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Research Article

Determination of active ingredients in commercial insecticides using spectral characteristics of Fourier transform infrared spectroscopy (FTIR)

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Abstract

Pesticides have become a basic necessity for yield development. This might be credited to the quickly expanding population, which has presented weight on the food creation industry.Fourier Transform Infra-red Spectroscopy utilizes sample with less course of action, less time consuming, simple, fast, non-destructive and environmental friendly infrared-based method. It makes use of Smart iTR window and pellets use on omnic transmission window. In FTIR the peaks formed for the representative sample are from 800 cm^{-1} to 4000 cm^{-1} of wavenumbers against the % transmittance. The FTIR spectra obtained for pesticide formulations were on par with the NIST (National Institute of Standards and Technology) spectra library. Comparing the commercial-grade spectra with the Spectrabase, NIST library and Bio-rad software showed the peak ranges for different functional groups of the compound and can be examined with KnowItAll software's ProcessItIR and AnalyseItIR. We can obtain the active principle of the peak, peak intensities. This method can be viewed as genuine choices to long and tedious chromatographic strategies as a rule suggested for quality control of commercially accessible pesticide formulations and check for adultered formulations that harm agricultural produce.

Keywords: FT-IR, Functional groups, Pesticides, Quality control, Wave numbers

INTRODUCTION

Agriculture is the world's major conservative movement, with over half of the total population being reliant upon agriculture for their livelihood. Pesticides empower the amounts and the nature of yields and food to be controlled and restrict the numerous human illnesses transmitted by insect or rodent vectors. In any case, despite their numerous benefits, pesticides are the absolute generally poisonous, residual and versatile substances in nature. Their unnecessary use deleteriously affects people and nature; their essence in food is especially hazardous. With their ecological security, the capacity to bio-accumulate and harmfulness, pesticides may put the human body in more danger of illness and harm (Fenik *et al*., 2011).

The enrollment, assembling and offer of a pesticide plan infer various controls among which its assessment, security and creation are the most significant. To portray a pesticide, it is important to have the option to decide its composition and chemical and physical properties. The main advantages of Near Infra-Red spectrometry are its nondestructive nature, the possibility to analyze products in real-time, the low cost of equipment maintenance, the fast response times and the possibility to measure directly solid samples, with no sample pre-treatment(Moros *et al*., 2006). Chromatographic methods have been the most broadly utilized techniques today. Regardless, the dynamic standards of the samples permit us that vibrational spectrometry-based systems could be utilized as a genuine option in the quality control of commercial pesticide formulations. Commercially available pesticides are being availed through different chemical formulations such as granular, wettable powder, liquid formulations etc. As the determination of these pesticides entails special extraction procedures which demand costly solvents, time consumable procedures and some other technical aspects to ascertain. By using FTIR spectroscopy, the easy, effective and short time determination of commercial-grade pesticide formulations can be carried out without any processing of samples like in GC-MS, LC-MS, etc. (Armenta *et al*., 2007)

Fourier transform infrared (FTIR) is a fast and micro-destructive spectroscopy method widely applied in the measurement of solid (Post *et al*., 1995), liquid (Van de Voort *et al*., 2004), and gas (Esler *et al*., 2000). This technique is used to identify the compounds' functional groups through different strategies, and FTIR works at a different range of spectra. For the identification of spectra of pesticides active ingredients, mostly the ATR-FTIR is used at mid-range. The connection between ATR-FTIR spectroscopy and other comparative strategies, of all the things considered known as vibrational spectroscopy (Lee *et al*., 2017).

FTIR method was found advantageous for Folpet and Metalaxyl, respectively, found comparable with liquid chromatography results with UV detection and involves a considerable decrease in solvent consumption (Quintas *et al*., 2003). Cyromazine determined with FT-IR and FT-Raman procedure were found statistically compared with reference liquid chromatography procedure and showed the FTIR methods were appropriate for quality control in commercial pesticide formulations (Armenta *et al*., 2004). The waste generation in FT-IR for diuron determination was 3.4 ml $CHCl_3$, in flow injection analysis 9.3ml $CHCl_3$ per sample and those methods consume less organic solvent than an HPLC method, which involves the use of 39 mL of acetonitrile per sample (Armenta *et al*., 2005b). By utilizing FTIR spectrometry, the immediate assurance of malathion in commercial pesticide formulations can be completed, with no pre-treatment of tests, with reproducibility and precision practically identical to those measured utilizing GC–FID, besides, decreasedtime and volume of chlorinated solvents utilized (from 35 ml of $CHCl_3$ to 2 ml) in the analysis (Quintás *et al*., 2004b).

The most well-known practice in the direct examination of solids by IR spectrometry is the utilization of disks arranged from the samples mixed in dry KBr. This method stays away from the utilization of any sort of dissolvable and does not require the analyte to be soluble. Be that as it may, it makes inconvenience for the assurance of the bandpass and for the most part, requires the utilization of an internal standard. That is the purpose behind the limited quantity of papers found in writing utilizing direct estimations on KBr plates (Armenta *et al*., 2005c)

To stimulate the determination of pesticides active ingredients with easy processing methods, less time consuming, environmentally friendly and reduced cost-effective techniques need to be recognized and adopted. Using the spectral characteristics to analyze the active ingredient in commercial pesticides is the best alternative to the ransom and time-consuming chromatography technique. Hence the present study was performed to investigate the applicability of FTIR technique and get the spectral region of sensitivity for the quick determination of active ingredient in various commercially available pesticides at Tiruchirappalli.

MATERIALS AND METHODS

Commercial grade chemicals used

Commercially available pesticides belonging to 21 groups/classes viz., abamectin, ketonenols, neonicotinoid, organochlorine, organofluorine, organophosphates, phenylpyrazole, pyrethroids, quinazoline and thiourea were analysed in FTIR to identify the active ingredients. The powdered and liquid formulations of pesticides were analyzed using transmission window and ATR-Diamond window, respectively. Spectra obtained for each pesticide formulation was processed using Bio-rad software and also compared with the Spectrabase and NIST library. The formulations utilized in the study are presented in Table 1.

Fourier transform infrared spectroscopy (FT-IR)

Fourier transform infrared spectroscopy (FT-IR) is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. An FTIR spectrometer simultaneously collects spectral data in a wide spectral range. The instrument FTIR spectrometry used was Nicolet iS10 using OMNIC spectra software. Two windows were used for sample analysis, such as Smart-iTR window and Omnic transmission window. Here the Spectral data were collected by a Bio-Rad Excalibur 3000 MX FTIR spectrometer and a helium-purged MTEC 300 photoacoustic cell. All the spectra were recorded over the 4000 – 400 cm^{-1} region at a spectral resolution of 8 cm^{-1} and with the 1024 scans co-added. The KBr was used as a pelleting material with powdered and granule formulations and liquid formulations were directly fed in the iTR window.

FTIR procedure

The details of the conditions under which the spectra of insecticides formulations obtained are presented in Table 2.

Omnictransmission window

The powder formulations of insecticides were compressed into a thin pellet for analyzes by FTIR. For the preparation of pesticide pellet samples, IR transparent material, namely KBr was mixed at the ratio of 2:1 in a mortar and pestle for 5 - 10 minutes. Then the mixture was converted into pellets by pressing the prepared

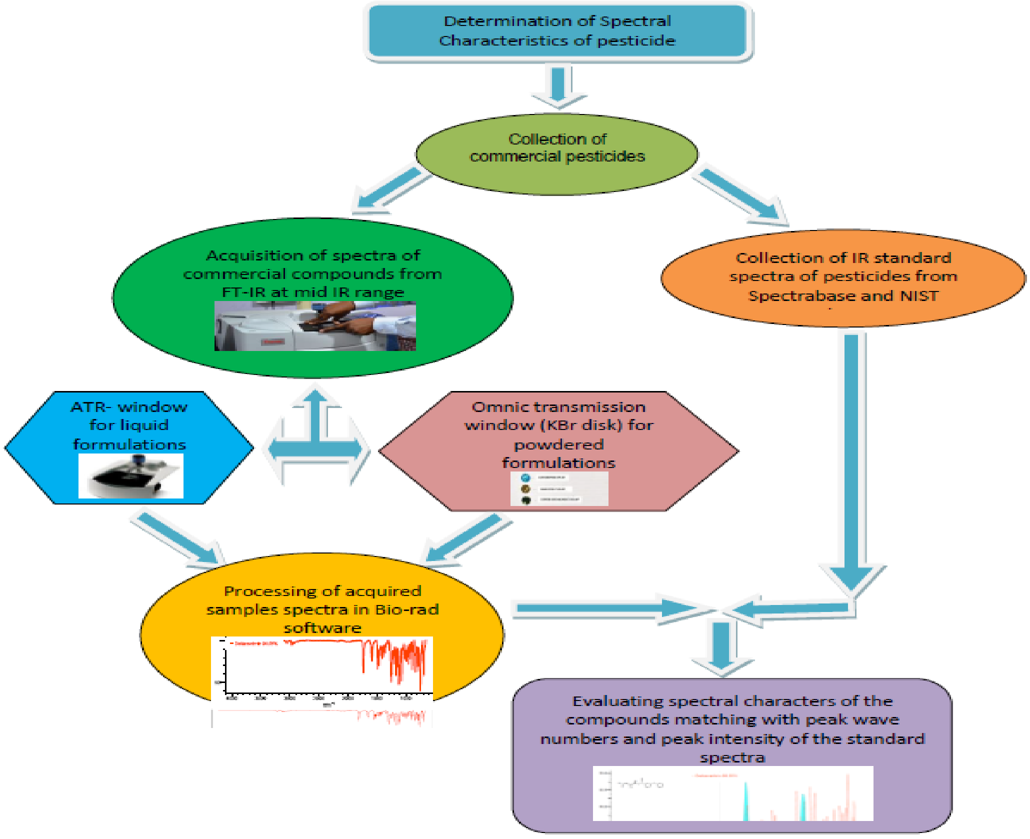

Fig. 1. *Flow Chart of the determination procedure.*

mixture with a hydraulic or hand press into a hard disk. A total laboratory hydraulic press creating a power (force) around 15 tons was used to make a pellet of ideally 0.5 to 1 mm thick, which was then placed in a transmission holder and scanned.

Attenuated total reflectance window

ATR can be used to analyze free-flowing aqueous solutions, viscous liquids, coatings, ecological materials. This technique is often the preferred method for liquid analysis because it simply requires a drop of liquid to be placed on the crystal. In the present study, the ATR window was used for the analysis of liquid pesticide formulations using the Diamond platform. A drop of the compound was placed on the platform in which the infra-red light was present and locked with the screw. Software Omni was used to get the spectrum which was compiled with instrument provides the compound spectrum within 30 to 40 seconds of their intact. It provides the spectrum in absorbance, transmission and other properties.

Processing and comparison of sample spectra with database

The sample spectra obtained from FTIR were compared with the NIST library and processed using the Bio-Rad KnowItAll software. The NIST (National Institute of Standards and Technology) provides Standard Reference Data, which spread a wide scope of logical orders including nuclear and sub-atomic material science, synthetic and precious stone structures, liquids, material properties, biotechnology, optical character acknowledgement and more. SpectraBase is a free online spectral vault from Bio-Rad Laboratories, Inc. The sample spectra can be processed through a huge number of spectra, including natural mixes, inorganic mixes, and polymers. The KnowItAll programming offers far-reaching answers for IR, Raman, NIR, NMR, MS, UV-Vis, and chromatography the flow chart of the determination procedure were given in Fig. 1. The product joined with the world's biggest spectral library, enables scientific experts to separate significantly more prominent information from their phantom information. The results of sample spectrabase processed are presented and discussed here.

RESULTS AND DISCUSSION

Results obtained are presented and discussed below.

Abamectin

It was observed that Emamectin 5% SG contained amines and alcohols as functional groups and have NH, NH_2, and NH_3 salts. The analyzedSpectra(Fig. 2a) showed bands at 1340-1250 cm^{-1} by medium symmetric primary amine NH_3 salt, secondary amine salt of NH at 2800-2000 cm^{-1} and NH_2 at 850-750 cm^{-1}. Alcohol group showed strong stretching of hydrogen-bonded OH at 3300-3280 cm^{-1}. It has NH_2 peak intensity of 69.76% at 759.82 cm^{-1} (Fig. 2b**).**

Ketoenols

Spiromesifen derives from a 1,3,5-trimethylbenzene and a 3,3-dimethylbutyric acid. The commercial compound spectrum(Fig. 3a**)** examined with the bio-rad's know-it-all software showed the peak ranges shown in Fig. 3b. Spiromesifen spectrum had absorption bands at 2959-2952 and 2866-2853 cm^{-1} due to asymmetric and symmetric stretching of CH bond in cyclopentyl group. It contained C=C bond variable stretching of alkane CCCH=CHCC groups at 1680-1620 cm^{-1}. The intensity of the peak at 1022.09 cm^{-1} showed 100% in ProcessItIR.

Neonicotinoids

Acetamiprid is a N-[(6-chloropyridin-3-yl) methyl]-N'-cyano-N-methylethanimidamide. FTIR analysis results of acetamiprid 20% SP (Fig.4a) showed the presence of C-Cl bond stretching at 830-600 cm^{-1}. The amine bonds of NH_2 and NH was located at 1620-1560, 850-750 and 2800-2000 cm^{-1} (NH). The peak at 1531.34 cm^{-1} due to N-H in plane deformation has 100% intensity which was very strong and characteristic of N atom attached to C atom of aromatic ring. The out-of-plane N-H deformation vibration at 900- 600 cm^{-1} was masked by absorption features of aromatic ring(Fig. 4b**).**

Imidacloprid is a systemic insecticide utilized as a foliar spray for the control of different sucking pests and other important bugs of cotton, paddy, chillies, sugarcane, sunflower, okra and mango. FT-IR spectra (fig. 5a) showed strong CH stretching at 2800-2900 cm^{-1} and 2690-2775 cm^{-1}. The signature bands(fig.5b**)** of 1667-1680, 1650-1550 and 830-600 cm^{-1} due to strong stretching of C=O bond, nitrile group (C-N=C) and halogen group C-Cl was seen in the spectra. The peak intensity is 100% at 1667.64 cm^{-1} and 32.03% at 1566.88 cm^{-1}. Quintás *et al*. (2004a) reported $-NO_2$ symmetric stretching band at 1300 – 1250 cm^{-1}.

Thiacloprid is a member of thiazolidines, a nitrile and a monochloropyridine. It derives from a 2-chlorop yridine and a cyanamide. The Thiacloprid 21.7 % SC spectrum (Fig.6a) examined in the KnowItAll software (Fig.6b) showed the presence of nitrile group C-N=C with strong stretched vibration C=N bond at 1550-1650 cm^{-1}. Spectrum also had strong stretching of halogen C-Cl bond at 600-830 cm^{-1}. The peak intensity observed with the spectrum showed 68.79% intensity at 1627.63 cm^{-1} and 100% at 652.59 cm^{-1} and confirmed the presence of nitrile and halogen functional groups.

Thiamethoxam is a xenobiotic and a neonicotinoid insecticide. It is an oxadiazane, a member of 1,3-thiazoles, an organochlorine compound and a 2-nitroguanidine derivative.Thiamethoxam 30% FS spectrum (Fig.7a)examined with the bio-rad's software (Fig.7b)showed medium stretching of C-N bond amine group at 1310-1360 cm^{-1} and strong stretching of C-Cl bond halogen group at 600-830 cm^{-1}. The observed peak intensity of 99.99% at 652.59 cm^{-1} and 46.13% at 1634.86 cm^{-1} showed the halogen and nitrile bonds vibration.

Organochlorines

Dicofol is a nonflowable fluid (or waxy strong), extending from dim to yellow-earthy color and is a viable acaricide controls mites, spider parasites on different yields. Dicofol 18.5% EC (Fig.8a) spectrum processed with ProcessItIR (Fig.8b) of the bio-rad software showed strong stretching bond of halogen group C-Cl in 830-600 cm^{-1}. It also had bands at 3400-3200 cm^{-1} and 1480-1410 cm^{-1} due to strong stretching and deformation of OH bond of $(R)_2CH-OH$, respectively. It showed the 100% intensity of C=O group stretching at 1094.41 cm^{-1}. Results are equated with the NIST spectrum.

Organofluorines

Flubendiamide is 1-*N*-[4-(1,1,1,2,3,3,3-heptafluoropropan-2-yl)-2-methylphenyl]-3-iodo-2-*N*-(2-methyl-1-methylsulfonylpropan-2-yl)benzene-1,2-dicarboxamide. The commercial formulations of 39.35% SC (Fig.9a) spectrum showed the presence of the P group, sulphur compounds and amine groups. The NH bond occurred in the range of 2320-2700 cm^{-1}, PH_2 bond stretching in the range of 2271-2440 cm^{-1} and sulphur bonds like SO_2, S-O and S-C occurs at 1342-1352 cm^{-1}, 891-910 cm^{-1} and 600-700 cm^{-1}(Fig.9b).

Organophosphates

Acephatebelongs to methamidophos is a mixed diacylamine, a phosphoramide, an organic thiophosphate and an organothiophosphate insecticide in which one of the hydrogen is replaced by an acetyl group. Acephate raw sample spectrum (Fig.10a) obtained from FTIR showed C=O stretching at 1697.36 $cm^{-1,}$ and sharp and strong absorption of P=O stretching frequency at 1219.71 cm^{-1} and were attributed to the presence of C=O and P=O bonds in the structure. As compared to the positions of the bonds in the spectrum of acephate, the presence of C=O (carbonyl) and P=O groups was confirmed in the structure of acephate. Fig.10e showed that the bands at 1697.05 cm^{-1} and 1034.14 cm^{-1} had an intensity of 32.98 and 100.00% was obtained using ProcessIt IR. The present results were comparable with the spectra of NIST library.

Chlorpyrifos is a crystalline organophosphate insecticide used on grain, cotton, field, fruit, nut and vegetable crops, and well as on lawns and ornamental plants.

Table 1. Details of insecticides formulations selected for the study.

Class / Group	Active ingredients	Formulations	Molecular formula	IUPAC name	Purpose
Abamectin	Emamectin	5% SG	$C_{56}H_{81}NO_{15}$	4”-deoxy-4”-methylamino derivative	Treatment of heartworm, hookworm, threadworm, and whipworm
Ketoenols	Spiromesifen	22.9% SC	$C_{23}H_{30}O_4$	[2-oxo-3-(2,4,6-trimethylphenyl)-1-oxaspiro[4.4]non-3-en-4-yl] 3,3-dimethylbutanoate	Control red spiders mite, white fly in tomato, chilli, brinjal, cotton and other crops.
Neonicotinoid	Acetamiprid	20%SP	$C_{10}H_{11}ClN_4$	N-[(6-chloropyridin-3-yl) methyl]-N’-cyano-N-methylethanimidamide	Foliar-feeding pests such as Aphids, Whiteflies, Leafhoppers, and Plant bugs.
	Imidacloprid	17.8% SC	$C_9H_{10}ClN_5O_2$	(*NE*)-*N*-[1-[(6-chloropyridin-3-yl)methyl]imidazolidin-2-ylidene]nitramide	Control aphids, thrips, whiteflies, scale, termites, turf and soil insects and some beetles.
	Thiacloprid	21.7% SC	$C_{10}H_9ClN_4S$	[3-[(6-chloropyridin-3-yl) methyl]-1,3-thiazolidin-2-ylidene]cyanamide	Control of a variety of sucking and chewing insects like aphids and whiteflies
	Thiamethoxam	30% FS	$C_8H_{10}ClN_5O_3S$	(NE)-N-[3-[(2-chloro-1,3-thiazol-5-yl)methyl]-5-methyl-1,3,5-oxadiazinan-4-ylidene]nitramide	Controls Stem borer, gall midge, leaf folder, brown plant hopper, Thrips in rice and also sucking pest in cotton
Organochlorine	Dicofol	18.5%EC	$C_{14}H_9Cl_5O$	2,2,2-trichloro-1,1-bis(4-chlorophenyl)ethanol	Used against red spider mite in cucumbers, ornamentals, and other fruits and vegetables.
Organofluorine	Flubendiamide	39.35% SC	$C_{23}H_{22}F_7IN_2O_4S$	1-*N*-[4-(1,1,1,2,3,3,3-heptafluoropropan-2-yl)-2-methylphenyl]-3-iodo-2-*N*-(2-methyl-1-methylsulfonylpropan-2-yl) benzene-1,2-dicarboxamide	Controls lepidopteron pests in rice, cotton, corn, grapes, other fruits and vegetables
Organophosphate	Acephate	75%SP	$C_4H_{10}NO_3PS$	*N*-[methoxy (methylsulfanyl) phosphoryl]acetamide	Used on food crops, citrus trees, as a seed treatment also kills cockroaches, crickets, firebrats earwigs, pillbugs, sowbugs, pantry pests, and wasps.
	Chlorpyrifos	20% EC	$C_7H_7Cl_3NO_3PS$	dimethoxy-sulfanylidene-(3,5,6-trichloropyridin-2-yl) oxy-lambda5-phosphane	Control cutworms, corn rootworms, cockroaches, grubs, flea beetles, flies, termites, fire ants, and lice
	Dimethoate	30% EC	$C_5H_{12}NO_3PS_2$	2-dimethoxyphosphinothioylsulfanyl-*N*-methylacetamide	Used against sucking insects like aphids, leafhoppers, and thrip
	Ethion	50% EC	$C_9H_{22}O_4P_2S_4$	diethoxyphosphinothioylsulfanylmethylsulfanyl-diethoxy-sulfanylidene-λ5-phosphane	Used to kill aphids, mites, scales, thrips, leafhoppers, maggots and foliar feeding larvae.
	Monocrotophos	36% SL	$C_7H_{14}NO_5P$	dimethyl [(E)-4-(methylamino)-4-oxobut-2-en-2-yl] phosphate	Control sucking, chewing and boring insects and spider mites on cotton, sugarcane, peanuts, ornamentals, and tobacco
	Profenofos	50% EC	$C_{11}H_{15}BrClO_3P$	4-bromo-2-chloro-1-[ethoxy(propylsulfanyl) phosphoryl]oxybenzene	Control over all sucking pests and foliar feeding larvae and control of mites on a variety of crops
	Triazophos	40% EC	$C_{12}H_{16}N_3O_3PS$	diethoxy-[(1-phenyl-1,2,4-triazol-3-yl)oxy]-sulfanylidene-lambda5-phosphane	Controls Aphids, thrips, midges, beetles, larvae, cutworms, and other soil insects in cereals, sugarbeets, sugarcanes, maize, soybeans, coffee, and grasslands.
	Quinalphos	25% EC	$C_{12}H_{15}N_2O_3PS$	diethoxy-quinoxalin-2-yloxy-sulfanylidene-lambda5-phosphane	Toxic against bollworms on cotton and stem borer, green leaf hopper, hispa on rice

Contd…..

Table 1. Contd…..

Phenylpyrazole	Fipronil	5% SC	$C_{12}H_4Cl_2F_6N_4OS$	5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-(trifluoromethylsulfinyl) pyrazole-3-carbonitrile	Used to control ants, beetles, cockroaches, fleas, ticks, termites, mole crickets, thrips, rootworms, weevils, and other insects
Pyrethroids	Cypermethrin	10% EC	$C_{22}H_{19}Cl_2NO_3$	[cyano-(3-phenoxyphenyl) methyl] 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane-1-carboxylate	To kill insects on cotton and lettuce, and to kill cockroaches, fleas, and termites in houses and other buildings.
	Lambda Cyhalothrin	5% EC	$C_{23}H_{19}ClF_3NO_3$	[(R)-cyano-(3-phenoxyphenyl)methyl] (1S,3S)-3-[(Z)-2-chloro-3,3,3-trifluoroprop-1-enyl]-2,2-dimethylcyclopropane-1-carboxylate	To control aphids, Colorado beetles and butterfly larvae
Quinazoline	Fenzaquin	10% EC	$C_{20}H_{22}N_2O$	4-[2-(4-*tert*-butylphenyl) ethoxy]quinazoline	Used against a broad spectrum of mites in grapes, pome fruit, citrus, peaches, cucurbits, tomatoes, cotton and ornamentals
Thiourea	Diafenthiuron	50% WP	$C_{23}H_{32}N_2OS$	1-*tert*-butyl-3-[4-phenoxy-2,6-di(propan-2-yl)phenyl] thiourea	It is toxic to cardamom borer, *Conogethes punctiferalis,*Guenee, Indian bees.

Table 2: Insecticide determination using FTIR Spectrometry in ATR and KBr method.

Insecticides	**Measurement mode**	**Wave number range (cm^{-1})**	**Baseline (cm^{-1})**	**Sample throughput (hr^{-1})**	**Waste generation**
Acephate	KBr disks	1700-1025	1750- 500	5-6	10-20 mg
Acetamiprid	KBr disks	1532-600	2200-500	5-6	10-20 mg
Chlorpyrifos	ATR	1022-580	1500-600	8-9	0.5-1 ml
Cypermethrin	ATR	2200-1500	1500	8-9	0.5-1 ml
Diafenthiuron	KBr disks	1740-1160	1200-500	5-6	10-20 mg
Dicofol	ATR	1480-600	3000-600	8-9	0.5-1 ml
Dimethoate	ATR	1070-580	1400-600	8-9	0.5-1 ml
Emamectin	KBr disks	2800-1250	2500-3500	5-6	10-20 mg
Ethion	ATR	2865-1375	1500-1000	8-9	0.5-1 ml
Fenzaquin	ATR	3080-1430	1600-1300	8-9	0.5-1 ml
Fipronil	ATR	1625-600	1800-600	8-9	0.5-1 ml
Flubendiamide	ATR	2700-910	3000-800	8-9	0.5-1 ml
Imidacloprid	ATR	1680-1550	1600-600	8-9	0.5-1 ml
Lambda Cyhalothrin	ATR	1300-1110	1500-900	8-9	0.5-1 ml
Monocrotophos	ATR	1680-1200	1700-1100	8-9	0.5-1 ml
Profenofos	ATR	1485-600	1400-600	8-9	0.5-1 ml
Quinalphos	ATR	1090-810	1100-800	8-9	0.5-1 ml
Spiromesifen	ATR	1680-1020	1200-100	8-9	0.5-1 ml
Thiacloprid	ATR	1650-1550	1600-1400	8-9	0.5-1 ml
Thiamethoxam	ATR	1635-1310	1500-900	8-9	0.5-1 ml
Triazophos	ATR	1525-1020	1500-600	8-9	0.5-1 ml

The halogen group showed a strong stretching of C-Cl bond at 830- 600 cm^{-1} and P=S bond showed variable strong stretching at 800-580 cm^{-1}. In most instances, when used alone, strong absorption at the cited regions was considered to be related to the stretching vibration of only a C-O- link. Another absorption feature of the spectrum that should be taken into consideration was C-O- absorption band, which was indicative of an ether group. For example, the absence of characteristic absorption features of those functional groups that contained the C-O- link (alcohol groups, ester groups, etc.) increases the probability of the C-O- absorption as indicative of an ether group. On equating chlorpyriphos 20%EC (Fig.10b)spectra with the NIST spectra and KnowitAll (Fig.10f) software, peak at 1022.57 cm^{-1} shows 100% intensity and at 1410.67 cm $^{-1}$ shows 69.13%. The absorption bands of C-N stretching, C-Cl stretching and P-S stretching for chlorpyriphos was also reported by Armenta *et al*. (2005a).

Dimethoate is a broadly utilized organophosphate bug spray and acaricide. Dimethoate 30% EC IR (Fig.10c) spectrum analyzed with bio-rad software (Fig.10g) showed that it had the strong stretching of P=S bond in the range of 800 to 580 cm^{-1} and the intensity was of 97.24 % at 783.92 cm^{-1}. 100% intensity is available at 1070.30 cm^{-1} band, which is corroborated with NIST library spectrum. Medium bending and stretching of NH and C-N bonds were observed at 1440-1490 and 1310-1350 cm^{-1}.

Ethion is used on a wide variety of food, fiber and ornamental crops, including greenhouse crops, lawns and turf. Ethion 50% EC (Fig.10d) contained P=S group and has a stretching at 800-580 cm^{-1} and string symmetric CH group at 2863-2843 cm^{-1}, medium symmetric CH group at 1380-1375 cm^{-1}. The intensity ranges from 48.87% to 82.95% in the area of P=S group as observed by ProcessItIR (Fig.10h) and Spectrabase. Similar vibration features of ethion at 720 and 1718 cm^{-1} due to P=S vibrations and S–P=S stretching, respectively was reported by Yang *et al.* (2019).

Monocrotophos 36% SL spectra showed (Fig. 11a) signature bands (Fig. 11e) of N-H stretching vibration near 3270 cm^{-1}, very strong C=O stretching vibration at 1680-1630 cm^{-1}, strong intensity of NH deformation and C-N stretching at 1570-1515 cm^{-1} and mixed C-N stretching and N-H bending at 1310-1200 cm^{-1}. Variable stretching of P-O-R bond was observed at 1050-970 cm^{-1}.

Profenofos (Fig. 11b) derived from a 4-bromo-2-chlorophenol showed antisymmetric stretching of CH bond at 2936-2916 cm^{-1}, symmetric stretching of CH bond at 2863-2843 cm^{-1}, and deformation of CH bond at 1485-1445 cm^{-1} in aromatic 1,2,3 trisubstituted ring. Strong stretching of halogen bonds of C-Br and C-Cl at

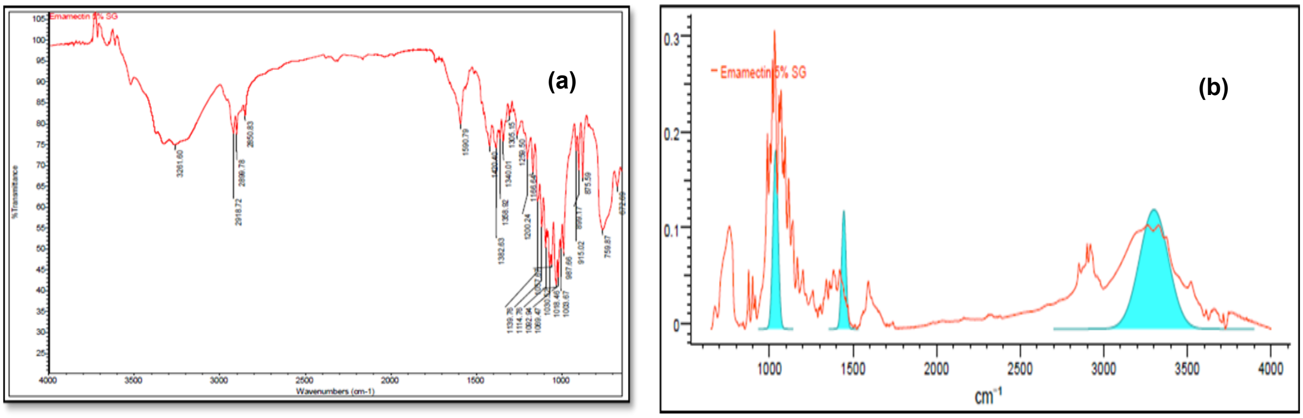

Fig. 2. *IR spectra of Emamectin (a- Original spectrum; b). Processed spectrum by KnowitAll).*

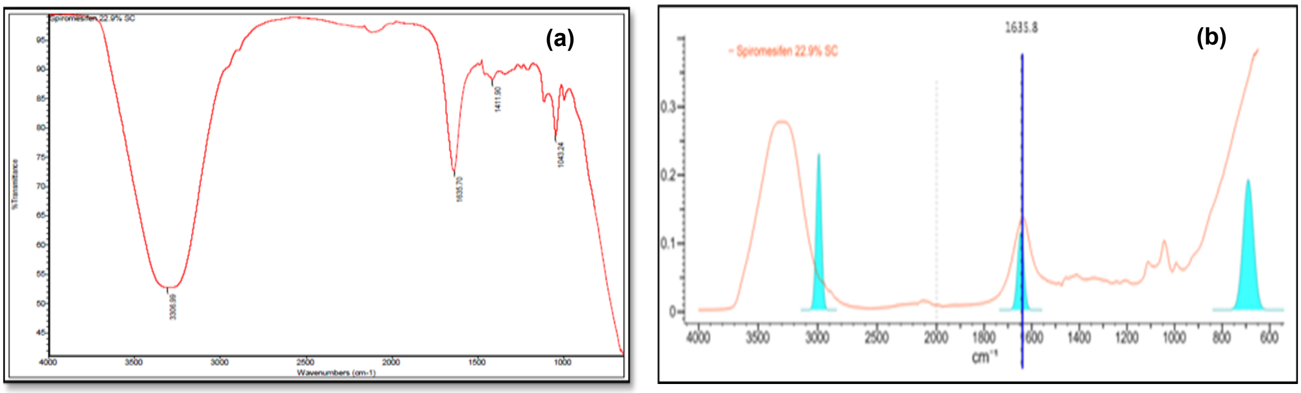

Fig. 3. *IR spectra of Spiromesifen (a). Original spectrum; b). Processed spectrum by KnowitAll).*

500-550 and 830-600 cm^{-1} respectively was also seen in spectra(Fig.11f). It showed 100% intensity at 1472.87 cm^{-1} for CH bond of alkanes.

Quinalphos (derives from a quinoxalin-2-ol)spectrum (Fig.11c)peak bands at 800-580, 810-870, 990-1090 and 2340-2790 cm^{-1} showed the presence of P=S group stretching, S-O bond stretching, S=O bond and O-H bond stretching, respectively (Fig.11g). The 100% peak intensity was obtained at 1023.05 cm^{-1}.

Triazophos is an acaricide,derived from a 1-phenyl-1H-1,2,4-triazol-3-ol. Triazophos 40% EC spectrum (Fig.11d)was compared with the spectrabase and bio-rad software (Fig.11h). It showed variable stretching of P=S bond at 580-800 cm^{-1}, strong bending of an aromatic ring at 690-710 cm^{-1} and strong antisymmetric C-H bond of alkanes at 2952-2972 cm^{-1}. It showed 100% intensity at 1019.38 cm^{-1}, 94.93% at 1524.73 cm^{-1} and 86.61 % at 1329.92 cm^{-1}.

Phenylpyrazoles

Fipronil is utilized to control ants, beetles, cockroaches, bugs, ticks, termites, mole crickets, thrips, rootworms, weevils, and different bugs. Fipronil 5% SC (Fig.12a) contains variable to medium stretching of aromatics ring group in the range of 1430 – 1625 cm^{-1} and halogen groups of C-Cl and C-F groups in the range of 830-600 cm^{-1} and 1300-900 cm^{-1} of strong and variable stretching. The peak intensity at 711.12 cm^{-1} showed

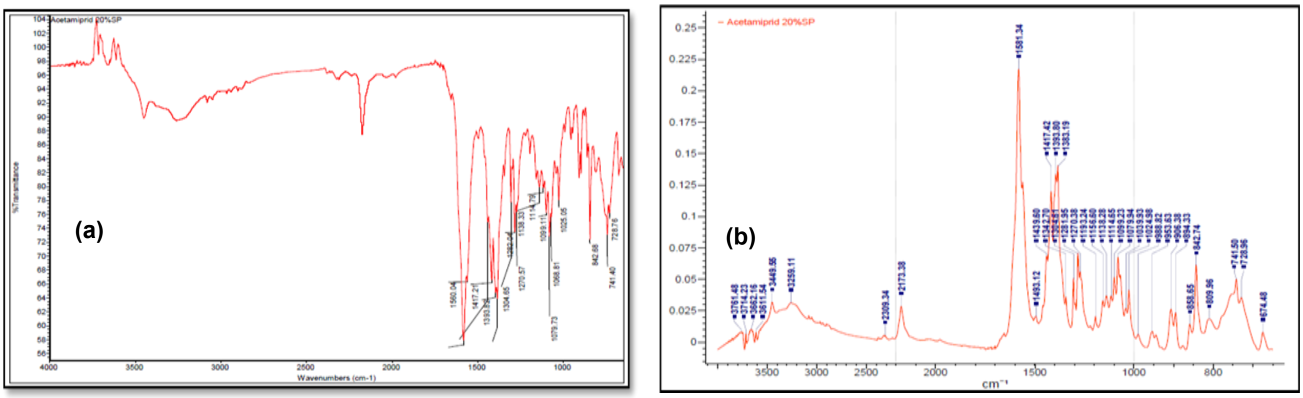

Fig. 4. *IR spectra of Acetamiprid (a). Original spectrum; b). Processed spectrum by KnowitAll).*

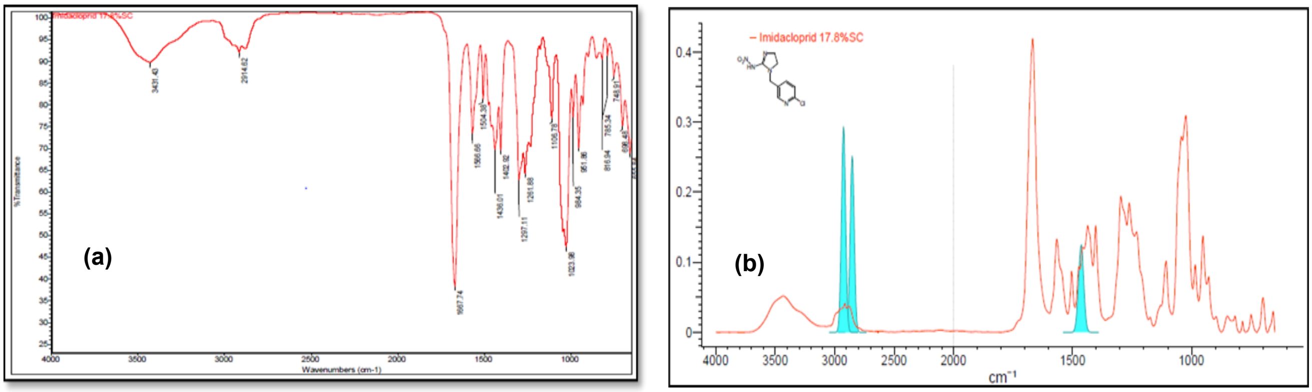

Fig. 5. *IR spectra of Imdiacloprid (a). Original spectrum; b). Processed spectrum by KnowitAll).*

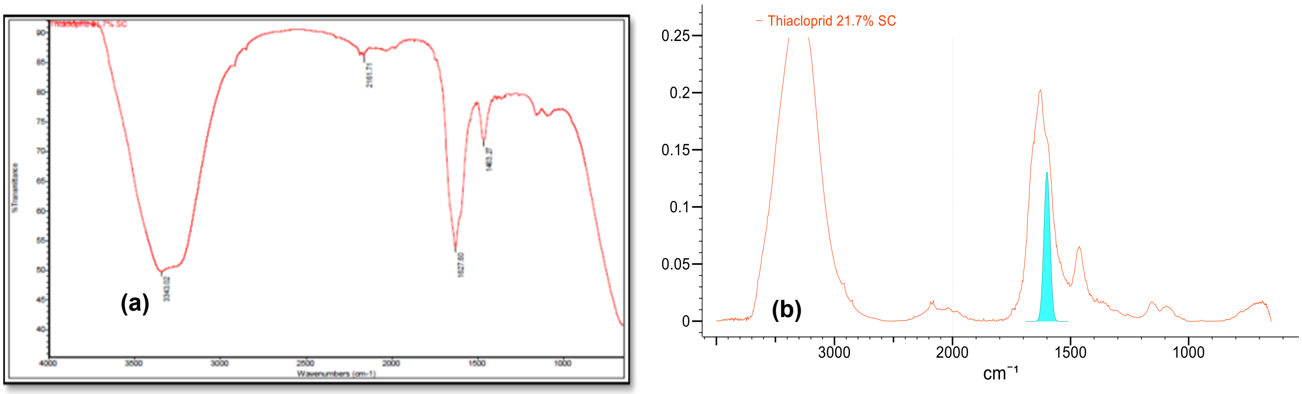

Fig. 6. *IR spectra of Thiocloprid (a). Original spectrum; b). Processed spectrum by KnowitAll).*

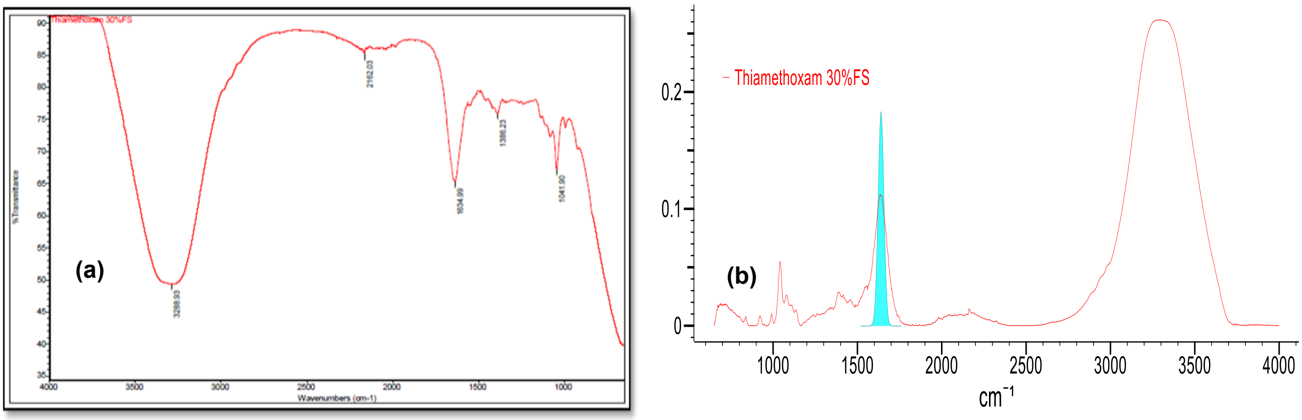

Fig. 7. *IR spectra of Thiomethoxam (a). Original spectrum; b). Processed spectrum by KnowitAll).*

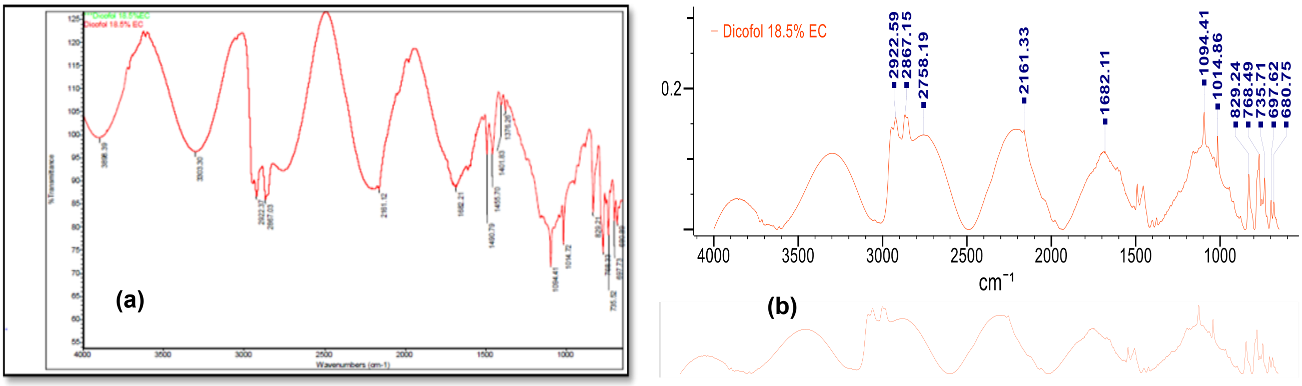

Fig. 8. *IR spectra of Dicofol (a). Original spectrum; b). Processed spectrum by KnowitAll).*

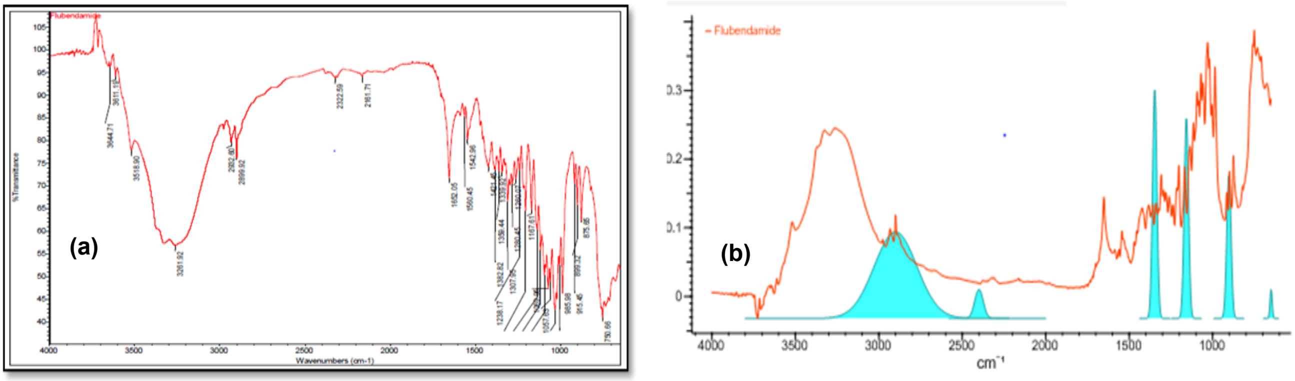

Fig. 9. *IR spectra of Flubendamide (a). Original spectrum; b). Processed spectrum by KnowitAll).*

100% by C-Cl group and 1070.30 cm^{-1} has an intensity of 23.06%. The commercial spectra were compared with the spectrabase and bio-rad software (Fig.12b) also. Two major absorption peaks at 1633 and 1319 cm^{-1}for fipronil was reported due to stretching vibrations of C–N bond and deformation vibrations of N–H bond, respectively(Qiu *et al*., 2013)

Pyrethroids

Cypermethrin is an engineered pyrethroid spray used to kill cockroaches, bugs, and termites in houses and different structures. Cypermethrin 10% EC (Fig.13a) Processing bybio-rad software (Fig.13b) shows the peak area from 860 - 2200 cm^{-1} which indicates the presence of C-Cl bond and the amine group in it. The finger print bands of cypermethrin at 865, 1454, 1586 cm^{-1} due to deformation vibrations of the cyclopropane ring, R-CH_2-CN deformation structure and C-C stretching of the aromatic rings as proposed by Segal-Rosenheimer and Dubowski (2007) was observed in this study. Additional important representing band of the molecule was observed at 1124 cm^{-1} and is related to the CN-O stretching of the cyanate group. Segal-Rosenheimer and Dubowski (2007) reported that the absorption bands at 1742, 1587,1488, 1449 and 1076 cm^{-1}, due to carbonyl stretching, C-C stretching in chloroalkenes, ring vibration of benzene, CH_2 deformation in R–CH_2–CN structure and (C O)–O– stretching, respectively for pure certified standard cypermethrin.

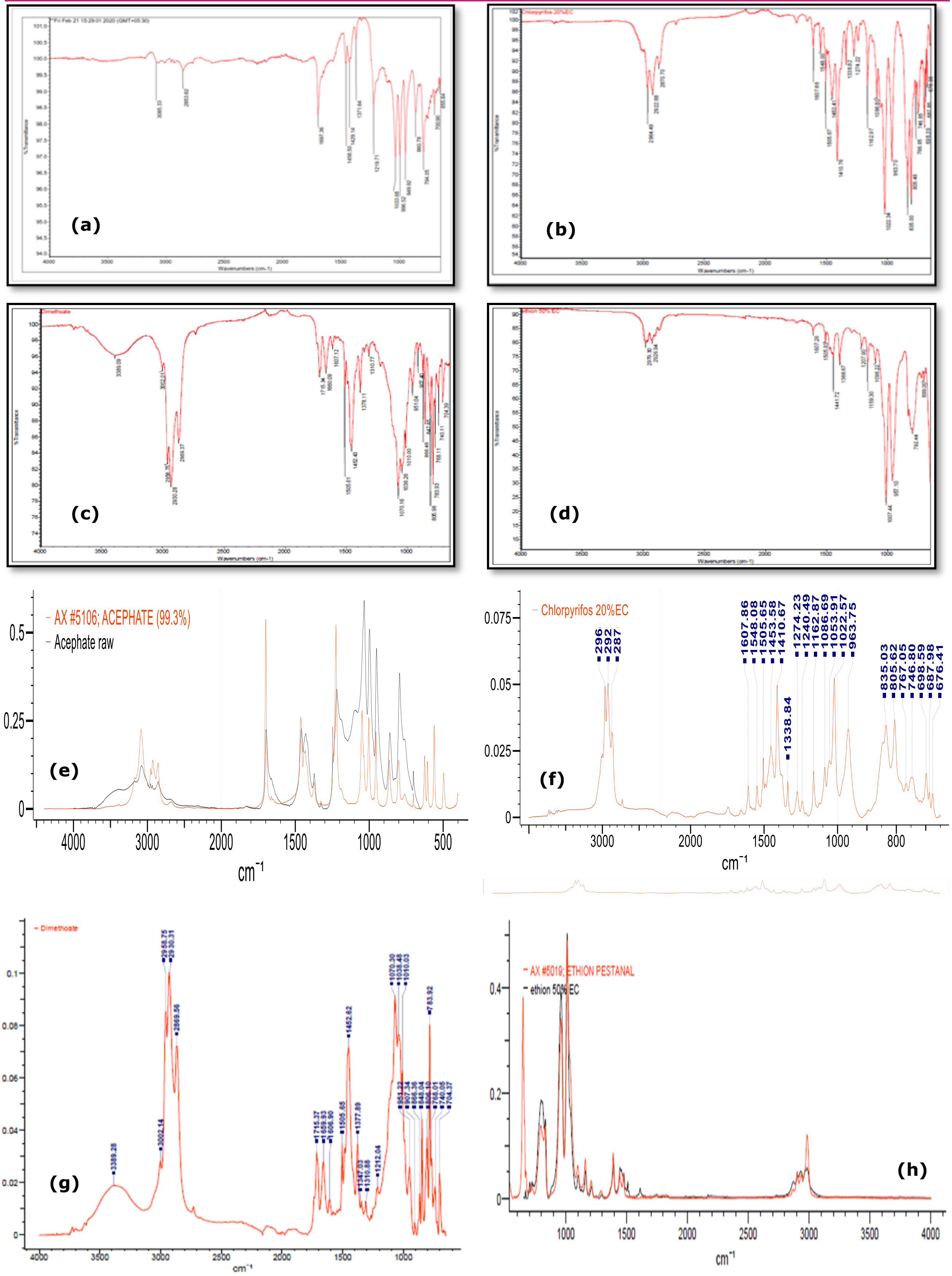

Fig. 10. *IR spectra of Acephate, Chlorpyrifos, Dimethoate and Ethion.(1).Original spectrum: a, b, c, d; 2).Processed spectrum by KnowitAll: e, f, g, h.*

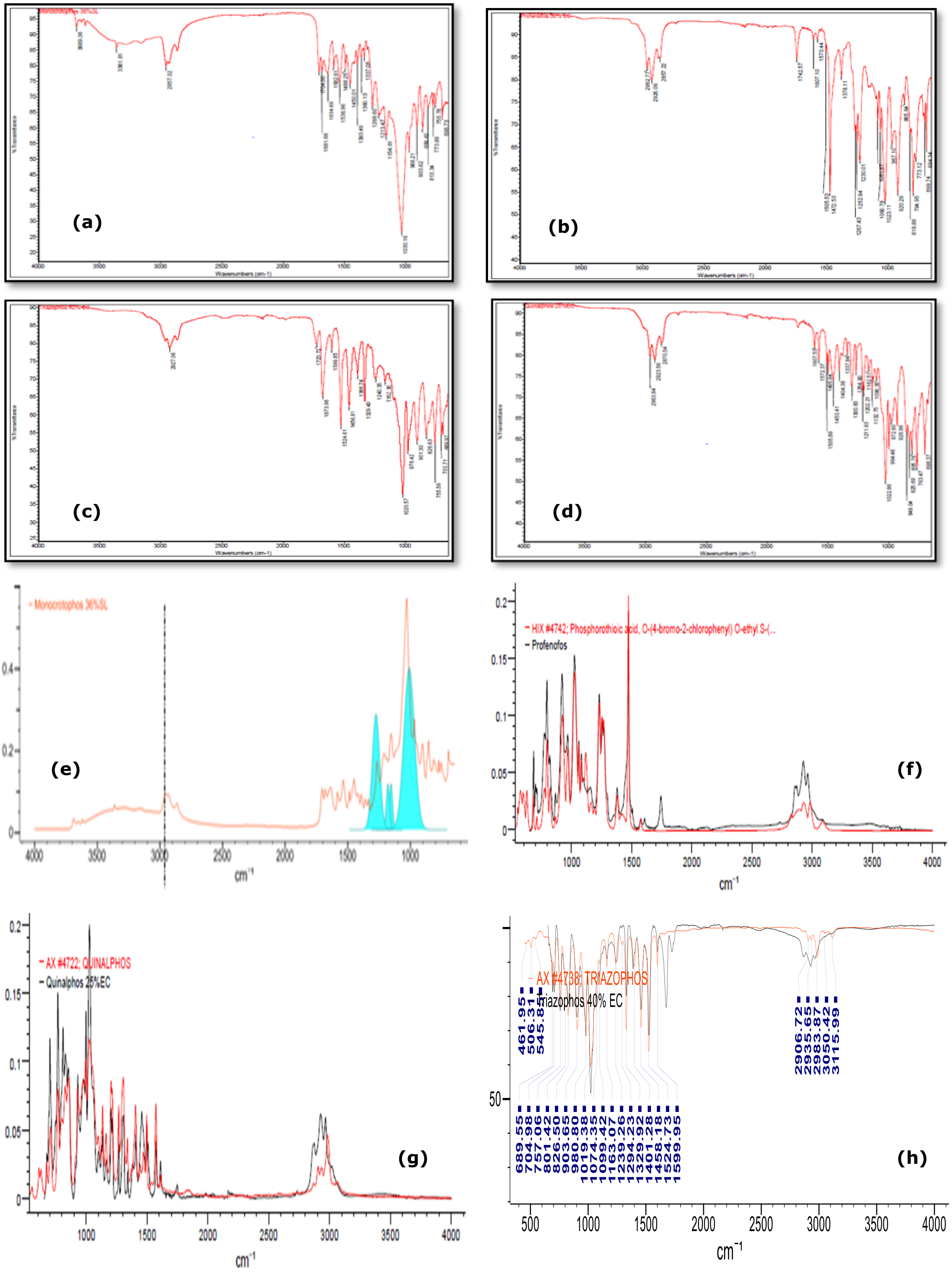

Fig. 11. *IR spectra of Monocrotophos, Profenofos, QuinalphosandTriazophos.(1).Original spectrum: a, b, c, d; 2). Processed spectrum by KnowitAll: e, f, g, h).*

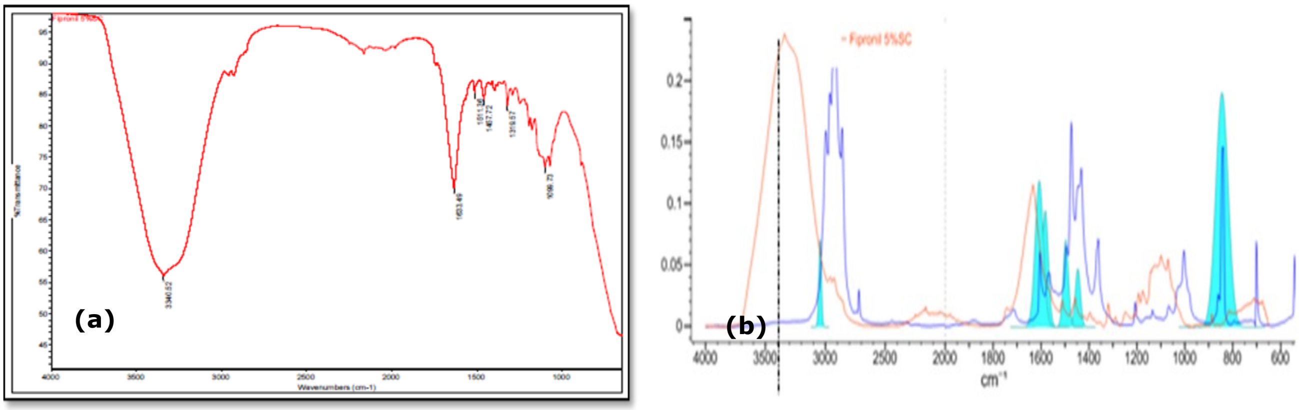

Fig. 12. *IR spectra of fipronil (a). Original spectrum; b). Processed spectrum by KnowitAll).*

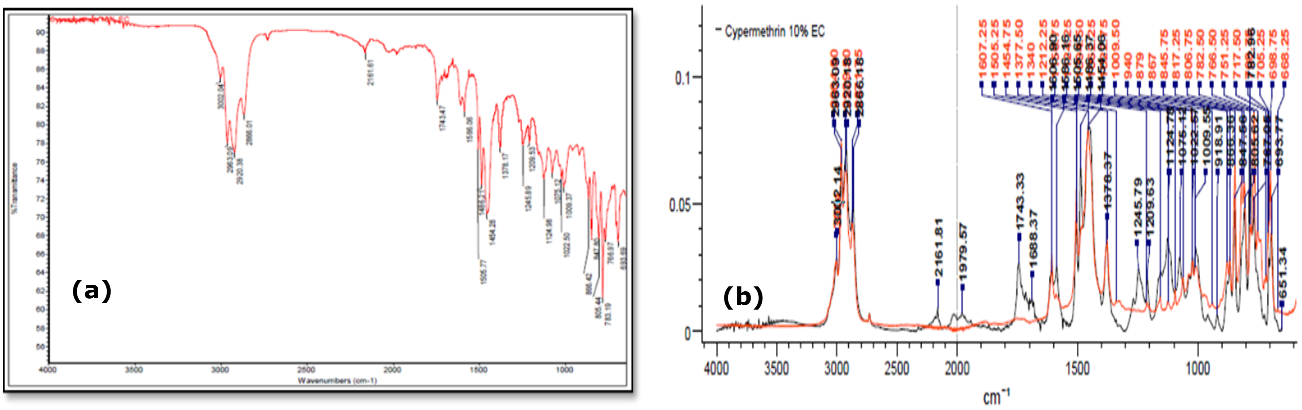

Fig. 13. *IR spectra of cypermethrin(a). Original spectrum; b). Processed matching spectrum by spectrabase.*

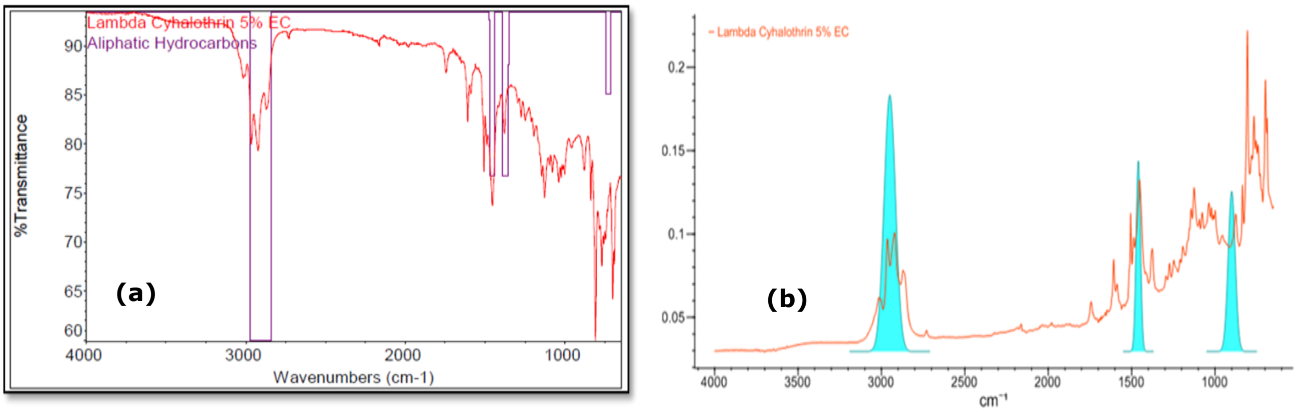

Fig. 14. *IR of cyhalothrin (a). Original spectrum; b). Processed spectrum by KnowitAll).*

Cyhalothrin, is a cyano-(3-phenoxyphenyl)methyl] 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane-1-carboxylate. Commercial product spectrum (Fig.14a and 14b) showed the presence of aliphatic hydrocarbons, halogen groups, sulphur and phosphorus compounds. Symmetric stretching of CH bond and deformation was observed at the band of 2900-3000 and 1490-1430 cm^{-1}respectively. The halogen C-F bond was present at 1350-1120 cm^{-1} and 780-680 cm^{-1} bands. The symmetric stretching of R-N=S=O at 1180-1110 cm^{-1} and P=N bond stretching at 1300-1100 cm^{-1} was observed as signature bands for cyhalothrin.

Quinazolines

Fenzaquin, a 4-[2-(4-*tert*-butylphenyl)ethoxy]quinazoline is the active ingredient of Fenzaquin10% EC (Fig.15a). FTIR Spectrum contains aromatics o-di-substituted ring (Fig.15b) in the peak range of 1430-1625 cm^{-1}, CH group stretching at 3079-3010 cm^{-1}. The peak intensity was 56.97% at 1495.53 cm^{-1} and 56.88% at 1454.06 cm^{-1} due to variable, medium stretching of aromatic string.

Thioureas

The absorbance FTIR spectra of diafenthiuron 50% WP in the wavenumber region from 4000 to 900 cm^{-1} was

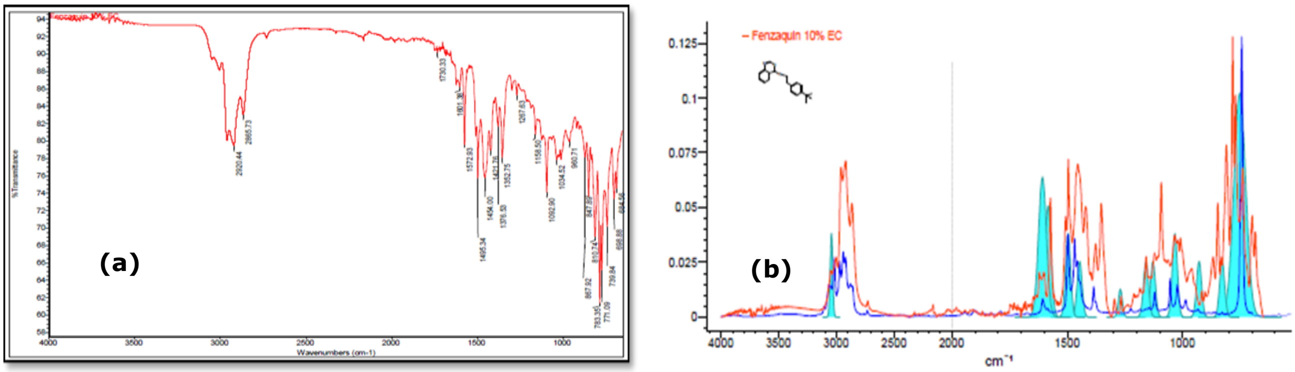

Fig. 15. *IR spectra of Fenzaquin (a). Original spectrum; b). Processed spectrum by KnowitAll).*

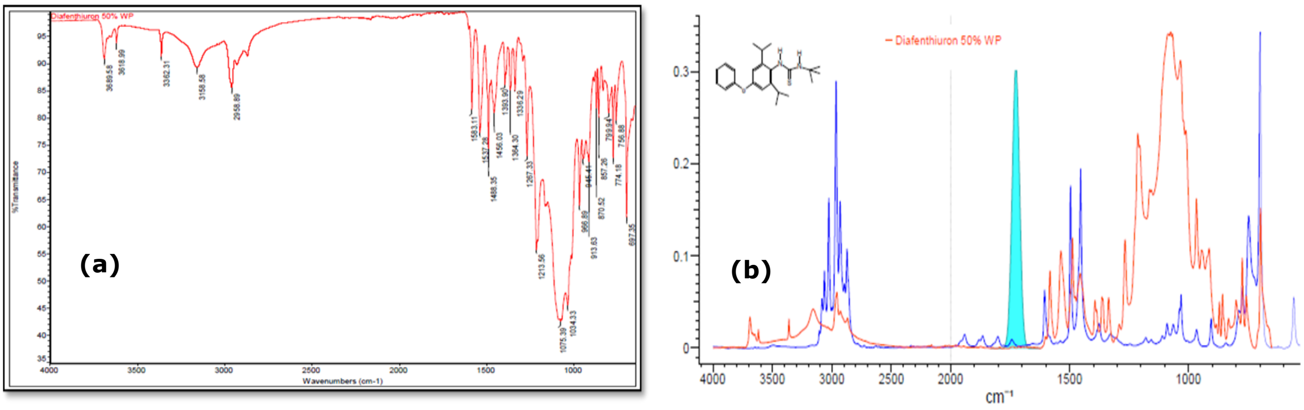

Fig. 16. *IR spectra of Diafenthiuron (a). Original spectrum; b). Processed spectrum by KnowitAll).*

shown in Fig.16a. In this Fig. 16b, the diafenthiuron spectrum has absorption bands at 3360-3100, 1740-1715, 1300-1160, 1200-1050 due to medium stretching of thioamide bond N=H, strong stretching of unsaturated ester bond C=O, strong stretching of unsaturated ester bond C-O, medium stretching bond C=S, respectively. The ProcessItIR spectrum showed 100% intensity at 1075.60 cm-1and 1034.14 cm-1 has 90.96%. Sample spectra provide the characteristic bands of the active principles additionally than some small bands coming from inert and solvent components of the pesticide formulations.

Conclusion

The suitability of the vibrational spectrometry for the determination of active ingredients in solid and liquid pesticide formulations at MIR regions indicated signature absorption bands of 1667-1680, 1650-1550, 1340-1250, 800-580 and830- 600 cm$^{-1,}$ respectively, for C=O, C-N=C, N-H, P=S and halogen bonds. Also, absorption bands of few pesticides were comparable spectra with the available NIST library and Spectrabase. Hence FTIR spectrometry for the direct determination of commercial pesticide formulations can be carried out without any pre-treatment of samples. So the proposed procedure was environmentally friendly for quality control analysis of formulated pesticides. These pesticide molecules provided specific characteristic absorption bands in the mid-IR, located at different wavenumbers providing the qualitative representation of the compounds. This work's principal target has been the advancement of quick and environmentally friendly techniques for the assurance of pesticides in agrochemical definitions utilizing vibrational spectroscopy like FTIR and extending to determine pesticide residue in plant and food material. This can be achieved after calibrating the signature bands for each compound.

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Conflict of interest

The authors declare that they have no conflict of interest.

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