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Analysis of Microplastics in Assorted Tea Ingredients Available in Wah Cantt Pakistan

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Abstract

Microplastics are considered as one of the most widespread environmental pollutants. The undertaken study presents an analysis of microplastics polymer in tea, powder milk and tea whitener in Wah Cantt Pakistan. Twenty-three samples of local and branded tea, powder milk and tea whitener were analyzed. Samples were examined via FTIR and SEM-EDX to detect presence of microplastics polymer. FTIR spectra of all samples revealed presence of various microplastic such as polyethylene, polyethylene terephthalate, polyvinyl alcohol, polystyrene, nylon, along with other toxic contaminants such as chromium hydroxide, phosphorus, polyamide. Moreover, SEM images show irregular, rod shape, fragments, thread like structure which were commonly observed in microplastics. The EDX spectra have further authenticated SEM results as it has shown carbon dominant peaks which are common attributes of microplastics polymers. Comparatively, local samples are more contaminated compared to branded samples. The microplastics polymers found in tea ingredients are reportedly highly toxic and capable of damaging nervous system, immune system, hormonal imbalances and causing cancer. The study recommends that use of plastic should be minimized particularly for packaging of tea, powder milk and tea whitener.

Keywords: Tea, whitener, milk, microplastics

1. Introduction

The word "plastic" encompasses a wide range of synthetic compounds, mainly produced by combining monomers through polymerization. These monomers often come from fossil and sources such as starch and castor oil (Leal Filho et al., 2019). Plastic production has significantly been augmented over the past few years, as of 2017 global plastic production was estimated approximately 348 metric tons (Geyer, 2020). Plastic pollution is a global environmental issue. Plastic pollution can impose detrimental impacts on environment, as it can negatively alter carbon cycle, nutrient cycle and ultimately it could cause havoc to wild life and keystone species (MacLeod et al., 2021). Plastic debris in the environment is classified based on size into macro-plastics (> 25 mm), meso-plastics (25 to 5 mm), micro plastics (5 mm to 0.1 μm), and nano-plastics (< 0.1 μm) (Andrady, 2011).

Humans are exposed to microplastics through different exposure sources (Koelmans et al., 2019) including drinking water (Oßmann et al., 2018), seafood (Smith et al., 2018), salt (Iñiguez et al., 2017) and milk (Kutralam-Muniasamy et al., 2020). Mason et al. (2018) revealed that tap water samples and bottled water samples are found contaminated with tested microplastics. Furthermore, Afrin et al. (2022) showed prevalence of macro-plastics in sugar samples collected from various cities of Bangladesh.

Similarly, Hernandez et al. (2019) concluded that tea bags when submerged in hot water release billions of microplastics and nano-plastics particles. The most common source of plastic debris in tea leaves are plastic waste arise from agricultural farms, plastic packaging of pesticide and various fertilizers, airborne micro and nano plastic particles (Bo et al., 2023). Li et al. (2022) showed evidence of presence of various microplastics in tea leaves samples collected from different regions in China and they have discovered two types of

microplastics polymers in samples i.e. polyethylene and polyethylene terephthalate. Furthermore, branded milk samples from various regions of Mexico, all had fragments and fibers shaped microplastics were observed in all the samples (Kutralam-Muniasamy et al., 2020; Hussain et al., 2020).

Tea is commonly termed as "chai" in local Pakistani language. It is anticipated that tea utilization in Pakistan will surges up to 250,755 tons by year 2027 (Khattak and Ali, 2015; Rameeza and Eun, 2022). There are different types of tea branded and local available in the Pakistani market having variation in their quality, but no study has yet been reported in Pakistan regarding compositional analysis of local tea brands in relation to quality (Adnan et al., 2013; Butt et al., 2022). Present study is focused on assessment of microplastics analysis of tea and ingredients like tea grains, powdered milk and tea whitener (both branded and local) available in Wah Cantt Punjab, Pakistan. This study will be a pioneer study for microplastic analysis in tea and its ingredients in Pakistan. This study will ensure social well-being and will enlighten pathways for future research in a particular field. The study will provide a qualitative analysis of (branded and non-branded) black tea grains, milk powder and tea whiteners. Finally, this study will help in facilitation of future research work in the same field.

2. Methodology

For current study of microplastics prevalence in tea and its ingredients, samples were collected from two major markets (Gol market Basti and Aslam market) of Wah Cantt (figure 1). Both of these markets are shown in figure 1. Wah Cantt is located at 33.7715° N, 72.7511° E, around approximately at 35 km northwest of Islamabad. Wah Cantt has a total area of about 14434.800 acres with a population size 380,103.

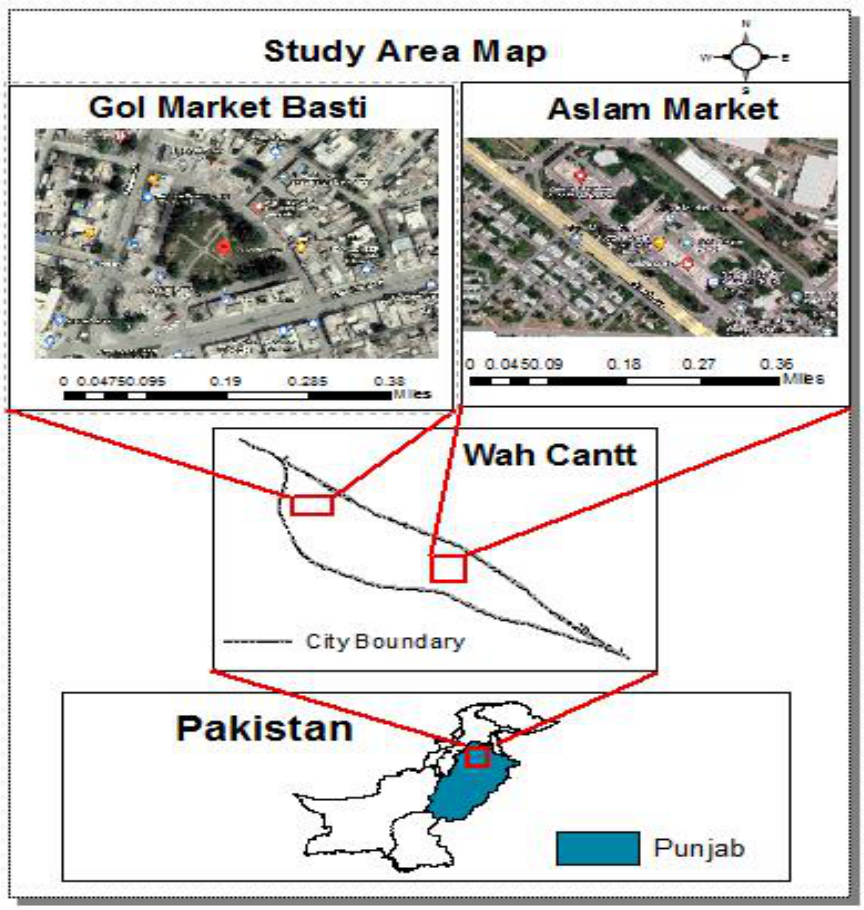


Fig. 1. Study area of the current research from where samples were collected from two major locations of Gol market Basti and Aslam market.

2.1 Consumer Preference Survey

It is important to consider information of participants regarding their preference for tea, tea whitener and powder milk, before diving into outcomes of microplastics in samples. For this purpose, 200 questionnaires were distributed among general public. This information was fetched by outcomes of questionnaire, which were filled by general public of Wah Cantt. Data regarding preferences of local people for tea, tea whitener and powdered milk were gathered. For ease, questions were designed to ask respondents to choose from a distinct set of pre-defined responses, such as "yes/no" or among a set multiple choice. The questionnaire contains questions about basic information for instance name, age group and gender. Besides that, it also contains specific information about costumer preferences for tea, whitener and powder milk such as branded/non-branded, brand of their preference. Lastly, it also proved to be fruitful to fetch data regarding daily consumption of tea/ individual.

2.2 Sample Collection

Altogether twenty-three samples were purchased randomly from these two markets. Out of these 23, eight samples were of tea and powder milk, whilst, seven samples of tea whitener were purchased respectively. Moreover, samples are further divided into two categories (branded and non-branded/local). Depending upon availability, four branded and four local samples of tea and powder milk were taken while, three samples of branded tea whiteners and 4 samples of local were collected as shown in table 1.

2.3 Sample Analysis

For evaluation of type of microplastics polymers in samples PerkinElmer Fourier Transform Infrared Spectroscopy (FTIR) was used (Liu et al., 2021; Teboul et al., 2021; Schlawinsky et al., 2022). The SEM-EDX was utilized for analysis morphological and structural analysis of microplastics in samples. EDX analysis is a fruitful technique in determination of carbon dominant particles, which were commonly observed in microplastics polymers. Before putting samples in SEM stubs for analysis, samples were coated with very thin and inert gold foil to dissipate charge and to enhance image quality and contrast (Tiwari et al., 2019).

Table 1: Particulars of collected samples

Name of sample (N=23)	Sampling Area	Branded Sample Codes	Local/Non-Branded Sample Codes
TEA (N=8=4+4)	Gol Market Basti	BT-I	LT-I
		BT-II	LT-II
		BT-III	LT-III
		BT-IV	LT-IV
TEA WHITENER (N=7=3+4)	Gol Market Basti	TWB-I	TWL-I
		TWB-II	TWL-II
		TWB-III	TWL-III
		N/A	TWL-IV
POWDERED MILK(N=8=4+4)	Aslam Market	BM-I	LM-I
		BM-II	LM-II
		BM_III	LM-III
		BM_IV	LM-IV

3. Results and Discussions

3.1 Survey outcomes

Results of questionnaire showed that 35% of respondents were female and 65% were male. Moreover, most of the participants were highly qualified and people of age group 20-70. 85% people prefer tea as their regular beverage instead of soft drink and other beverages. Moreover, 90% of respondents showed their affection towards branded tea ingredients whilst, 10% participants are purchasers of local tea ingredients. On average people consume 2 to 3 cups of tea daily. Further, people take tea to make them stress free, get themselves energized and relaxed. These details are further depicted in table 2 below.

3.2 Microplastic Identification

Microplastics polymers were detected in all twenty-three samples under observation, regardless they were branded or not. Further details of microplastics polymers analyzed in samples are given below.

3.2.1 Microplastics in Branded Tea Ingredients

Microplastics polymers were detected in all eleven branded samples of tea, tea whitener and powder milk.

Microplastics polymer, polyethylene terephthalate was detected in all the four branded (BT-I, BT-II BT-III and BT-IV) tea samples. IR spectra of all four branded tea samples were quiet identical, indicated presence of ethylene (C_3H_6) group and BT-III and III show strong peaks in region of 1600 cm^{-1} which indicates presence of aromatic benzene ring. Saturated aliphatic esters identifies at 1190 cm^{-1} with antisymmetric stretching vibration, which probably could be propionates ($R\text{-}COOCH_2CH_3$). Moreover, 1022 cm^{-1} depicts stretching vibration of primary aliphatic amines v(C-N). In all the samples sharp-medium peak was observed at 953 cm^{-1} which indicate aliphatic NH_2 group. Next peak for all samples were weak-medium at 880 cm^{-1} which shows wagging vibration of CH_2 group attached to aromatic ring. Spectra of samples BT-I, BT-III and BT-IV show strong-medium peaks at 804, 813 and 808 cm^{-1} which exhibit rocking vibrations of carbonyl group along with C-O bond deformation and manifest presence of polyethylene terephthalate (PET) in compliance with reference spectra (Hummel, 2002; Noda et al., 2007). Polyethylene terephthalate and polyethylene is considered as one of the most common microplastics detected in black tea (Li et al., 2022), tea beverages and in tea bags (Mei et al., 2022). On the other hand, the presence of γ (NH2) and v(C-N) group in spectra could be because it is one of the main constituents of black tea or may act as contaminants if present in bulk quantity. IR spectra of all four branded tea samples are depicted in figure 2.

Table 2 Customer preferences and consumption patterns of tea

Consumer Preference of Tea Ingredients (N=200)				
Literacy Rate	Graduated-65%	Undergrad-25%	Intermediate-9%	Primary-1%
Economic Class	Upper Class-20%	Middle Class-80%		
Beverage	Tea-85%	Soft Drink-10%	Coffee-5%	
Milk type	Liquid-60%	Powder-40%		
Tea whitener	Prefer-50%	Not Preferred-50%		
Manufacturer	Branded Tea-90%	Branded Dry milk-90%	Branded Tea whitener-90%	Non-Branded Tea, Tea whitener and powder milk-10%
Average Daily tea intake	2-3 Cups daily			

The spectra of powder milk samples showed that it contains polyethylene as it shows CH_2 symmetric stretch at 2921 cm^{-1}, CH_2 antisymmetric stretch at 2852 cm^{-1} in all four BM samples, another peak in region of 1370-1395 cm-1 depicts presence of symmetric deformation of cyclic CH_3 group, Medium-weak peak in region of 875-890 in all samples which represents ring structure that is rocking vibration of n-hexyl group and rocking vibrations of CH_2 group at 704 cm^{-1}, 703 cm^{-1} 702 cm^{-1} and 703 cm^{-1} were observed in spectra of all four BM samples , collectively in compliance with reference spectra (Hummel, 2002; Noda et al., 2007; Jung et al., 2018). Moreover, presence of carbonyl C=O group at 1740 cm-1, vibrating stretching of NH2 amide bond at 3197 and 3266 cm-1 in all samples and vinyl group R-C=C at 1644 cm^{-1} revels presence of polyacrylamide. Furthermore, spectra of all BM samples except BM-III shows medium-weak peak at 1535 cm^{-1} which indicates presence of 5-membered aromatic-ring structure with carbon and nitrogen atoms and this structure is termed as "pyrroles". Medium peak at 1150 cm^{-1} indicates presence of stretching vibration of carbon-oxygen (peroxide) bond in all samples and strong peak at 1075 cm^{-1} was observed in all samples which indicates anti symmetric vibrating stretch of saturated aliphatic esters which could probably denote presence of adipates which are plasticizers and are toxic but less than that of phthalates. These adipates are used in production of various plastic products such as food containers and they have ability to accumulate in soil but are biodegradable in nature (Vikhareva et al., 2021). Sharp and strong peak at 1022and 1023 cm^{-1} were found in all four samples which depicts presence of saturated aliphatic carbonates vas (C=O) ring particularly lactones group, which were commonly found in processed milk samples and use for aroma in milk and its products such as yogurt (Furlani et al., 2015). IR spectra of all four BM samples are depicted in figure 2.

Broad U-shaped peak at 3200 cm^{-1} to 3330 cm^{-1} were observed in IR spectra of all three samples of branded tea whitener which denotes presence hydroxyl group (OH). Two sharp peaks at 2920 cm^{-1} and 2850 cm^{-1} in IR spectra of all samples which indicates symmetric stretch and antisymmetric stretch of CH_2 group. Afterwards, a sharp peak at 1744 cm^{-1} followed by a medium-weak peak at 1642 cm^{-1} in all three samples indicates presence of carbonyl C=O group and vinyl group R-C=C. Medium-weak peak at 1545 and 1546 cm^{-1} depicts five membered C-N ring structure termed as pyrroles (Xiang et al., 2021). Spectra of sample TWB-III show CH_2 bend at 1460 cm^{-1}. While, peak of medium-weak intensity at 1377 cm^{-1} in all three samples indicates antisymmetric deformation vibration of CH_3 group. In region of 1022, 1018 and 1038 cm^{-1} strong peak was observed which denotes presence of lactones group as indicated earlier in powder milk as well. TWB-I shows rocking vibration of isobutyl at 922 cm^{-1}. TWB-III at show rocking vibration of hexyl group at 892 cm^{-1}. Medium peak at region of 871 cm^{-1} in spectrum of TWB-I and at 867 cm-1 in spectrum of TWB-III show out of plane wagging motion of CH group attached to aromatic group. A weak-medium peak at 700 cm^{-1} denotes deformation motion of carboxylate group (COO) Altogether, these functional reveals presence of polyethylene and polyethylene terephthalate in all samples. IR spectra of all three samples exhibit band at 1240 cm^{-1} which show C-O, which indicates presence of antisymmetric aliphatic esters. Moreover, weak peaks at 1141 and 1148 cm^{-1} show presence of v(C-N) primary aliphatic amine group. At 1065 cm-1 asymmetric stretch of esters C-O was observed in TWL-III. IR spectra of samples TWB-I and III exhibits weak band at 537 which show presence of nitriles, these functional groups could exist naturally in tea whiteners. IR spectra of TWB samples are depicted in figure 2.

3.2.2 Microplastics in Local (Non-branded) Tea Ingredients

As of branded samples, microplastics polymers were also found in all local samples of tea whitener, tea and powder milk which were purchased from sampling sites. Local tea samples were found contaminated with microplastic polymers. IR spectra of samples LT-I and LT-II reveals presence of nylon polymer. Spectra of these two samples shows: strong NH2 band at 3363 cm^{-1} and 3397 cm^{-1}, antisymmetric of CH_2 at 2786 cm^{-1}, deformation of amide ring structure at 1588 cm^{-1},

asymmetric deformation of CH_3 at 1467 cm^{-1}, symmetric deformation of cyclic $–C(CH_3)_2$- at 1374 cm^{-1}, sharp peak at 1020 cm^{-1} depicts antisymmetric stretching of aliphatic carbonates C=O, weak peak at 954 cm^{-1} which is indicative of presence NH group. These all functional groups are constituents of nylon-6, Noda et al. (2007) which is a harmful microplastic polymer and could have deteriorating impact on human lungs (Zarus et al., 2023). Sample LT-III spectra also indicates nylon-6 as it shows absorbance at 3364 cm^{-1} for NH2, 1598 cm^{-1} for deformation of amide ring structure, 1021 cm^{-1} for antisymmetric stretching of aliphatic carbonates C=O, NH group at 955 cm^{-1}. These functional groups are present in nylon-6 as stated earlier. However, LT-III show additional medium-strong peak at 654 cm^{-1} which reveals presence of vibrating stretch of aliphatic chlorine v(C-Cl). Chlorine could impose toxicological impacts on human, when ingested with edibles (Amir et al., 2019). Spectrum of LT-IV also indicate Nylon-6, it shows: vibrating stretch of NH_2 at 3447 cm^{-1}, (C6H6) at 1603 cm^{-1}, antisymmetric stretching vibration of saturated aliphatic esters at 1190 cm^{-1}, peak at 1022 cm^{-1} depicts presence of aliphatic amines. Peak at 953 cm^{-1} indicates out of phase deformation vibration of aliphatic NH_2 group, Peak at 880 cm^{-1} reveals wagging vibration of CH_2 group attached to aromatic ring and rocking vibrations of carbonyl group along with C-O bond deformation was observed at 817 cm^{-1} (Hummel, 2002). IR spectra of all four samples are depicted below in figure 2.

Non-branded local powder milk was also found deteriorated with microplastics polymers. The samples LM-I and LM-II contains Polyvinyl alcohol and polyethylene. IR spectra of LM-I and LM-II reveals OH stretching at 3312 and 3303 cm^{-1}, symmetric stretch of CH_2 at 2915 cm^{-1}, medium-weak peak at 1643 show presence of vinyl group R-C=C, at 1374 cm-1 symmetric deformation vibration of cyclic CH_3, these all functional groups indicates polyvinyl alcohol. Sample LM-I and II beside these peaks show other peaks like strong and sharp antisymmetric stretch of aliphatic carbonates vas (C=O) ring at 1015 and 1014 cm^{-1} which probably represent lactones (also stated earlier in branded milk samples), which is commonly found in processed milk (Furlani et al., 2015). Alongside that, LM-I spectra show three more functional groups, a peak of strong intensity at 989 cm-1 indicates presence of deformation vibration of aromatic heterocyclic ring structure which are probably pyridines which are highly toxic and could impose neurotoxic and carcinogenic effects to humans (Bellamri et al., 2023). Two more weak peaks in LM-I were also present at 908 and 867 cm^{-1}. Medium-weak peak at 908 cm^{-1} show presence of phosphorous. Phosphorous intake could impose detrimental effects on human health such as osteoporosis, renal failure, cardiovascular disorders, kidney disorders (Chang and Anderson, 2017). While, sharp-weak peak at 867 cm^{-1} indicate presence vibrating stretch of (O-O) bond which could be naturally present in powder milk. Spectra of samples LM-III and IV are exactly identical to each other they show, broad stretch of OH group at 3298 cm^{-1} and 3301 cm^{-1}, symmetric and antisymmetric stretch of CH_2 at 2920 cm^{-1} and 2851 cm^{-1}, vibrating stretch of carboxylic anhydrides C=O at 1742 cm^{-1}, vinyl group R-C=C at 1641 and 1642 cm^{-1} these functional groups indicates presence of polyvinyl alcohol PVA in samples. Furthermore, presence of n-hexyl group and symmetric deformation of cyclic CH_3 group indicates presence of polyethylene polymer in samples LM III and LM IV. Two weak medium peaks of v(C-N) at 1542 cm^{-1} indicates ring structure, which denotes pyrroles group as stated earlier in BM. IR spectra of local milk samples are depicted below in figure 2.

All the local tea whitener samples were found deteriorated with microplastics polymers. Sample TWL-I show presence of Nylon-6, as its spectrum shows peak of NH_2 at 3463 cm^{-1}, symmetric and antisymmetric stretch of CH_2 group at 2920 cm^{-1} and 2851 cm^{-1}, sharp peak at 1742 cm^{-1}, v(C-N) stretching at 1079 cm^{-1} show primary amine group, stretching vibration of carbonyl group C=O at 1742 cm^{-1} and wagging motion of CH_2 at 771 cm^{-1}. Moreover, presence of vinyl group R-C=C at 1644 cm^{-1}, antisymmetric stretch of $(CH_2)_4$ at 1221 cm^{-1} and deformation motion of benzene derivative ring at 856 cm^{-1}, these functional groups are commonly found in polystyrene. Polystyrene is one of the most lethal

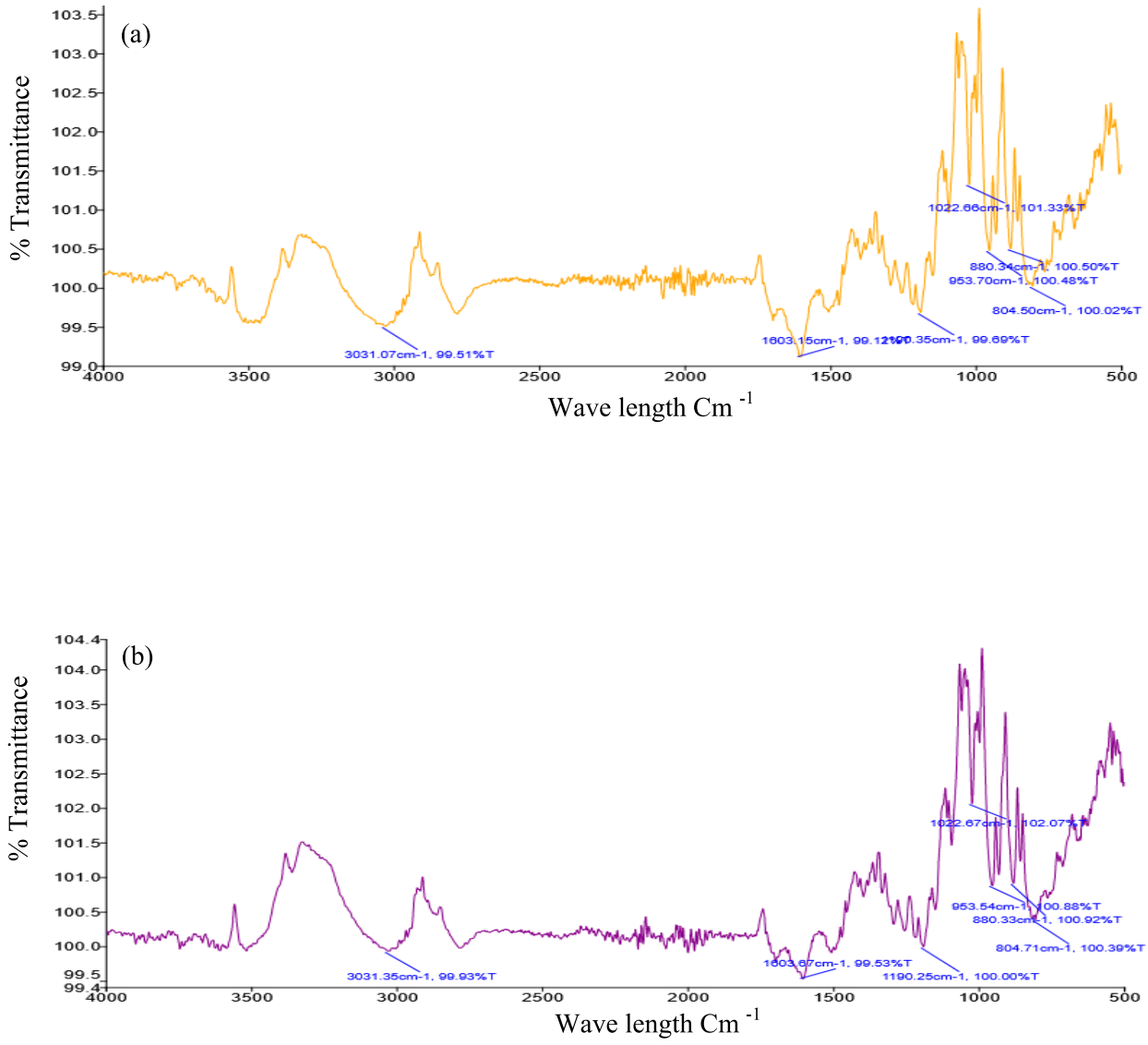
microplastics, it can be ingested in human body through edibles and produce cytotoxic, carcinogenic and neurotoxic impacts to human beings (Hwang et al., 2020). Furthermore, a medium peak at 1523 cm^{-1} indicates presence of benzamidazoles group which has wide range of applications for instance it could be used in pesticides and as an antibiotic for animals to kills dangerous parasites such as tapeworms, lungworms, roundworms. Use of heavy dosage of benzamidazoles either to plants as parasites or to animals as an antibiotic could transfer its residue to their milk and through milk to humans via food chain and could cause deleterious effects to human health (Tejada-Casado et al., 2018). There are few other functional groups also present such as strong and sharp peak at 1021 cm^{-1} of lactones which is constituent of tea whitener as indicated earlier. Weak-medium peak of fatty esters at 988 cm^{-1} (HC=CH) and v(C-O) at 1148 cm^{-1} are considered as constituents of tea whitener, as indicated by Priyanka et al. (2022) in their research study, as indicated earlier in LM-1 sample phosphorus is also detected in TWL-I sample at 930 cm^{-1}. Sample TWL-II shows symmetric and antisymmetric stretch of CH_2 group at 2920 cm^{-1} and 2851 cm^{-1}, very strong peak of C=O at 1744 cm-1, vibrating stretch of carbon oxygen bond v(C-O) at 1150 cm^{-1}, ring structure of benzene derivative at 856 cm^{-1}, these functional groups pointing towards presence of polyethylene terephthalate (Jung et al., 2018). While medium-strong peak at 1092 cm-1 show presence of pyrrole group in sample TWL-II. Sharp strong peak at 1022 cm^{-1} indicates presence of lactones which are present in milk and also a constituent in tea whitener powder (Obi et al., 2018). Another sharp medium peak at 958 cm-1 and 931 cm^{-1} indicates presence of aliphatic CCl and phosphorus group, both these compounds are toxic for human if ingested as indicated by Chang and Anderson (2017) and Amir et al. (2019) in their studies. Lastly, a weak medium peak at 880 cm^{-1} indicates deformation vibration of ring structure of pyrroles in tea whitener sample (Hummel, 2002). Spectra of TWL-III and IV were almost same they show band of NH_2 group at 3324 cm^{-1}, CH_2 symmetric and asymmetric at 2920 and 2850 cm^{-1}, carboxylic anhydride C-O-CO at 1743 cm^{-1}, CH_3 deformation at 1428 cm^{-1} in TWL-IV, CH at 1343 cm^{-1} show Nylon-6. Moreover, $(CH_2)_4$ cyclic at 1237 cm^{-1}, wagging vibration of CH2 at 907 cm-1 in TWL-III and benzene derivative ring at 866 cm^{-1} these functional groups show presence of Polystyrene. Furthermore, in both samples TWL-III and IV at 1048 cm^{-1} indicates deformation vibration of benzamidazole ring structure and it could be deleterious to human health as indicated earlier in TWL-I. Astonishingly, these two samples TWL-III and IV also show peaks at 848, 681which indicate presence of chromium hydroxide CrO(OH) and fluorine. Chromium hydroxide which is highly toxic and impose detrimental effects on humans and environment (Alam et al., 2023). While, aromatic fluorine at 518 cm^{-1}, which could have deleterious impacts on human kidneys (Dharmaratne, 2019). Both samples indicate phosphorus group at 941 cm^{-1}. TWL-IV also show two peaks at 1115 and 1066 cm-1 which indicates presence of trimellitates, which also falls in category of emerging plasticizers and are toxic in nature (Qadeer et al., 2024). IR spectra of TWL samples are depicted below in figure 2.

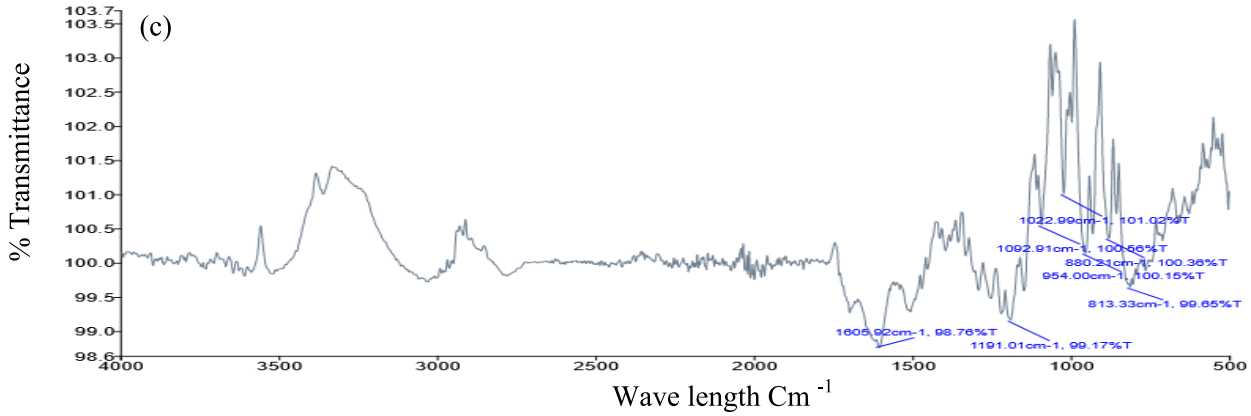
3.3 Morphology and elemental composition of microplastics

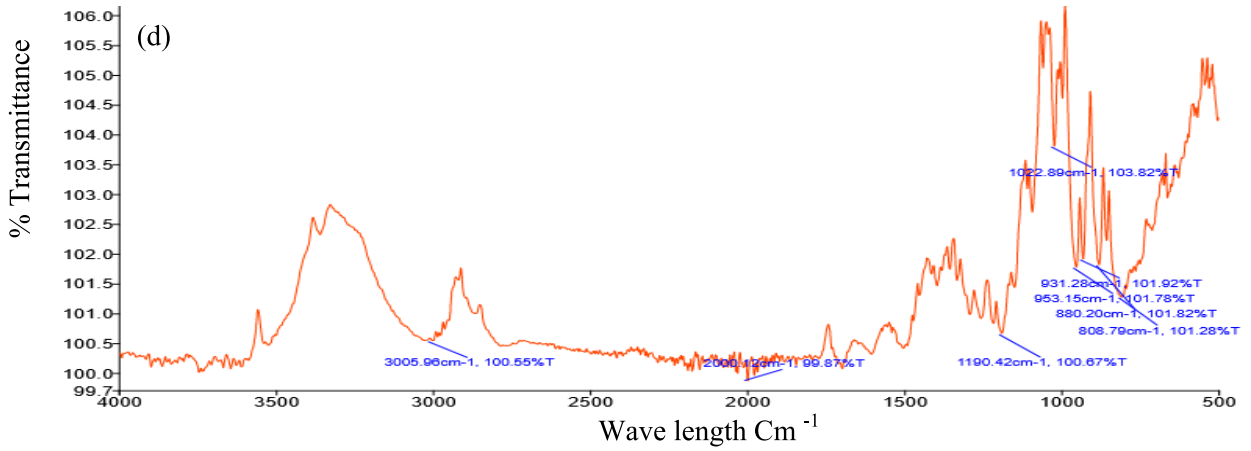
For examination of morphology, surface structure and in depth qualitative analysis of samples for microplastics detection, scanning electron microscopy SEM equipped with EDX energy dispersive x-ray spectroscopy was utilized. As, FTIR results have already revealed presence of synthetic microplastic polymers in all samples, so for SEM-EDX analysis only six representative samples were selected. Outcomes of SEM images show various shapes of microplastics polymer and EDX spectra analysis of samples revealed presence of prodigious amount of carbon in all six samples along with few other contaminants in all samples as shown below in table 1. Moreover, these carbon and oxygen ratio of EDX results were found exceeded than natural amount of carbon and oxygen (25% in tea and 37% in powder milk/ tea whitener) present in tea, milk powder and tea whitener as indicated by Łuczaj and Skrzydlewska (2005) and Mehta (2015).

3.3.1 Morphological and elemental analysis of milk samples

SEM-EDX analysis of selected branded and local milk samples BM-I and LM-I contains polyethylene and polyvinyl alcohol polymers. SEM images of sample BM-I shows irregular shaped debris morphology for polyethylene as indicated by (Da Costa et al., 2021). Moreover, EDX analysis of sample BM-I and LM-I indicates high percentages of carbon and oxygen, as aforementioned in table 2, which indicates presence of synthetic microplastic polymer (Mphaga et al., 2023). Sample LM-I also indicated presence of few other elements such as chlorine, phosphorus, potassium and calcium. Presence of chlorine and phosphorus may be considered as contaminants in this sample, because they are not commonly present in milk. Moreover, presence of phosphorus in LM-I sample was also confirmed earlier by results of FTIR analysis. While presence of calcium and potassium in LM-I sample can be considered as milk constituents. SEM images along with EDX spectra of these two samples are depicted in figure 3.




(c)
% Transmittance
Wave length Cm -1
1605.92cm-1, 98.76%T
1191.01cm-1, 99.17%T
1092.91cm-1, 100.56%T
954.00cm-1, 100.15%T
813.33cm-1, 99.65%T


(d)
% Transmittance
Wave length Cm -1
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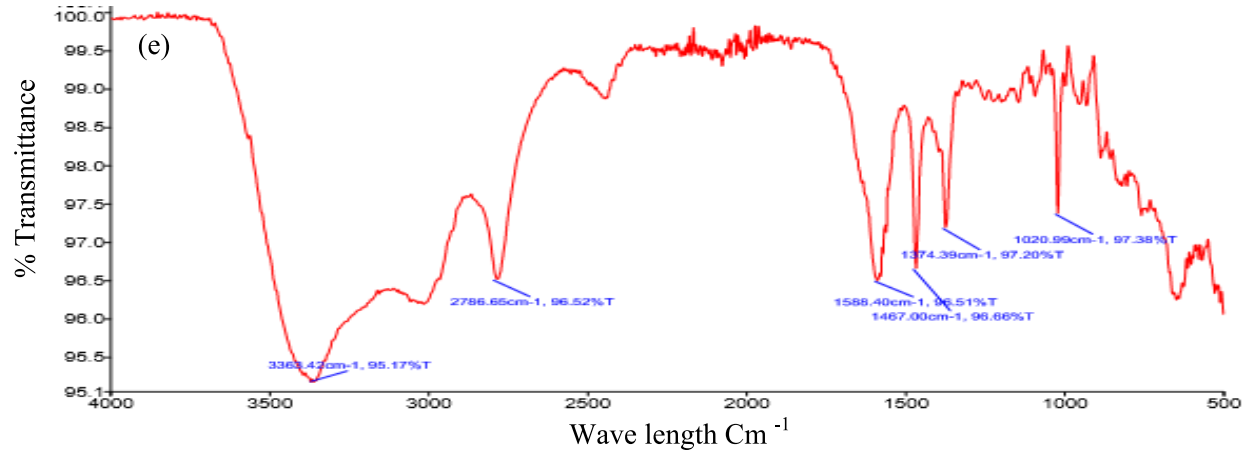
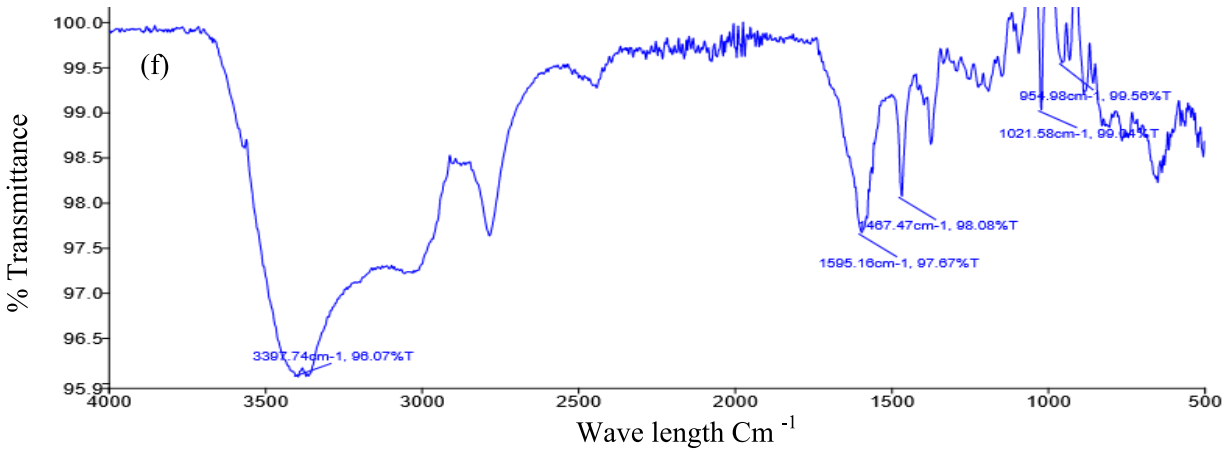
1190.42cm-1, 100.67%T
931.28cm-1, 101.92%T
953.15cm-1, 101.78%T
880.20cm-1, 101.82%T
808.79cm-1, 101.28%T


(e)
% Transmittance
Wave length Cm -1
2786.65cm-1, 96.52%T
1588.40cm-1, 96.51%T
1467.00cm-1, 96.66%T
1374.39cm-1, 97.20%T
1020.99cm-1, 97.38%T


(f)
% Transmittance
Wave length Cm -1
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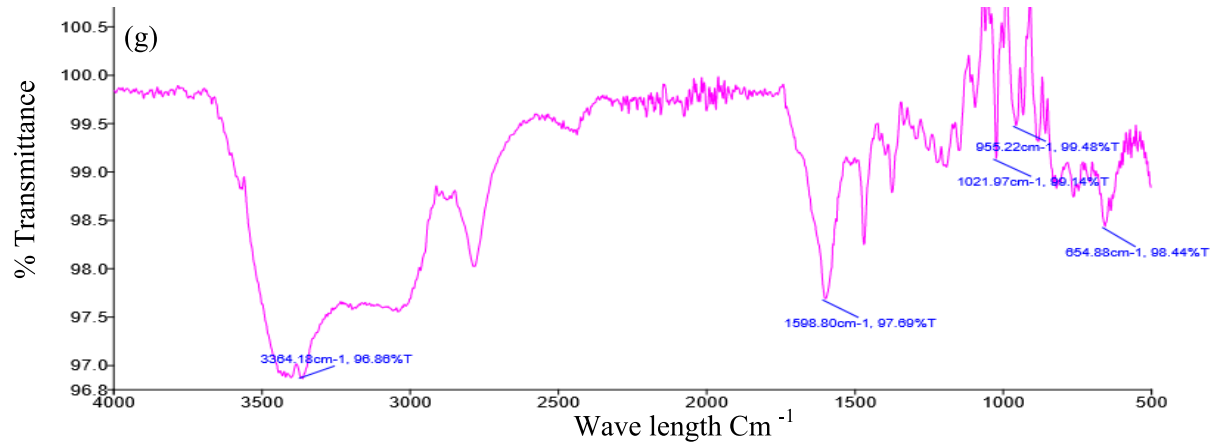
1595.16cm-1, 97.67%T
1467.47cm-1, 98.08%T
954.98cm-1, 99.56%T
1021.58cm-1, 99.44%T


(g)
% Transmittance
Wave length Cm -1
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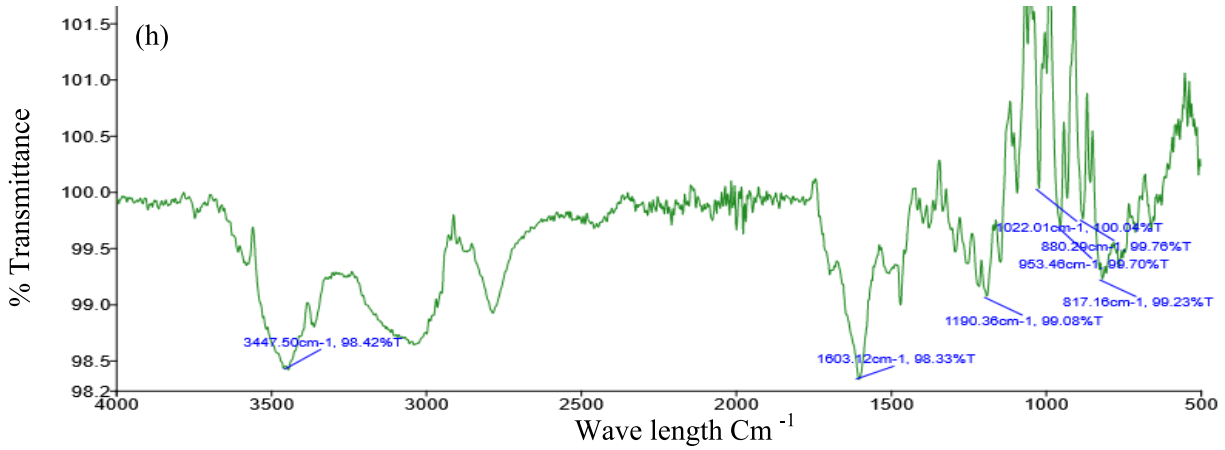
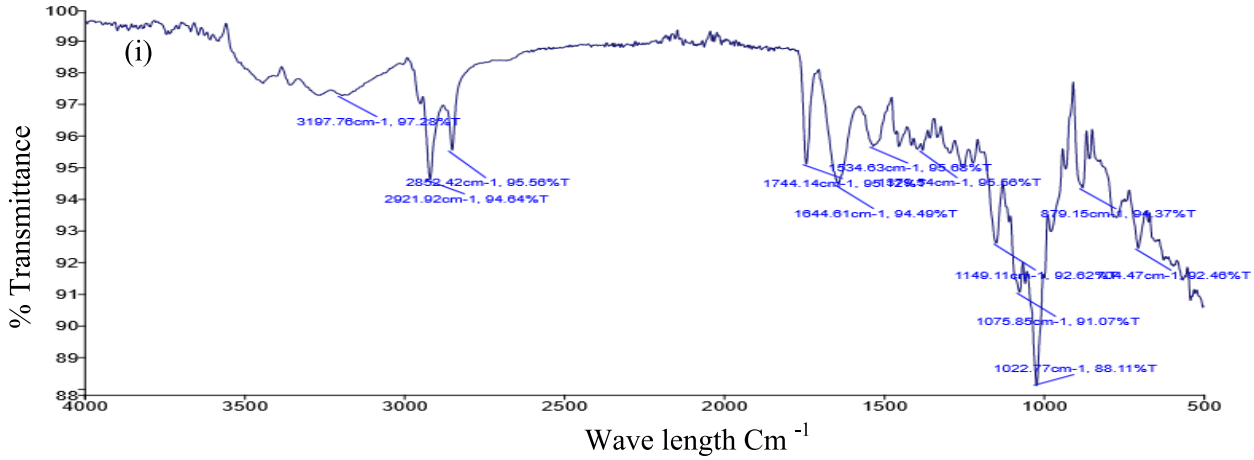
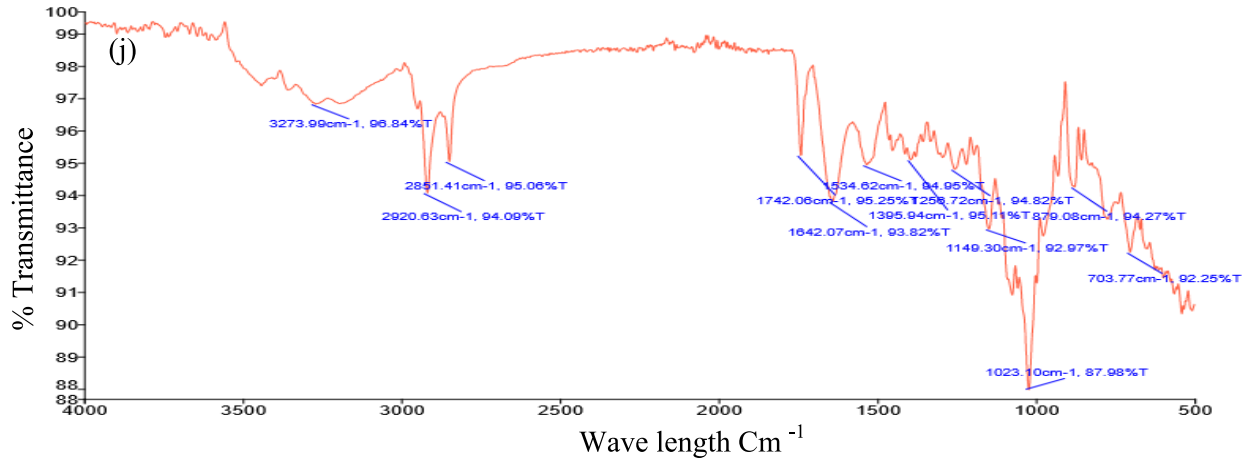
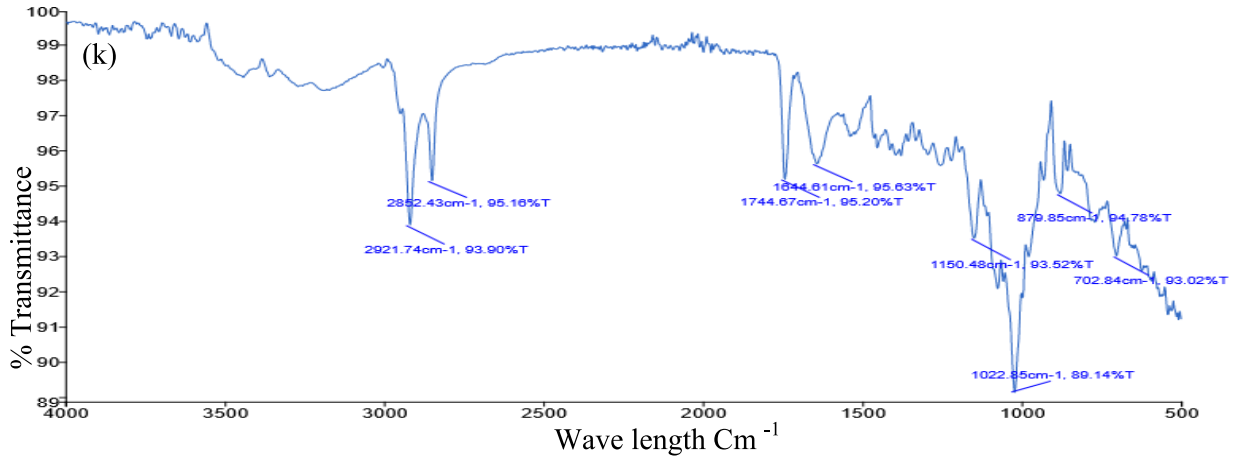
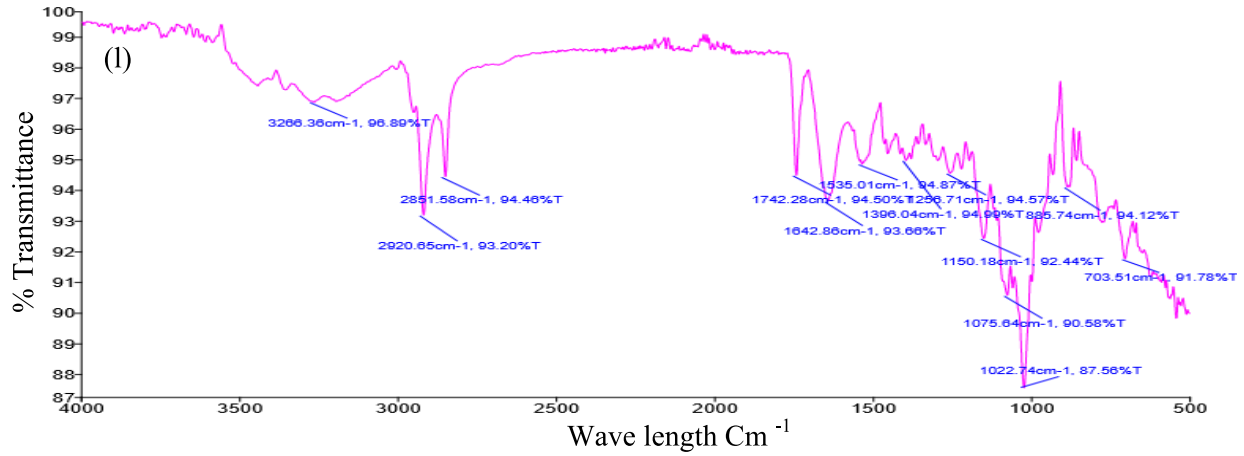
1598.80cm-1, 97.69%T
955.22cm-1, 99.48%T
1021.97cm-1, 99.14%T
654.88cm-1, 98.44%T

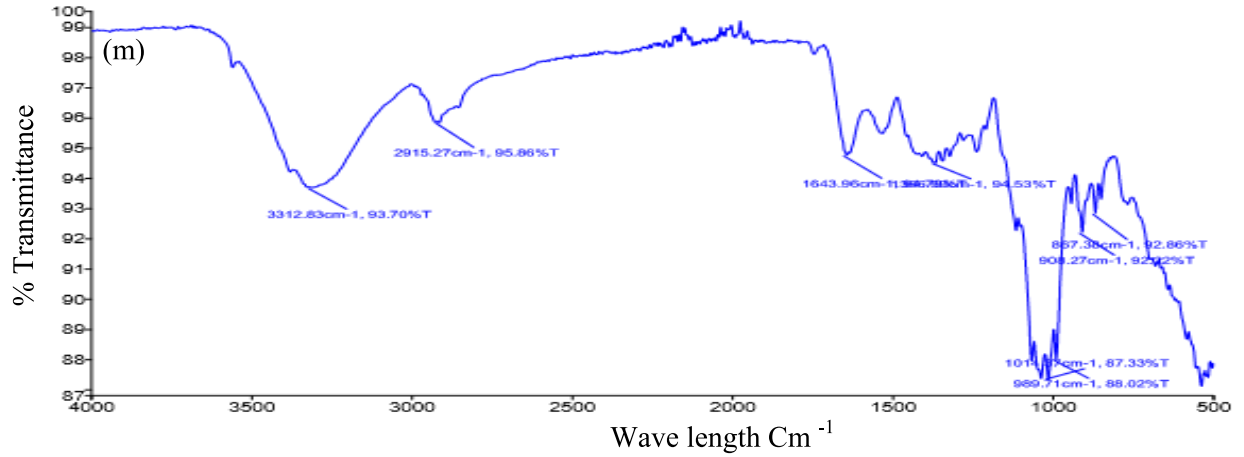

(h)
% Transmittance
Wave length Cm -1
3447.50cm-1, 98.42%T
1603.12cm-1, 98.33%T
1190.36cm-1, 99.08%T
1022.01cm-1, 100.04%T
880.29cm-1, 99.76%T
953.46cm-1, 99.70%T
817.16cm-1, 99.23%T

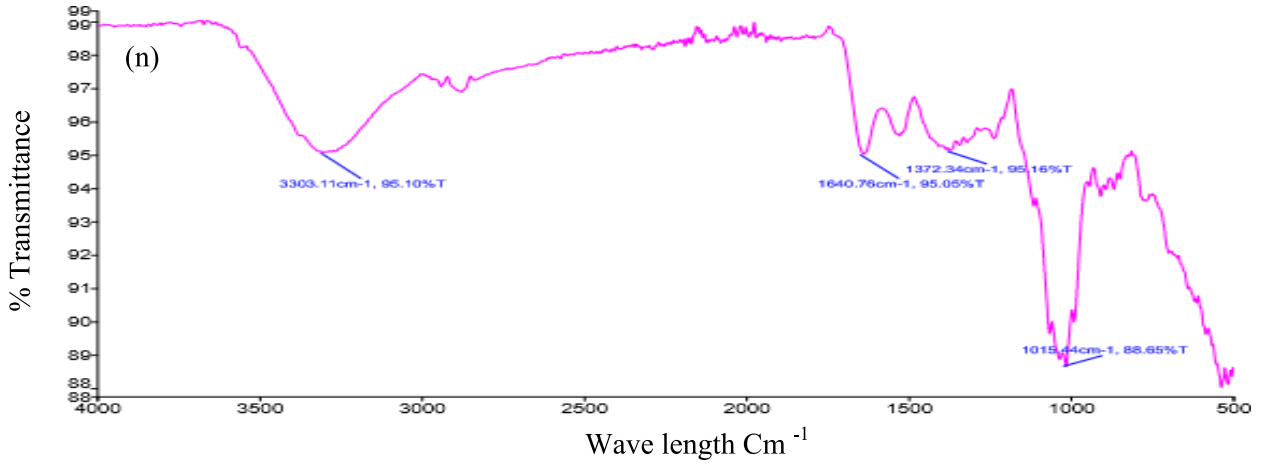

(i)
% Transmittance
Wave length Cm -1
2852.42cm-1, 95.56%T
2921.92cm-1, 94.64%T
1644.61cm-1, 94.49%T
1075.85cm-1, 91.07%T
1022.77cm-1, 88.11%T

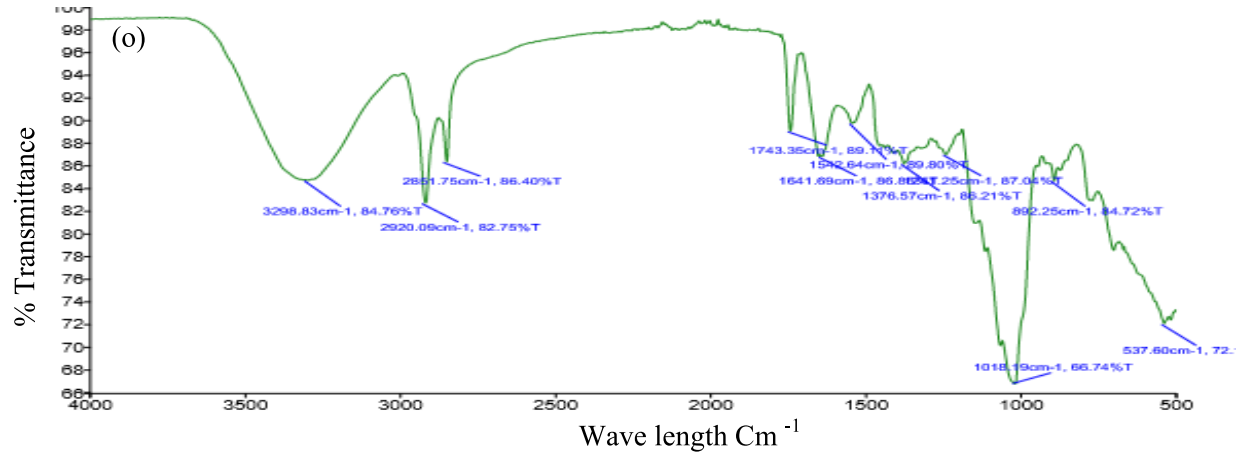

(j)
% Transmittance
Wave length Cm -1
3273.99cm-1, 96.84%T
2851.41cm-1, 95.06%T
2920.63cm-1, 94.09%T
1642.07cm-1, 93.82%T
1149.30cm-1, 92.97%T
703.77cm-1, 92.25%T
1023.10cm-1, 87.98%T

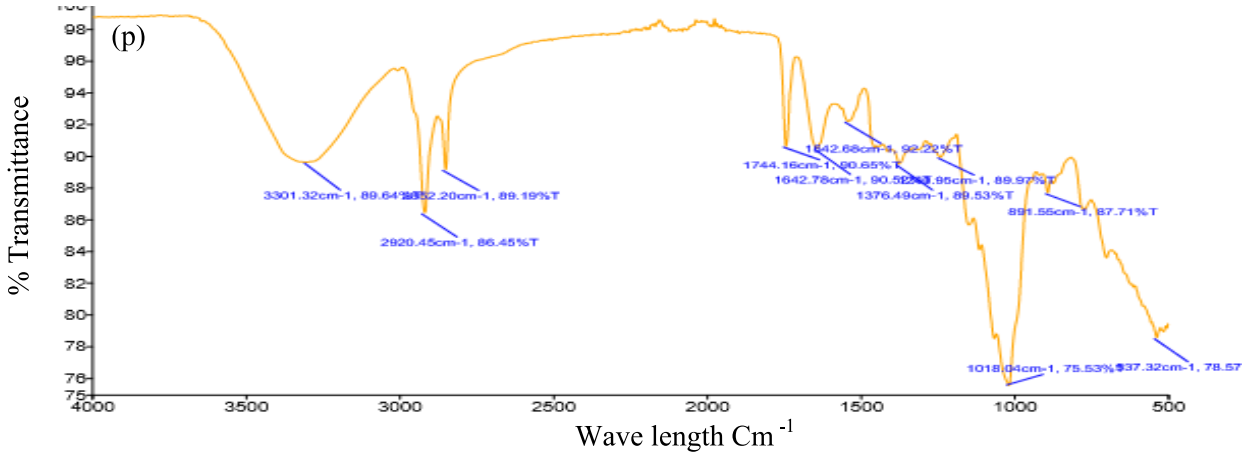

(k)
% Transmittance
Wave length Cm -1
2852.43cm-1, 95.16%T
2921.74cm-1, 93.90%T
1744.67cm-1, 95.20%T
1150.48cm-1, 93.52%T
702.84cm-1, 93.02%T
1022.85cm-1, 89.14%T

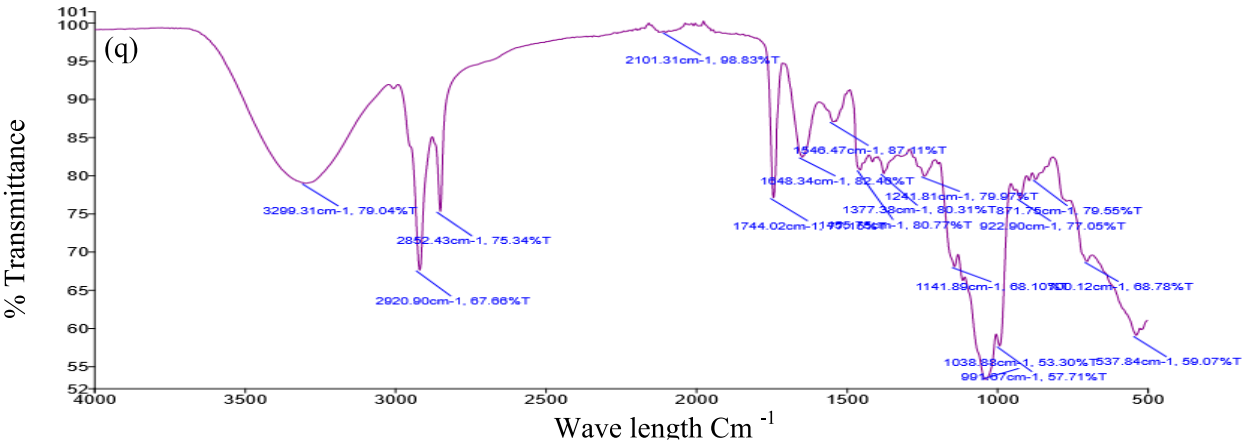

(l)
% Transmittance
Wave length Cm -1
3286.36cm-1, 96.89%T
2851.58cm-1, 94.46%T
2920.65cm-1, 93.20%T
1742.28cm-1, 94.50%T
1642.86cm-1, 93.66%T
1150.18cm-1, 92.44%T
1075.64cm-1, 90.58%T
1022.74cm-1, 87.56%T
703.51cm-1, 91.78%T

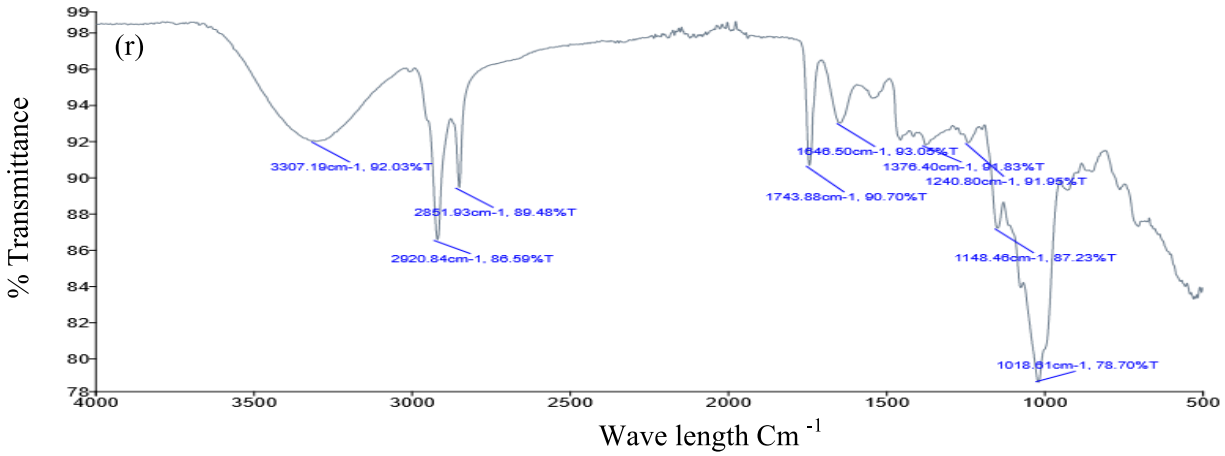

(m)
% Transmittance
Wave length Cm -1
3312.83cm-1, 93.70%T
2915.27cm-1, 95.86%T
1643.96cm-1, 94.53%T
989.71cm-1, 88.02%T

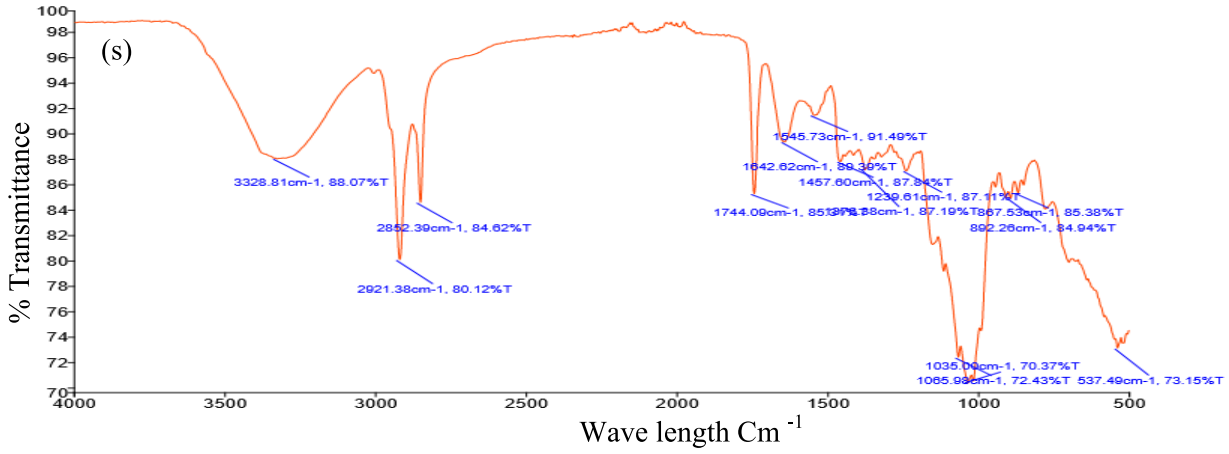

(n)
% Transmittance
Wave length Cm -1
3303.11cm-1, 95.10%T
1640.76cm-1, 95.05%T
1372.34cm-1, 95.16%T
1015.44cm-1, 88.65%T

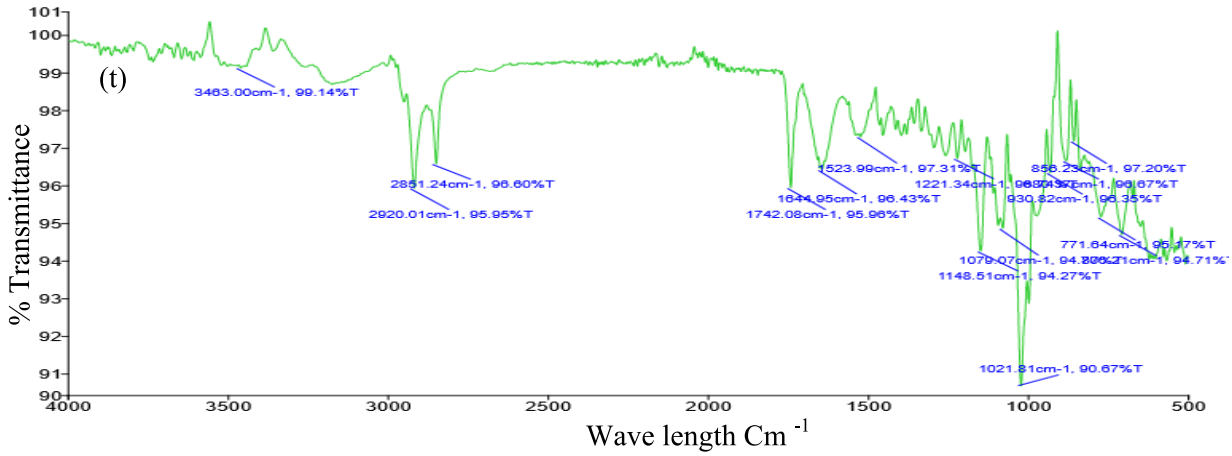

(o)
% Transmittance
Wave length Cm -1
3298.83cm-1, 84.76%T
2920.09cm-1, 82.75%T
2851.75cm-1, 86.40%T
1743.35cm-1, 89.17%T
1642.64cm-1, 89.80%T
1641.69cm-1, 86.85%T
1376.57cm-1, 88.21%T
892.25cm-1, 84.72%T
1018.19cm-1, 66.74%T
537.60cm-1, 72.


(p)
% Transmittance
Wave length Cm -1
3301.32cm-1, 89.64%T
2920.45cm-1, 86.45%T
1744.16cm-1, 90.65%T
1642.68cm-1, 92.22%T
1642.78cm-1, 90.52%T
1376.49cm-1, 89.53%T
891.55cm-1, 87.71%T
1018.04cm-1, 75.53%T
537.32cm-1, 78.57


(q)
% Transmittance
Wave length Cm -1
3299.31cm-1, 79.04%T
2920.90cm-1, 67.66%T
2101.31cm-1, 98.83%T
1744.02cm-1, 80.77%T
1377.38cm-1, 80.31%T
922.90cm-1, 77.05%T
1038.88cm-1, 53.30%T
991.07cm-1, 57.71%T
537.84cm-1, 59.07%T


(r)
% Transmittance
Wave length Cm -1
3307.19cm-1, 92.03%T
2851.93cm-1, 89.48%T
2920.84cm-1, 86.59%T
1646.50cm-1, 93.05%T
1743.88cm-1, 90.70%T
1376.40cm-1, 91.83%T
1240.80cm-1, 91.95%T
1148.46cm-1, 87.23%T
1018.61cm-1, 78.70%T


(s)
% Transmittance
Wave length Cm -1
3328.81cm-1, 88.07%T
2852.39cm-1, 84.62%T
2921.38cm-1, 80.12%T
1545.73cm-1, 91.49%T
1642.62cm-1, 89.39%T
1457.60cm-1, 87.84%T
1239.61cm-1, 87.11%T
1744.09cm-1, 87.19%T
867.53cm-1, 85.38%T
892.26cm-1, 84.94%T
1035.09cm-1, 70.37%T
1085.93cm-1, 72.43%T
537.49cm-1, 73.15%T


(t)
% Transmittance
Wave length Cm -1
3483.00cm-1, 99.14%T
2851.24cm-1, 96.60%T
2920.01cm-1, 95.95%T
1523.99cm-1, 97.31%T
1644.95cm-1, 96.43%T
1742.08cm-1, 95.96%T
1221.34cm-1, 96.67%T
930.82cm-1, 96.35%T
856.23cm-1, 97.20%T
771.64cm-1, 96.47%T
1079.07cm-1, 94.71%T
1148.51cm-1, 94.27%T
1021.81cm-1, 90.67%T

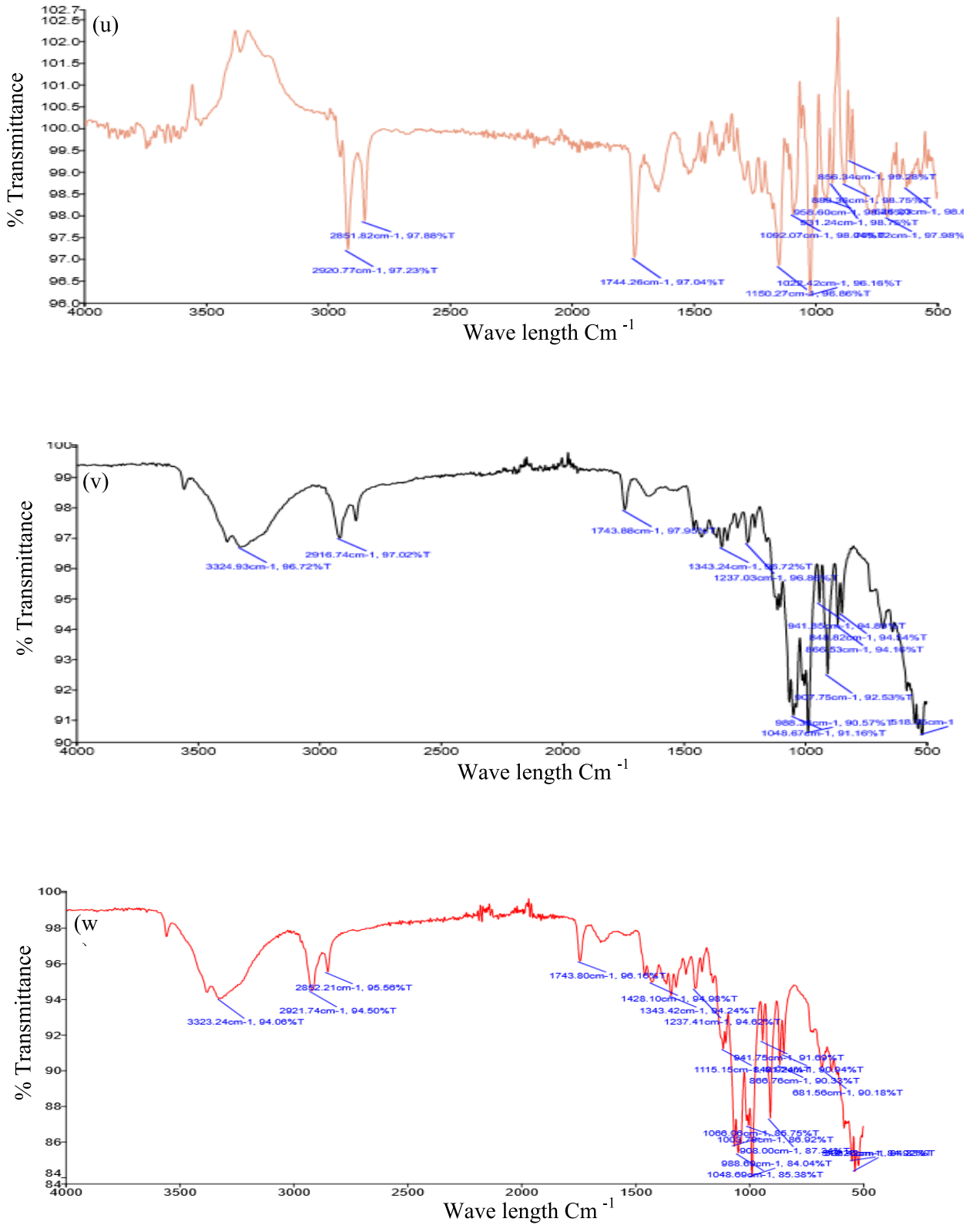
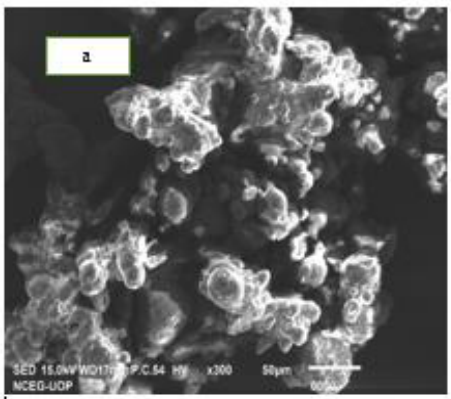
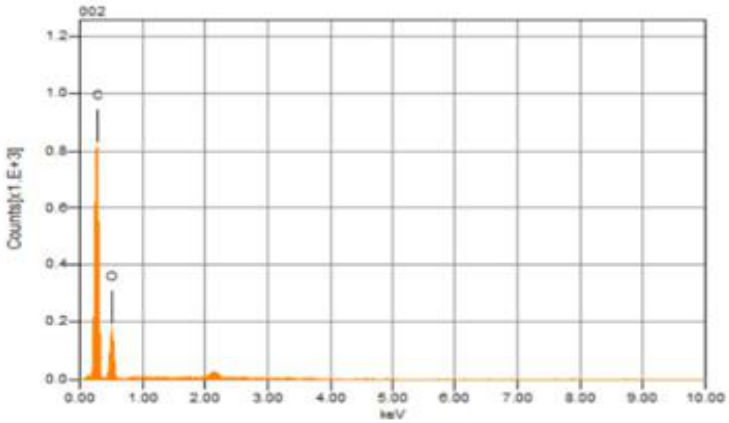
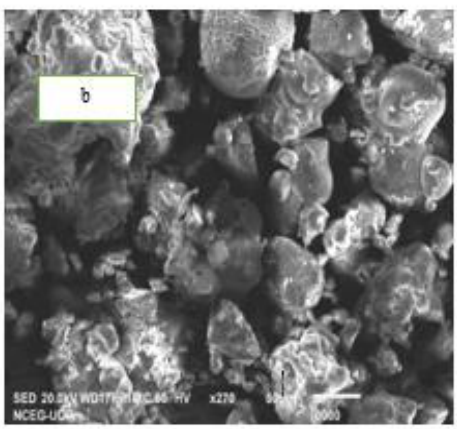
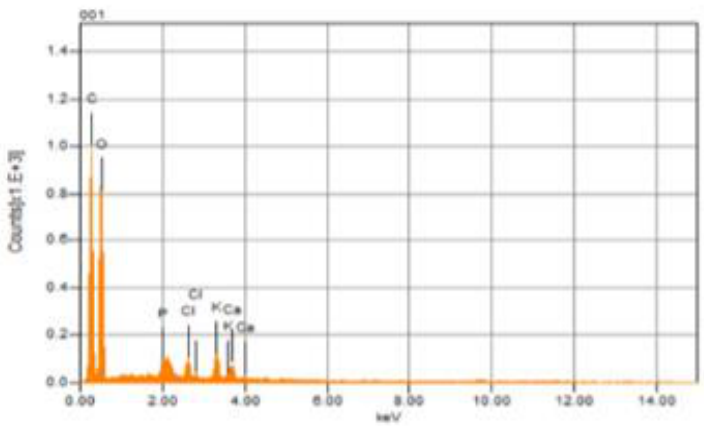


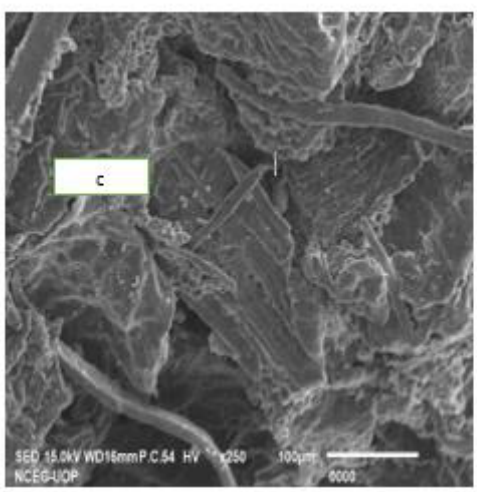
Fig. 2. FTIR Spectra of Branded Tea: a) BT-1, b) BT-II, c) BT-III, and d) BT-IV; FTIR Spectra of Branded Milk: e) BM-I, f) BM-II, g) BM-III, and h) BM-IV; FTIR Spectra of Branded Tea Whiteners: i) TWB-I, j) TWB-II, k) TWB-III; FTIR Spectra of Local Tea: l) LT-I, m) LT-II, n) LT-III, and o) LT-IV; FTIR Spectra of Local Milk: p) LM-I, q) LM-II, r) LM-III, and s) LM-IV); and FTIR Spectra of Local Tea Whitener: t) TWL-I, u) TWL-II, v) TWL-III, and w) TWL-IV.

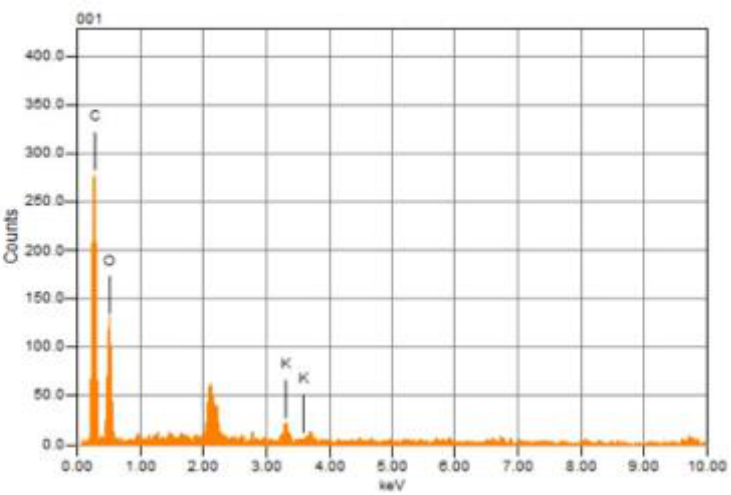

a


002
C
O
Counts[x1 E+3]
keV


b


001
C
O
P
Cl
Cl
K
Ca
K
Ca
Counts[x1 E+3]
keV


c


001
C
O
K
K
Counts
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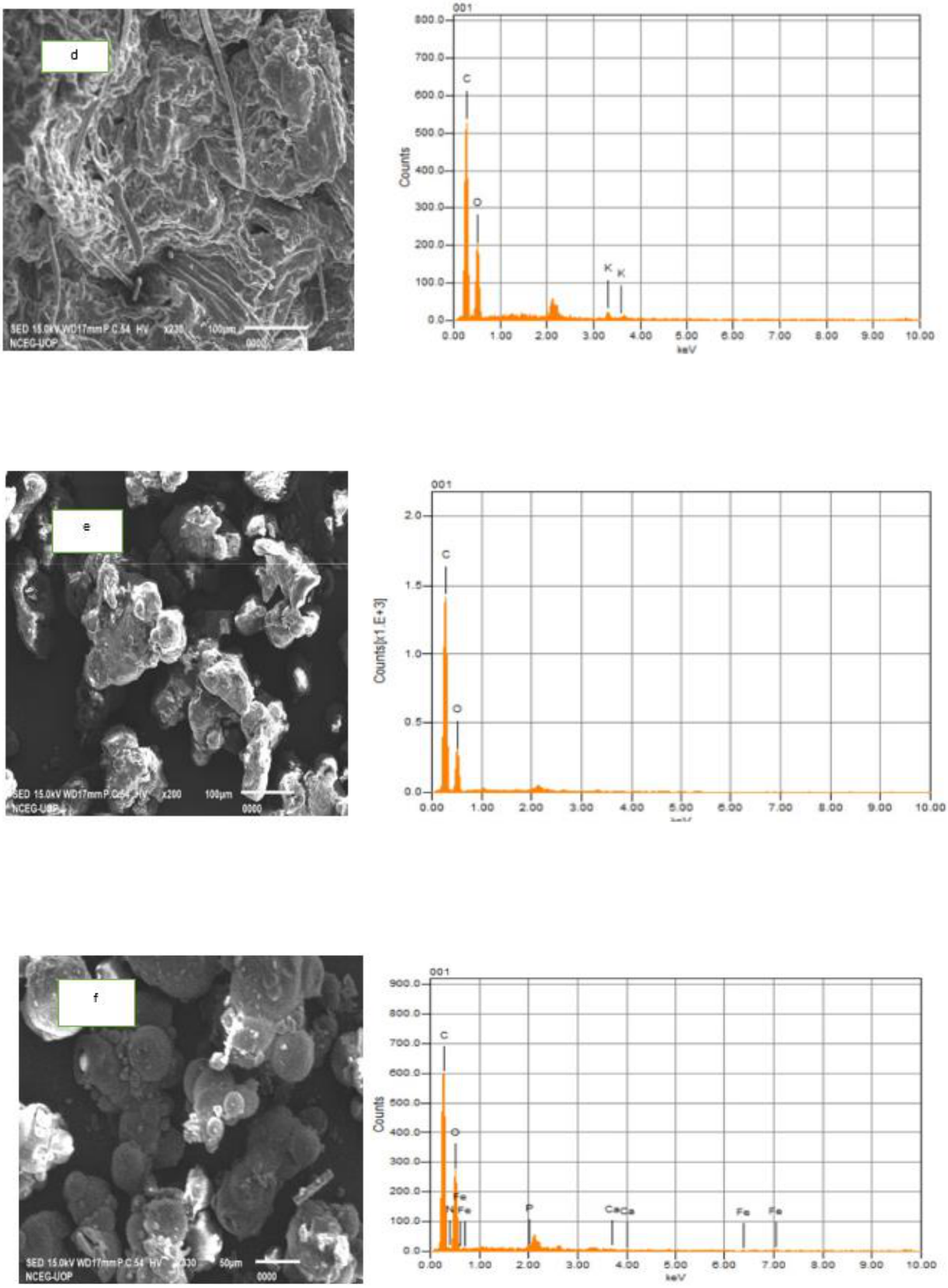

Fig. 3. SEM image and EDX spectra of a) Branded Milk- BM1, b) Local Milk - LM1, c) Branded Tea – BT-3, d) Local Tea – LT-2, e) Branded Tea Whitener- TWB-1, f) Local Tea Whitener- TWL-1.

3.3.2 Morphological and elemental analysis of tea samples

Representative samples of branded and local tea samples show presence of polyethylene terephthalate and nylon. SEM image analysis of samples BT-III and LT-II reveals fiber shape for PET and thread and rod/thread shaped image for nylon. EDX spectra of BT-III show hefty peaks for carbon followed by oxygen. The atomic percentage of carbon was 61.01% and 37.98% of oxygen was observed. Alongside, that 1.01% of potassium atom was also found in BT-III sample, this indicates presence of PET. PET is commonly used as packing material and it is also observed in tea bag samples (Hernandez et al., 2019). SEM-EDX analysis of LT-II reveal presence of nylon. SEM image indicates rod shaped and thread like structure which is commonly observed in nylon polymer. EDX spectra show intense peaks for carbon and oxygen with atomic percentage of 61.95 % for carbon and 37.43% for oxygen respectively. While, atomic percentage of potassium was 0.62 in sample. SEM images and EDX spectra of both samples are shown in figure 2.

3.3.3 Morphological and elemental analysis of tea whitener samples

SEM image of branded tea whitener, TWB-I sample exhibit irregular debris structure which denotes presence of polyethylene. EDX spectra has further confirm presence of polyethylene in sample as it shows gigantic carbon peak followed by oxygen peak, with 71.32 % of carbon and 28.62 % of oxygen. On the other hand, local tea whitener sample TWL-I shows rod like shape structure and spheres which are typically associated with nylon and polystyrene polymers (Hawng et al., 2020). Furthermore, EDX spectra of sample TWL-I reveals prodigious carbon peak followed by oxygen peak. Atomic percentage of carbon was 61.02 and oxygen was 37.94. While, few other elements were also detected in trace amounts such as nitrogen (0.81%), iron (0.11%), calcium 0.09% and phosphorus 0.03%. SEM image and EDX spectra of both samples are shown in figure 2.

4. Conclusions

The study revealed the presence of various types of microplastic polymers in samples such as PE, PET, PVA, Nylon and PS. Moreover, beside microplastics various other pollutants such as adipates, hydroxyethyl methacrylate, chromium, phosphorus, chlorine, these all are toxic their ingestion could impose devastating impacts on human health. Elemental makeup and morphological analysis of samples have further confirmed the presence of microplastics contaminants. SEM image shows fiber, rod shape, irregular shape which were commonly observed in microplastics, Moreover, EDX spectra have also shown high percentages of carbon in all samples (more than natural amount of carbon present in tea, dry milk and tea whitener). So, presence of excess amount of carbon than natural amount may indicates presence of microplastics polymer in samples. In comparison, the branded samples contain two types of microplastics polymers namely polyethylene and polyethylene terephthalate. However, along with polyethylene and polyethylene terephthalate local samples also contaminated nylon, polystyrene and polyvinyl alcohol. It is concluded that according to survey outcomes 90% people prefer branded tea, tea whitener and dry milk for their daily tea preparation over non-branded. So, it is concluded that people consuming branded tea, dry powder and tea whitener are at less risk comparatively to people consume non-branded ones, as non-branded samples contains more toxic MP's than branded ones.

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Authors' Contribution

Fiza Sarwar, proposed the main concept and supervised the study throughout. Muhammad Zuhair Asif was involved in data collection, analysis and write up. Amara Dar assisted in methodology and results interpretation. Syed Umair Ullah Jamil worked on figures and approved the writeup. Waqar-

un-Nisa provided relevant literature, and review and proof read of the manuscript.

Conflict of Interest

All authors declare no conflict of interest.

Data Availability Statement

The data sets generated and analyzed during the current study are available in the main body of the paper.

References

Adnan, M., Ahmad, A., Ahmed, A., Khalid, N., Hayat, I., Ahmed, I., 2013. Chemical composition and sensory evaluation of tea (Camellia sinensis) commercialized in Pakistan. Pakistan Journal of Botany, 45(3), 901-907.

Afrin, S., Rahman, M. M., Hossain, M. N., Uddin, M. K., Malafaia, G., 2022. Are there plastic particles in my sugar? A pioneering study on the characterization of microplastics in commercial sugars and risk assessment. Science of the Total Environment, 837, 155849.

Alam, M. A., Mondal, A. K., Uddin, M. T., Razzaq, M. A., Chowdhury, M. J., Saha, M. S., 2023. Chemical Investigation and Separation of Chromium from Chrome Cake of BSCIC Tannery Industrial Estate at Hemayetpur, Dhaka, Bangladesh. Journal of Environmental and Public Health, 2023.

Amir, M., Ahmad, N., Sarfaroz, M., Ahmad, W., Ahmad, S., Mujeeb, M., Pottoo, F. H., 2019. Tamarindus indica fruit: Pharmacognostical standardization, detection of contaminant, and in vitro antioxidant activity. Journal of Pharmacy and Bio Allied Sciences, 11(4), 355.

Andrady, A. L., 2011. Microplastics in the marine environment. Marine Pollution Bulletin, 62(8), 1596-1605.

Bellamri, M., Brandt, K., Cammerrer, K., Syeda, T., Turesky, R. J., Cannon, J. R., 2023. Nuclear DNA and mitochondrial damage of the cooked meat carcinogen 2-amino-1-methyl-6-phenylimidazo [4, 5-b] pyridine in human neuroblastoma cells. Chemical Research in Toxicology, 36(8), 1361-1373.

Bo, L. J., Li, B., Zhang, K., Ma, R. H., Li, Y., Wang, Y. Q., Liu, Y. Y., 2023. Distribution, sources, and behavioral characteristics of microplastics in farmland soil. Huan Jing Ke Xue, 44(4), 2375-2383.

Butt, I., Fatima, M., Bhalli, M. N. U. M., Ali, M., 2020. Evaluation of drinking water quality and waterborne disease prevalence in children at Shah di Khoi, Lahore, Pakistan. Journal of Himalayan Earth Science, 53(1), 118-125.

Chang, A. R., Anderson, C., 2017. Dietary phosphorus intake and the kidney. Annual Review of Nutrition, 37, 321-346.

Dharmaratne, R. W., 2019. Exploring the role of excess fluoride in chronic kidney disease: a review. Human and Experimental Toxicology, 38(3), 269-279. doi:10.1177/0960327118814161

Furlani, R. P., Dias, F. F., Nogueira, P. M., Gomes, F. M., Tfouni, S. A., Camargo, M. C. 2015. Occurrence of macrocyclic lactones in milk and yogurt from Brazilian market. Food Control, 48, 43-47.

Geyer, R., 2020. Chapter 2-Production, use, and fate of synthetic polymers. In: Trevor, M. L. (eds) Plastic waste and recycling. Academic Press, 13-32. https://doi.org/10.1016/B978-0-12-817880-5.00002-5.

Hernandez, L. M., Xu, E. G., Larsson, H. C., Tahara, R., Maisuria, V. B., Tufenkji, N., 2019. Plastic teabags release billions of microparticles and nanoparticles into tea. Environmental Science and Technology, 53(21), 12300-12310.

Hummel, D.O., 2002. Infrared Spectrometry. In: Atlas of Plastics Additives. Springer, Berlin, Heidelberg. https://doi.org/10.1007/978-3-642-56211-2_3.

Hussain, R., Khattak, S. A., Sattar, S., Ali, L., Ullah, Z., Muhammad, N., 2020. Evaluation of the contaminated soil and its impacts on Tobacco (Nicotiana tabacum L.) crops in Swabi, Pakistan. Journal of Himalayan Earth Science, 53(1), 34-48.

Hwang, J., Choi, D., Han, S., Jung, S. Y., Choi, J., Hong, J., 2020. Potential toxicity of polystyrene microplastic particles. Scientific Reports, 10(1), 7391.

Iñiguez, M. E., Conesa, J. A., Fullana, A., 2017. Microplastics in Spanish table salt.

Scientific Reports, 7(1), 8620.
Jung, M. R., Horgen, F. D., Orski, S. V., Rodriguez, V., Beers, K. L., Balazs, G. H., Lynch, J. M., 2018. Validation of ATR FT-IR to identify polymers of plastic marine debris, including those ingested by marine organisms. Marine Pollution Bulletin, 127, 704-716.
Koelmans, B., Pahl, S., Backhaus, T., Bessa, F., Calster, G.V., Contzen, N., Cronin, R., Galloway, T.S., Hart, A., Henderson, L., Kalčíková, G., Kelly, F.J., Kołodziejczyk, B., Marku, E., Poortinga, W., Rillig, M.C., Sebille, E.V., Steg, L., Steinhorst, J., Steidl, J., Syberg, K., Thompson, R.C., Wagner, M., Wezel, A.P., Wyles, K.J., Wright, S.L., 2019. A Scientific Perspective on Microplastics in Nature and Society. SAPEA, Berlin, publisher 173 pp. Doi 10.26356/microplastics.
Khattak, M. S., Ali, S., 2015. Assessment of temperature and rainfall trends in Punjab province of Pakistan for the period 1961-2014. Journal of Himalayan Earth Sciences, 48(2), 42-61.
Kutralam-Muniasamy, G., Pérez-Guevara, F., Elizalde-Martínez, I., Shruti, V. C., 2020. Branded milks–Are they immune from microplastics contamination. Science of the Total Environment, 714, 136823.
Leal Filho, W., Saari, U., Fedoruk, M., Iital, A., Moora, H., Klöga, M., Voronova, V., 2019. An overview of the problems posed by plastic products and the role of extended producer responsibility in Europe. Journal of Cleaner Production, 214, 550-558.
Li, Y., Peng, L., Fu, J., Dai, X., Wang, G., 2022. A microscopic survey on microplastics in beverages: the case of beer, mineral water and tea. Analyst, 147(6), 1099-1105.
Liu, Y., Li, R., Yu, J., Ni, F., Sheng, Y., Scircle, A., Zhou, Y., 2021. Separation and identification of microplastics in marine organisms by TGA-FTIR-GC/MS: A case study of mussels from coastal China. Environmental Pollution, 272, 115946.
Łuczaj, W., Skrzydlewska, E., 2005. Anti-oxidative properties of black tea. Preventive Medicine, 40(6), 910-918.
MacLeod, M., Arp, H. P. H., Tekman, M. B., Jahnke, A., 2021. The global threat from plastic pollution. Science, 373(6550), 61-65.
Mason, S. A., Welch, V. G., Neratko, J., 2018. Synthetic polymer contamination in bottled water. Frontiers in Chemistry, 6, 389699.
Mehta, B. M., 2015. Chemical Composition of Milk and Milk Products. In: Cheung, P., Mehta, B. (eds) Handbook of Food Chemistry. Springer, Berlin, Heidelberg. https://doi.org/10.1007/978-3-642-36605-5_31
Mei, T., Wang, J., Xiao, X., Lv, J., Li, Q., Dai, H., Pi, F., 2022. Identification and evaluation of microplastics from tea filter bags based on Raman imaging. Foods, 11(18), 2871.
Mphaga, T., Mhlongo, T. N., Zikalala, S., Topkin, J. 2023. Identification and quantification of microplastics in wastewater treatment plants by spectroscopic and microscopic techniques in Johannesburg East, South Africa. Water Practice and Technology, 18(12), 3124-3140.
Noda, I., Dowrey, A. E., Haynes, J. L., Marcott, C., 2007. Group Frequency Assignments for Major Infrared Bands Observed in Common Synthetic Polymers. In: Mark, J.E. (eds) Physical Properties of Polymers Handbook. Springer, New York, NY. https://doi.org/10.1007/978-0-387-69002-5_22.
Obi, J., Yoshinaga, K., Tago, A., Nagai, T., Yoshida, A., Beppu, F., Gotoh, N., 2018. Simple quantification of lactones in milk fat by solvent extraction using gas chromatography– mass spectrometry. Journal of Oleo Science, 67(8), 941-948.
Oßmann, B. E., Sarau, G., Holtmannspötter, H., Pischetsrieder, M., Christiansen, S. H., Dicke, W., 2018. Small-sized microplastics and pigmented particles in bottled mineral water. Water Research, 141, 307-316. https://doi.org/10.1016/j.watres.2018.05.027.
Qadeer, A., Anis, M., Warner, G. R., Potts, C., Giovanoulis, G., Nasr, S., Shuhang, W., 2024. Global environmental and toxicological data of emerging plasticizers: current knowledge, regrettable substitution dilemma, green solution and future perspectives. Green

Chemistry. https://doi.org/10.1039/D3GC03428C

Rameeza, F., Eun, J. B., 2022. Production, Consumption, and Trading of Tea in Pakistan. The Korean Tea Society, 28(2), 45-51. https://doi.org/10.29225/jkts.2022.28.2.45

Schlawinsky, M., Santana, M. F., Motti, C. A., Martins, A. B., Thomas-Hall, P., Miller, M. E., Kroon, F. J., 2022. Improved microplastic processing from complex biological samples using a customized vacuum filtration apparatus. Limnology and Oceanography: Methods, 20(9), 553-567.

Smith, M., Love, D. C., Rochman, C. M., Neff, R. A., 2018. Microplastics in seafood and the implications for human health. Current Environmental Health Reports, 5, 375-386.

Teboul, E., Orihel, D. M., Provencher, J. F., Drever, M. C., Wilson, L., Harrison, A. L., 2021. Chemical identification of microplastics ingested by Red Phalaropes (Phalaropus fulicarius) using Fourier Transform Infrared spectroscopy. Marine Pollution Bulletin, 171, 112640.

Tejada-Casado, C., del Olmo-Iruela, M., García-Campaña, A. M., Lara, F. J., 2018. Green and simple analytical method to determine benzimidazoles in milk samples by using salting-out assisted liquid-liquid extraction and capillary liquid chromatography. Journal of Chromatography B, 1091, 46-52. https://doi.org/10.1016/j.jchromb.2018.05.024.

Tiwari, M., Rathod, T. D., Ajmal, P. Y., Bhangare, R. C., Sahu, S. K., 2019. Distribution and characterization of microplastics in beach sand from three different Indian coastal environments. Marine Pollution Bulletin, 140, 262-273.

Vikhareva, I. N., Aminova, G. K., Mazitova, A. K., 2021. Ecotoxicity of the adipate plasticizers: Influence of the structure of the alcohol substituent. Molecules, 26(16), 4833.

Xiang, J.; Liu, F.; Wang, B.; Chen, L.; Liu, W.; Tan, S., 2021. A Literature Review on Maillard Reaction Based on Milk Proteins and Carbohydrates in Food and Pharmaceutical Products: Advantages, Disadvantages, and Avoidance Strategies. Foods, 10(9), 1998. https://doi.org/10.3390/foods10091998

Zarus, G. M., Muianga, C., Brenner, S., Stallings, K., Casillas, G., Pohl, H. R., Gehle, K., 2023. Worker studies suggest unique liver carcinogenicity potential of polyvinyl chloride microplastics. American journal of industrial medicine, 66(12), 1033-1047.