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Physicochemical Properties and Characterisation Of Wax Extracted From Cassava Byproducts – Peels And Bagasses

Chioma Vivian Abiaziem* & Evelyn Ufoma Adebisi
Department of Science Laboratory Technology, The Federal Polytechnic Ilaro, Ogun State, Nigeria.
*chioma.abiaziem@federalpolyilaro.edu.ng; evelyn.adebisi@federalpolyilaro.edu.ng

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Abstract
Waxes were extracted from byproducts of cassava processing (peels and bagasses), characterised and analyzed for their physicochemical properties to determine their industrial potential uses as a way of environmental pollution otherwise caused by indiscriminate deposal. The characterisation was done using FTIR, UV-visible spectroscopy and SEM. The physicochemical properties were done using standard methods. The results obtained were; yield (8.51±0.19% and 9.86±0.16% (w/w), melting point (63.5±0.06 and 62.50±0.09ºC), saponification value (103.42±0.19 and 275.01±0.01 mg/KOH/g), acid value (23.40±0.20 and 29.15±0.02 mg/KOH/g), ester value (80.02±0.15 and 245.85±0.12 mg/KOH/g), free fatty acid (11.77±0.07 and 14.66±0.10 mg/KOH/g) and iodine value (90.03±0.03 and 22.54±0.04 mg/KOH/g), respectively. Also, the waxes were viscous liquid at room temperature, colourless, odourless and free of adulterants. Although both waxed differed significantly in the chemical properties, both exhibited similar properties as beeswax. It was concluded that waxes from both byproducts can find useful industrial applications as beeswax in pharmaceutical, cosmetics, paints and food industries. Also, it will reduce their effects on environmental degradation otherwise caused by inappropriate disposal of the wastes.
Keywords: Agricultural wastes, Cassava bagasse, Cassava peel, Wax.

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1. Introduction

Cassava (*Manihot esculenta*), a root tuber tropical crop is wildly grown in Nigeria. Indeed, the crop is cultivated in almost two-thirds of the geopolitical regions of Nigeria. The tuber is eaten boiled or as processed products - 'gari', 'fufu' and 'lafun' in the southwestern and southeastern regions of the country (SENCE Agric, 2013). Nigeria is the world's largest producer of cassava. The country's 59 million tonnes production accounts for a fifth of the global production in 2017 (Otekunrin & Sawicka, 2019). Quite apart from being a valuable source of dietary carbohydrate and energy for Nigerians, the tuber is cherished by the industry for its starch. For example, cassava starch is used for textile, pharmaceuticals, adhesives, and alcohol production. Also, the byproducts of cassava processing including the peels and bagasse are relished by livestock – pigs and ruminants. Unfortunately, the animal feeding value of the carbohydrate-rich wastes is limited by the low protein content and poor digestibility (Pallar, Elakkiya, Tennety & Devip, 2012). Besides, raw cassava waste contains toxic hydrocyanic acid. Consequently, only an insignificant fraction of the byproducts are used for animal feeding. A greater proportion is discarded as agricultural wastes, which in most cases were improperly disposed of, therefore causing environmental pollution and thus constituting health hazard.

Recycling or re-utilization of wastes generated from the cassava processing may be the solution to the problem of poor agricultural waste management in the country. Consequently, the application of the cassava wastes as alternate substrates for bioprocesses will address the challenge of environmental pollution to some degree. Numerous methods have been advanced to exploit cassava peel and cassava bagasse to generate value-added products such as organic acids, ethanol, aroma, and mushroom among others (Bekele, Desalegn & Mitiku, 2015). This study reports the extraction of waxes from cassava peel and bagasse and their physiochemical properties and characterization intending to find acceptable use for them.

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2. Materials And Methods

2.1 Sample Collection

Cassava peels and bagasse samples used in this study were collected from a cassava processing factory in Ilaro, Ogun State, Nigeria. The samples were washed with clean distilled water to remove dirt, dried to constant weight in a hot air oven at 80^{o}C, pulverized into fine powder in a mill and then kept in labelled sealed air-tight polyethene containers at room temperature until required for wax extraction and further tests. All reagents used were AR grade chemicals.

2.2 Wax Extraction

Physicochemical Parameters and Statistical Analysis

The physicochemical analysis of samples of waxes extracted from cassava peels and bagasse were conducted using the method described by Anuj, Yuvraj, Veena and Nishi (2014). Fat constants including acid value, free fatty acids, saponification value, ester value, and iodine value were determined. The melting points of the waxes were determined using the capillary method adopted by Bekele *et al.* (2016). All determinations were done in three replications. Mean values of the parameters and their standard deviations were subsequently presented. Comparison of the mean values using Student t-test of Statistical Toolkit (Microsoft Excel) was done to ascertain significant differences between chemical characteristics of both waxes.

Characterization of Waxes

The characterisation of the waxes extracted was carried out using Fourier transform infrared spectroscopy (FT-IR), Ultraviolet-Visible spectroscopy (UV-Vis) and Scanning electron microscope (SEM).

3. Results and Discussion

The percent yield of wax from cassava bagasse (9.86±0.16%) was slightly higher than that from cassava peels (8.51± 0.19%). The wax yields obtained in this study were higher compared to those obtained by Gaoxiang *et al.*, 2016 (1.2%) and Attard *et al.* (2015) (0.53%). The higher yield of wax from cassava byproducts in this study might be due to the inefficient cassava processing which did not remove flesh completely from the peels and the fibrous core. Indeed, the traditional method of processing is adopted at the cassava factory, the source of the wastes. Besides, differences in the cassava varieties, physical structure and chemical composition used in this study and the earlier studies might be responsible for the difference in the yields.

The results of the physicochemical characteristics of the extracted waxes from cassava byproducts presented in Table 1 indicated that the waxes were viscous liquids at room temperature and they had good odour. The melting points were 63.50±0.06 and 62.50±0.09^{o}C for the peel and the bagasse wax, respectively. The melting points observed in this study were within the same range as the earlier reported values by Mangesh & Lele (2012); Bekele *et al.* (2016). The physical characteristics exhibited by the extracted waxes appeared to signify that they are clear of foulness and can be used for various purposes.

The chemical characteristics including acid values, saponification values, ester values, free fatty acid contents and iodine values of the experimental waxes are presented in Table 1. The results showed that except for iodine value, other fat constants determined were significantly higher in cassava bagasse wax than in cassava peel wax.

Table 1: Physicochemical characteristics of crude cassava peel and bagasse wax

	Cassava peel wax	Cassava bagasse wax
Physical characteristics		
Odour	Agreeable odour	Agreeable odour
Nature	Viscous	Viscous

	Mean	±SD	Mean	±SD
Percentage yield (%)	8.51	0.19	9.86	0.16
Melting point (°C)	63.50	0.06	62.50	0.09
Chemical characteristics				
Acid value (mgKOH/g)	23.40[b*]	0.20	29.15[a]	0.02
Saponification value (mgKOH/g)	103.42[b]	0.19	275.01[a]	0.01
Ester value (mgKOH/g)	80.02[b]	0.15	245.85[a]	0.12
Iodine value (g I/100 g)	90.03[a]	0.03	22.54[b]	0.04
Free fatty acid (mg/100 g)	11.77[b]	0.07	14.66[a]	0.10

*Mean in a row denoted by different superscripts are significantly different ($p<0.05$)

The acid value is a relative measure of acidity due to free acidity, the product of the hydrolytic breakdown of glycerides (Bekele *et al.***,** 2016). It, therefore, indicates the state of hydrolysis of the product. The range of acid values obtained for the experimental waxes in this study 23.4±0.20 mgKOH/g (cassava peel wax) and 29.15±0.02 mg/KOH/g (cassava bagasse wax) are close to the 22.33 mg/KOH/g reported for beeswax by Bekele *et al.* (2016).

The saponification value indicates the number of acids and ester group found in the waxes (Bernal *et al*., 2005), and is a measure of the milligram of alkali required to completely saponify a gram of the substance. The saponification values for the experimental waxes were 103.42±0.19 mgKOH/g and 275.01± 0.01 mgKOH/g for peel and bagasse waxes, respectively. Both fell within the international standard of saponification value for beeswax which is >65 mgKOH/g. The results obtained affirmed absence of anomalous value indicating that the extracted waxes were free from adulterants waxes (Bekele *et al.,* 2016).

The ester value of wax indicates the amount of KOH used up in the course of saponification of esters (Bekele *et al***.,** 2016). The ester value obtained was 80.02±0.15 mg/KOH/g for cassava peel and 245.85±0.12 mgKOH/g for cassava bagasse. The ester value of the peel wax was within the international limit for beeswax (72-80 mgKOH/g) while the bagasse wax was exceedingly higher and this can be attributed to high saponifiable matter.

The iodine value is expressed as the grams of Iodine absorbed per 100 g of lipid, it indicates the degree of unsaturation. The higher the iodine value, the greater the number of C=C double bonds present. A rise in iodine value shows high exposure of lipid to oxidative rancidity owing to a high degree of unsaturation (Gaoxiang *et al.,* 2016). The iodine values obtained in this study were 90.03±0.03 and 22.54±0.04 g/100 for cassava peel and bagasse wax, respectively.

Fourier Transform-Infrared (FT-IR) Analysis Results

Wax is a long chain mixtures of aldehydes, long chain primary alcohols, fatty acids, hydrocarbons and esters. Upon extraction of the native waxes, a spectroscopic analysis was performed to determine its chemical composition. FT-IR analysis of the wax samples showed the presence of various functional group present in the waxes showing their corresponding compounds. The contrast of the absorption frequency of different organic functional group revealed bands at 2928 and 2911 cm^{-1} for cassava peel and bagasse, respectively, which is characteristic of -CH stretch and bend, whereas bands at 1035 and 1381 cm^{-1} for cassava peel wax and 1028 and 1464cm^{-1} for cassava bagasse wax signifying the presence pf sp^2 and sp^3 bonds. Bands at 3324 and 3382 cm^{-1} for peel and bagasse wax, respectively, indicated the presence of hydroxyl group in the wax samples. Similarly, bands at 1708 cm^{-1} for cassava peel wax and 1717 cm^{-1} for cassava bagasse wax were attributed to the presence of carbonyl group. Similar findings were reported in sugarcane bagasse characterisation by Mangesh & Lele (2012). According to Gaoxiang *et al.* (2016), the sugarcane bagasse FT-IR characterisation revealed the existence of several functional groups, which include alkanes, alcohol, fatty acids, aldehyde and a small amount

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of lignin derivatives.

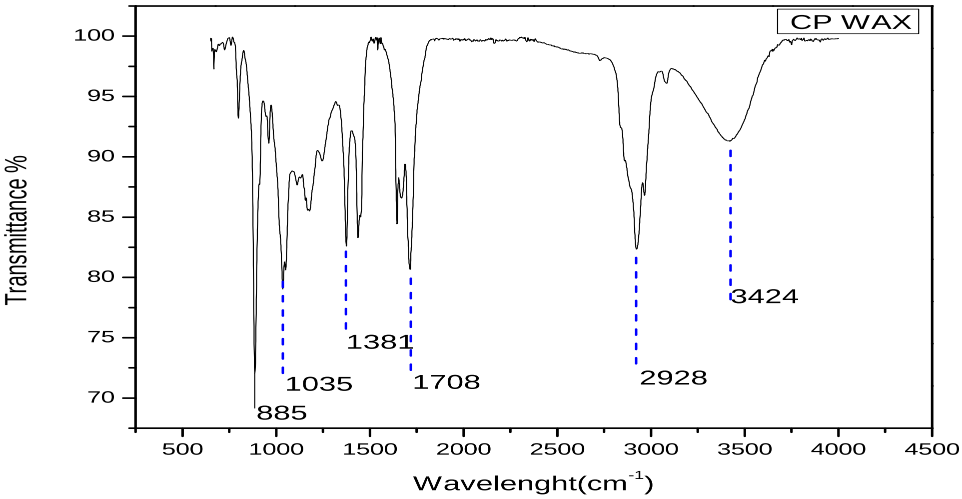

Figure 1: FT-IR spectra of extracted cassava peel wax

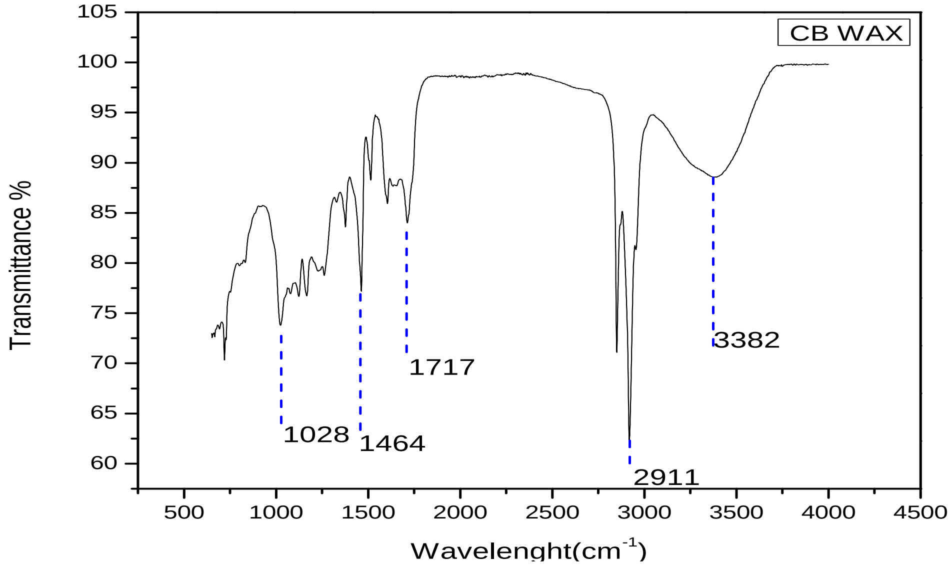

Figure 2: FT-IR spectra of extracted cassava bagasse wax

Ultraviolet-Visible Spectroscopy (UV-Vis) Analysis Results

Fatty acids, conjugated dienes, and hydroperoxide were formed by lipid oxidation and absorb UV light around 230 nm. In the UV region (100- 400 nm), cassava peel wax exhibited an absorption peak at 255 nm while cassava bagasse wax had an absorption peak at 245 nm, this implies the existence of conjugated dienes and trienes. Mangesh & Lele (2012) reported a close λ_{max} of 230 nm. This finding was also similar to that reported by Athukorala, Mazza, & Oomah (2009) where wax from flax (*Linum usitatissium*) straw exhibited a similar pattern.

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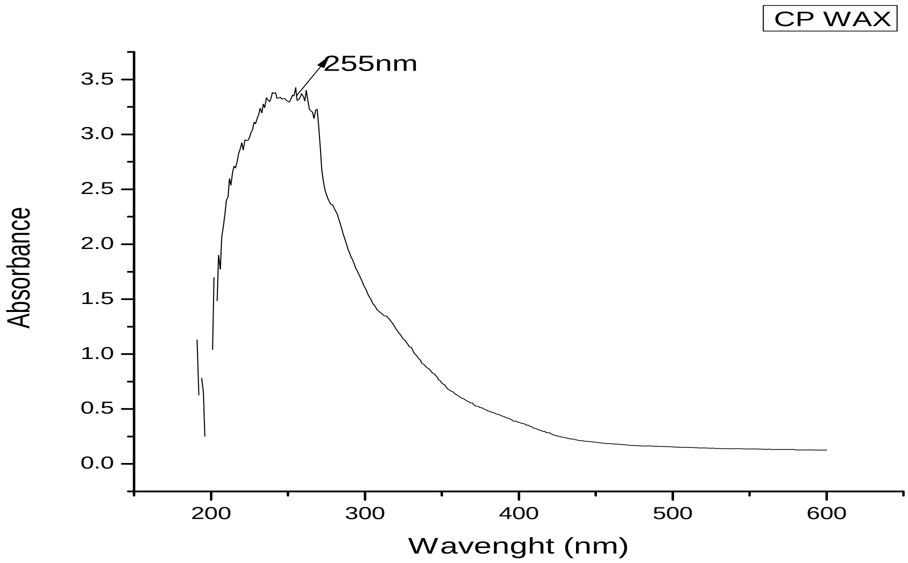

Figure 3: UV-Vis spectra of extracted cassava peel wax

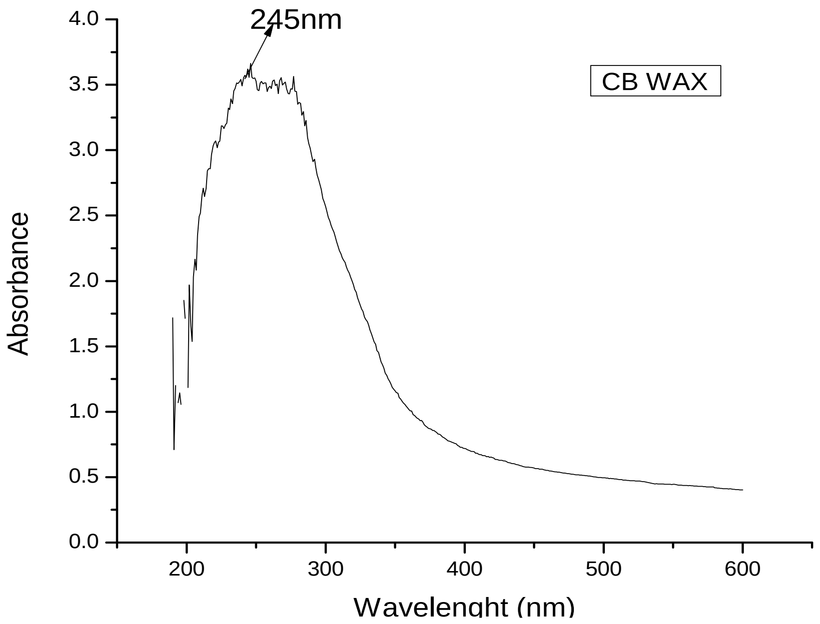

Figure 4: UV-Vis spectra of extracted sugarcane bagasse wax

Scanning Electron Microscope (SEM) Results

The smooth surface of the untreated (raw) cassava peel and bagasse samples in Figures 5a and 6a, respectively were due to the presence of some non-fibrous components in the structure of the fibre such as lignin, hemicellulose, wax, pectin, oil etc (Adewuyi and Vargas, 2017). Figures 5b and 6b showed the surface morphology of dewaxed cassava peel and bagasse, respectively, which appeared to be rough, with a reduction in size that may have resulted from the removal of lignin, hemicellulose and other non-cellulosic constituents showing a defibrillated fibrils (Hongjia, Yu, Longhui and Xiong, 2013).

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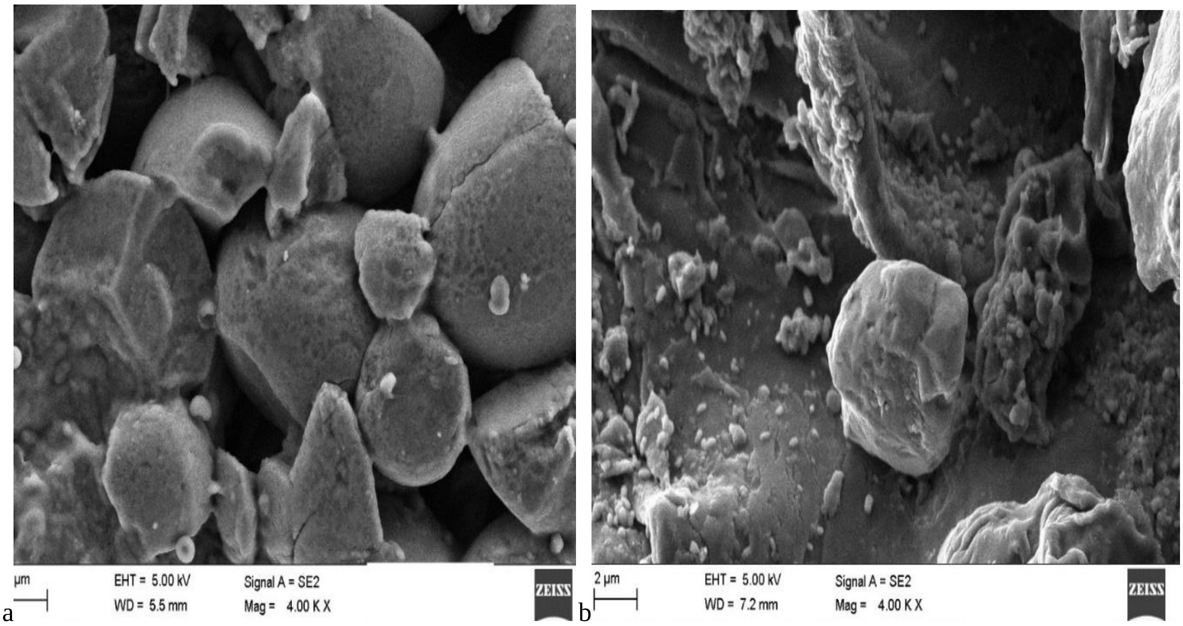

Figure: 5a and 5b: Scanning electron micrograph of raw and dewaxed cassava peel

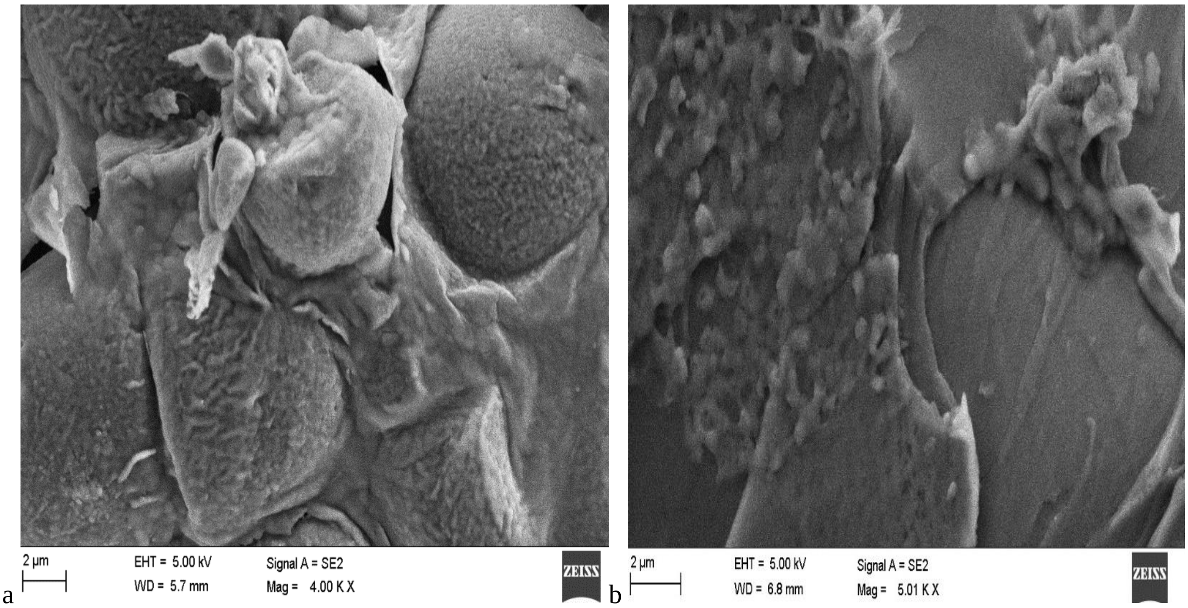

Figure: 6a and 6b: Scanning electron micrograph of raw and dewaxed cassava bagasse

4. Conclusion

The crude waxes obtained from cassava peel and bagasse revealed several classes of the compounds like alkanes, ester, alcohol and fatty acids. The main component is secondary butyl isothiocyanates, which has numerous valuable effects that can be used for different medicinal purposes. Besides, fatty acid play important roles in human nutrition. Aside from the therapeutic and nutritional us, cassava peel and bagasse wax may be used as an eatable covering for fruits' and vegetables' preservation. The waxes obtained in this study were good smelling, free of adulterants, and are similar to beeswax in physicochemical properties and hence can find useful industrial applications as beeswax, for example, pharmaceutical, cosmetics, paints and food industries. Both waxes have compounds of organic and industrial significance, hence, wax extracted from both cassava wastes will be a possible substitute for beeswax in industries. Also, it will reduce their environmental degradation otherwise caused by inappropriate disposal of the wastes.

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