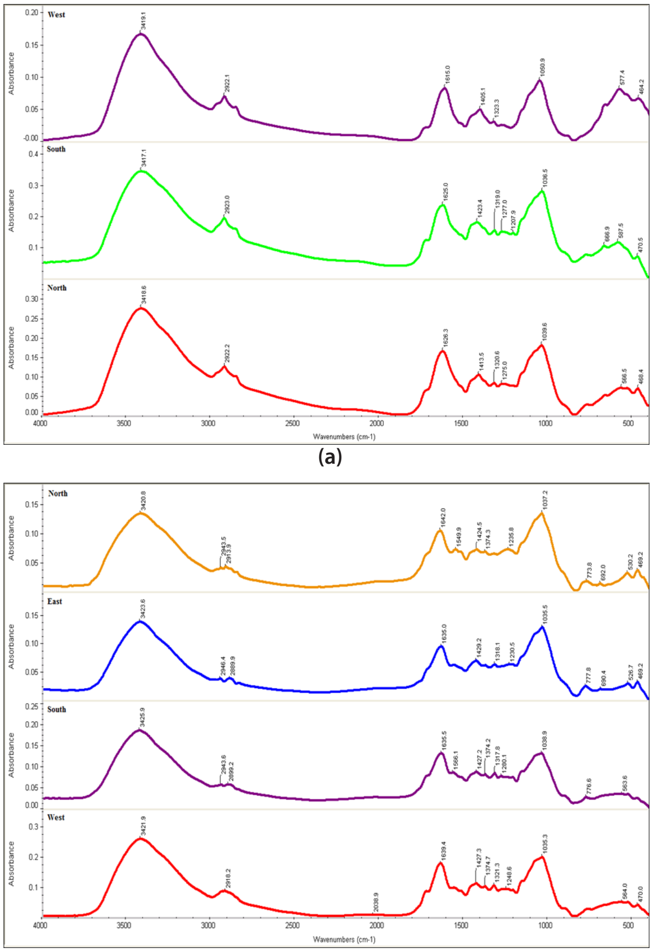


Figure 2: Thallus of Lichen Species *Pyxine cocoes* (Sw.) Nyl.



(a)

(b)

Figure 3: Direction-wise FTIR spectra of lichen species *P. cocoes* (a) Panki Thermal Power Plant, Kanpur; and (b) Feroze Gandhi Unchahar National Thermal Power Corporation, Raebareli

Table 2: Band assignments for FTIR spectra of lichen species *P. cocoes* around Thermal Power Plants

S. No.	*Range of wave number (cm^{-1})*	*Panki Thermal Power Plant, Kanpur Band Position (in cm^{-1})*			*Feroze Gandhi Unchahar Thermal Power Corporation, Raebareli Band Position (in cm^{-1})*				*Band Assignment*
		North	*South*	*West*	*North*	*East*	*South*	*West*	
1	3500-3300	3418.6	3417.1	3419.1	3420.8	3423.6	3425.9	3421.9	N-H stretching (primary, secondary, amines and amides), O-H stretching (alcohols, phenols groups) (Ramrakhiani *et al.* 2011)
2	3300-2500	2922.2	2923.0	2922.1	2943.5	2946.4	2943.6	-	O-H stretching (carboxylic acids)
					2913.9	2889.9	2899.2	2918.2	
3	2200-2000							2038.9	C≡N stretch (nitriles), -C≡C- stretch (alkynes), NH$_3^+$ torsional vibration (Mohan 2005)
4	1760-1665	1626.3	1625.0	1615.0				-	α, β-unsaturated aldehydes, ketones; (Singh *et al.* 2020) C=O stretching (Carbonyls group)
5	1680-1640				1642.0	1635.0	1635.5	1639.4	-C≡C- stretch (alkenes), Amide- I, C=O stretching (Jilie and Shaoning 2007)
6	1560-1530				1549.9	-	1566.1	-	Amide- II, CN stretching, NH bending (Jilie and Shaoning 2007)
7	1450-1400	1413.5	1423.4	1405.1	1424.5	1429.2	1427.2	1427.3	C=O symmetric stretching –COO$^-$ (Naumann 2000)
8	1370-1350				1374.3	-	1374.2	1374.7	C-H rock (alkanes)
9	1350-1300	1320.6	1319.0	1323.3	-	1318.1	1317.8	1321.3	components of α- helix proteins (Adriana and Gabi 2011)
10	1250-1220	1275.0	1277.0	-	1235.8	1230.5	1280.1	1248.6	P=O stretching (asym.) of PO$_2^-$ phosphodiesters (Naumann 2000)
		-	1207.9	-					
11	1080-1010	1039.6	1036.5	1050.9	1037.2	1035.5	1038.9	1035.3	SO$_3$ asymmetric (Cirik *et al.* 2012); C-O bonding due to polysaccharides (Das and Guha 2007)
12	900-600	-	666.9	-					O-CH$_3$ stretching of methoxy groups (Movasaghi *et al.* 2008)
13	800-640				773.8	777.8	776.6	-	C-H out of plane bending vibrations (Jilie and Shaoning 2007)
14	770-620				692.0	690.4	-	-	Amide- V, Out of plane NH bending (Jilie and Shaoning 2007)
15	690-515	566.5	587.5	577.4	530.2	526.7	563.6	564.0	C-Br stretching (alkyl halides)
16	530-400	468.4	470.5	464.2	469.2	469.2	-	470.0	Al-O stretching (AlO$_8$ Octahedral, isolated) (Tarte 1962, 1964)

Variation in frequency, which govern both bond dissociation and bond formation crucial for metal chelation, were monitored through FTIR analysis (Clark *et al.* 2019). This spectroscopic technique furnishes evidence of compounds involved in metal absorption, with alterations in the IR region unveiling the pollutant's influence on the functional groups of lichen species (Figure 3 a, b).

Measurement by FTIR spectra of P. cocoes around Panki Thermal Power Plant, Kanpur

The strong absorbance bands 3500- 3300 cm^{-1} were found for the lichen *P. cocoes* (Table 2; Figure 3a) at 3418.6 cm^{-1} (north), 3419.1 cm^{-1} (west), 3417.1 cm^{-1} (south), which indicated the stretching of bonded N-H/ O-H and the presence of alcohol and phenol groups (Ramrakhiani *et al.* 2011).

The spectral band ranged between 3300-2500 cm^{-1} due to O-H stretching in the presence of carboxylic acid at 2922.2 cm^{-1} (north), 2922.1 cm^{-1} (west), 2923.0 cm^{-1} (south). The absorbance bands observed ranged between 1760-1665 cm^{-1} due to C=O stretching (carbonyl group) and α, β-unsaturated aldehydes, ketones (55) and observed at 1626.3 cm^{-1} (north), 1625.0 cm^{-1} (south), 1615.0 cm^{-1} (west). The bonded C=O symmetric stretching absorbed infrared at 1423.4 cm^{-1} (south), 1413.5 cm^{-1} (north), 1405.1 cm^{-1} (west) respectively (Naumann 2000). The absorbance bands observed at 1323.3 cm^{-1} (west), 1320.6 cm^{-1} (north) and 1319.0 cm^{-1} (south) showed components of α- helix protein (Adriana and Gabi 2011). The absorbance bands ranged between 1250-1220 cm^{-1}were attributed to P=O asymmetric stretching and phosphodiesters at 1275.0 cm^{-1} (north), 1277.0 cm^{-1}, and 1207.9 cm^{-1} (south) respectively (Naumann 2000). The range of wave number 1080-1010 cm^{-1} showed SO_3 asymmetric stretching (Cirik *et al.* 2012); and C-O bonding due to polysaccharides at 1036.5 cm^{-1} (south), 1039.6 cm^{-1} (north) and 1050.9 cm^{-1} (west) respectively (Das and Guha 2007). The range of wave number 900-600 cm^{-1} showed O-CH_2 stretching of methoxy groups only in the south direction at 666.9 cm^{-1} (Movasaghi *et al.* 2008). The peaks range between 690-515 cm^{-1}resulted in absorption due to the vibration modes of C- Br stretching coupled to alkyl halides at 566.5 cm^{-1} (north), 577.4 cm^{-1} (west) and 587.5 cm^{-1} (south) respectively. This phenomenon is principally involved in metal absorption by the formation of chelatesor bond dissociation due to the presence of phytotoxic gases mainly SO_2. The biodeterioration of granite monuments is available using FT Raman Spectroscopic studies on several lichens (Prieto *et al.* 2000). The peaks observed at 468.4 cm^{-1} (north), 470.5 cm^{-1} (south) and 464.2 cm^{-1} (west) showed the presence of vibrational frequencies of Al-O stretching (AlO_8 Octahedral; isolated) (Tarte 1962, 1964). The observations are useful to detect rapidly and characterize the occurrence of lichen *P. cocoes* with different levels of metal accumulation around the thermal power plants.

Measurement by FTIR spectra of P. cocoes around Feroze Gandhi Unchahar National Thermal Power Corporation (FGUNTPC), Raebareli

For lichen *P. cocoes* around Feroze Gandhi Unchahar National Thermal Power Corporation (FGUNTPC), Raebareli (Table 2; Figure 3b), the major absorbance bands ranged between 3500- 3300 cm^{-1}at 3420.8 cm^{-1} (north), 3421.9 cm^{-1} (west), 3423.6 cm^{-1} (east), 3425.9 cm^{-1} (south) and showed the stretching of N-H/ O-H groups and due to asymmetrical vibration of C-H showed the presence of protein and phospholipids (Ramrakhiani *et al.* 2011). The wave numbers observed at 2923.5 & 2913.9 cm^{-1} (north), 2946.4 & 2889.9 cm^{-1} (east), 2943.6 & 2899.2 cm^{-1} (south) and 2918.2 cm^{-1} (west) ranged between absorbance bands 3300-2500 cm^{-1}due to O-H stretching (carboxylic acids). The absorbance bands observed ranged between 2200- 2000 cm^{-1} due to NH_3^+ torsional vibration and C≡N stretch (nitriles), -C≡C- stretch (alkynes), at absorbance value 2038.9 cm^{-1} only in west direction of the study area (Mohan 2005). The wave numbers observed at 1635.0 cm^{-1} (east), 1635.5 cm^{-1} (south), 1639.4 cm^{-1} (west), and 1642.0 cm^{-1} (north) ranged between absorbance bands 1680- 1640 cm^{-1}due to Amine-I, C=O stretching and -C≡C- stretch (alkenes) (Jilie and Shaoning 2007). The wave numbers observed 1560-1530 cm^{-1} due to Amide- II, CN stretching, NH bending at 1549.9 cm^{-1} (north) and 1566.1 cm^{-1} (south) respectively (Jilie and Shaoning 2007). The bonded C=O symmetric stretching absorbed infra-red at wave number 1450-1400 cm^{-1}at all at 1429.2 cm^{-1} (east), 1427.3 cm^{-1} (west), 1427.2 cm^{-1} (south) and 1424.5 cm^{-1} (north) (Naumann 2000). The spectra observed at 1374.7 cm^{-1} (west), 1374.3 cm^{-1} (north) and 1374.2 cm^{-1} (south) showed stretching of C-H rock (alkanes) in the bands ranged from 1370-1350 cm^{-1}. The absorbance bands ranged 1350-1300 cm^{-1} showed components of α- helix protein at 1317.8 cm^{-1} (south), 1318.1 cm^{-1} (east) and 1321.3 cm^{-1} (west) (Adriana and Gabi 2011). The absorbance bands ranged between 1250-1220 cm^{-1} at 1280.1 cm^{-1} (south), 1248.6 cm^{-1} (west), 1230.5 cm^{-1} (east) and 1235.8 cm^{-1} (north) and 1080-1010 cm^{-1}were attributed to P=O asymmetric stretching and phosphodiesters at 1038.9 cm^{-1} (south), 1037.2 cm^{-1} (north) 1035.5 cm^{-1} (east), 1035.3 cm^{-1} (west) (Naumann 2000) and asymmetric stretching of SO_3 (14) as well as C-O bonding due to polysaccharides in all directions respectively (Das and Guha 2007).

The wave numbers 777.8 cm^{-1} (east), 776.6 cm^{-1} (south), and 773.8 cm^{-1} (north) showed C-H out-of-plane bending vibrations. The bands range 770-620 cm^{-1} represents N-H bending with the presence of amine-V at absorbance values 692.0 cm^{-1} (north) and 690.4 cm^{-1} (east) respectively (Jilie and Shaoning 2007). The peaks ranged between 690-515 cm^{-1} resulted in absorption due to the vibration of C-Br stretching (alkyl halides) at 564.0 cm^{-1} (west), 563.6 cm^{-1} (south), 530.2 cm^{-1} (north) and 526.7 cm^{-1} (east) respectively. The peaks observed at 470.0 cm^{-1} (west) and 469.2 cm^{-1} in each (i.e., north and east) direction showed Al-O stretching (AlO_8 Octahedral; isolated) (Tarte 1962, 1964).

The absence of secondary metabolites may explain the large number of bands seen in *P. cocoes.* Due to the presence of more -COOH and -OH groups with varying levels of absorption throughout the study area. The presence of both metabolites in *P. cocoes* increases the chance of detecting the IR band in the 3500-2800 cm^{-1} range. The effect of pollutants on the functional group chemistry of the species is shown by changes in the functional group bands in the IR region of FTIR analysis (Table 2). This mechanism is mostly involved in metal absorption via chelation or bond dissociation caused by the presenceof phytotoxic gases primarily SO_2.

Comparative assessment of FTIR spectral analysis of both TPPs

Comparing the FTIR spectra data of *P. cocoes* collected around the Panki Thermal Power Plant in Kanpur and the Feroze Gandhi Unchahar National Thermal Power Corporation (FGUNTPC) in Raebareli reveals distinct variations in absorbance bands and chemical composition within the lichens. In the vicinity of the Panki Thermal Power Plant, strong absorbance bands were observed in the range of 3500-3300 cm^{-1}, indicating the stretching of bonded N-H/O-H groups and the presence of alcohol and phenol groups. Spectral bands between 3300-2500 cm^{-1} were linked to O-H stretching associated with carboxylic acid, while absorbance bands in the range of 1760-1665 cm^{-1} indicated C=O stretching and the presence of α, β-unsaturated aldehydes and ketones. Moreover, various absorbance bands corresponding to protein and phospholipids were evident across different spectral regions. Vibrational frequencies linked to metal absorption, such as Al-O stretching, were also detected.

Conversely, around the FGUNTPC in Raebareli, major absorbance bands were observed primarily within the 3500-3300 cm^{-1} range, indicative of N-H/O-H groups stretching. Similar to the findings at the Panki site, absorbance bands between 3300-2500 cm^{-1} were associated with O-H stretching in carboxylic acids. Additionally, various absorbance bands corresponding to protein and phospholipids were observed, indicating the presence of similar functional groups as observed in the Panki site. Notably, differences in absorbance bands related to metal absorption and structural vibrations were observed between the two study sites.

Overall, these differences in absorbance bands and chemical composition highlight variations in metal accumulation levels and environmental conditions between the two study sites, providing valuable insights into the impact of thermal power plants on lichen species. Table 2 represents the comparison of band assignments for FTIR spectra of *P. cocoes* around TPPs.

Conclusion

The present study investigated the presence of metabolites within *P. cocoes*, a toxitolerant lichen species collected from areas surrounding two thermal power plants in Uttar Pradesh, India. The study reveals the presence of metabolites in *P. cocoes* spectra, with distinct IR bands observed within specific wavelength ranges. These bands, ranging from 3500-3300 cm^{-1} (related to N-H and O-H functional groups) to 530-400 cm^{-1} (linked with Al-O stretching), signify variations in functional groups potentially influenced by environmental stressors such as pollution. The observed alterations in functional groups, encompassing changes in carbonyl, hydroxyl and aliphatic groups, suggest a responsive mechanism of *P. cocoes* to pollution-induced stress. These alterations, controlled by bond dissociation and formation, indicate the lichen's adaptability to environmental disturbances, highlighting its resilience in a polluted environment. The findings underscore the significance of FTIR spectroscopy as an effective tool for assessing the impacts of environmental pollution on biological systems. By establishing baseline data through FTIR analysis of *P. cocoes* in the vicinity of thermal power plants, this study sets the stages for future investigations into the biochemical mechanisms underlying stress responses in lichen species. Such insights are crucial for guiding conservation strategies aimed at mitigating the detrimental effects of pollution on ecosystems.

Declarations

- All authors are members.
- The manuscript contains unpublished data in the related field of research.
- There is no conflict of interest among authors or with any publisher concerned.

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