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A Review on the Development of oil Palm, Pineapple and tea Leaves as Adsorbent for Arsenic, Zinc, Aluminium and Mangenese Removal From Wastewater

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Abstract: This review paper was to review the characteristics and the potential of oil palm, pineapple and tea leaves as activated carbon in removing heavy metal such as arsenic, manganese, zinc and aluminum from wastewater as activated carbon had been widely used. Leaves waste which is one of the wastes of agricultural, are abundantly accessible since there is a high agricultural activity. In addition, leaf-based products contain a range of organic and inorganic compounds, including cellulose, hemicellulose, pectin and lignin. The activated carbon will be analyze as stated in the previous study such as Fourier Transform Infrared Spectroscopy (FTIR) spectra result, Field Emission Scanning Electron Microscopy (FESEM) and Thermogravimetric Analysis (TGA). To produce activated carbon there are two ways, which is physical activation and chemical activation. In this review paper, the most leaves waste among three species of leaves and heavy metal that had been found is tea waste and zinc, respectively. Overall, leaves waste can be suggested to be used as activated carbon in the elimination of heavy metals from industrial wastewater.

Keywords: Leaves Waste, Activated Carbon, Heavy Metals

1. Introduction

Wastewater with heavy metal loading should be treated before discharge to the receiving environment. Adsorption of heavy metals using adsorbent is one of possible method in treating wastewater with heavy metals. Adsorption was discovered to be a highly efficient method for treating heavy metals in effluents [1]. An attempt is by using adsorbent from natural waste material.

The use of natural material waste as precursor in activated carbon preparation is more environmentally friendly method. Therefore, there is a need to explore factors affecting activated carbon production from leaveswaste.

Agricultural wastes and products that are high in molecular weight components like cellulose, hemicelluloses, and lignin might provide a significant amount of adsorbent or biomass. Furthermore, these components are high in functional groups, they can form multiple types of bonds. According to a

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review of the literature, waste biomasses can be used in their natural state whether untreated or intact [2] or activated carbon that produced physically or chemically [3].

Leaf-based materials have attracted greater attention from the tested adsorbents, partly as they are affordable and accessible in large numbers in practically all parts of the world [4]. Furthermore, the utilization of leaf-based materials from various trees contains a variety of inorganic and organic compounds.

The aim of this review is to acknowledge in deep the potential of leaves waste as activated carbonfor heavy metal removal. The objectives were to review the characteristics of oil palm, pineapple and tea leaves as activated carbon. These also were proven by previous study by many researchers. Moreover, this review paper is to review the potential of oil palm, pineapple and tea leaves activated carbon on arsenic, zinc, aluminium and manganese removal.

2. Literature Review

2.1 Heavy Metals

These heavy metals may have harmful impacts on human well-being, flora and fauna. As eachof these heavy metals has a particular toxicity profile, the successful recovery of heavy metals from waste sources is known to be critical as each of these heavy metals exhibits a specific toxicity profile [5]. The treatment of industrial wastewater effluent has been given considerable importance, as local and foreign authorities. Requires that prior to discharge into water bodies, commercial wastewater should be processed to meet a set level [5].

The allowable limits of heavy metals in drinking and wastewater by WHO are shown in Table1 meanwhile the requirements for effluent discharge of heavy metals are set out in the Environmental Quality Act (EQA) 1974: Standard A for discharge upstream of any raw water intake and Standard B for discharge downstream of any raw water intake, as stated in Table 2.

Table 1: Allowable Limits of heavy metals in Wastewater by World Health Organization

Heavy Metal	Impact	WHO (mg/L)
Arsenic	Cancer, skin damage, circulatorysystem problems	0.01
Manganese	The central nervous system, the lungs, and the liver aredamage	0.5
Aluminium	Depression, lethargy, neurological signs and nervous system.	3
Zinc	Alzheimer, autism spectrum disorders and bone disease	0.2

Table 2: Discharge of Industrial Effluent of Standards A and B (Malaysian Sewage Industry, 2016)

Parameter	Unit	Standard	
		A	B
Arsenic	mg/L	0.05	0.1
Manganese	mg/L	0.20	1
Aluminium	mg/L	2	2
Zinc	mg/L	10	15

2.2 Type of Leaves

In addition, leaf-based products contain a range of organic and inorganic compounds, including cellulose, hemicellulose, pectin, lignin, etc. These molecules have different functional groups, such hydroxyl, carbonyl, amino and nitro, [6] in their composition and may represent binding sites in processes of adsorption. Leaf-based materials have attracted considerable attention among the studied adsorbents, mostly due to the fact that they are inexpensive and readily available in large numbers in practically all places throughout the world. Table 3 shows the previous studies on leaves waste are used as adsorbent.

Table 3: Previous Studies on Leaves Waste as Adsorbent

Author	Leaves Wastes	Heavy Metals	Operating Parameters	
			pH	Percentage Removal (%)
[7]	Cattail	Pb (II)	6.32	37.4
			6.18	97.4
			5.76	92.3
			5.32	91.9
[8]	Neem	Brilliant Green	6.5	98
[9]	Spent Tea	Chromium	10	95.42
[10]	Oil Palm	Methylene Blue	6	88.72
[11]	Coconut	Methylene Blue	4.10	86.38
[12]	Pineapple	Methyl Violet	5	n.a

2.3 Preparation of Leaves as Adsorbent

The pre-treatment procedure of the starting material involves carbonization and activation to improve the production of activated carbon. Waste leaves are generally charred and activated by physical and chemical activation [13]. Many researches have been conducted using variety of wasted leaves to generate adsorbents, which have then been used as adsorbents for the removal of organic andinorganic contaminants from wastewater.

Physical activation is an activation method in two stages including high temperature carbonization and activation. Physical activation also a pyrolytic double-stage process comprising carbonization and activation [14]. Due to the ease of the process and the capacity to generate activated carbon with highly developed micro porosity and acceptable physical qualities such as strongphysical strength, physical activation is frequently used for commercial production [15].

Chemical activation is a stage activation process that involves the use of chemical additives inthe inert environment to saturate and carbonate the precursor to create activated carbon at lowtemperatures of about 300°C to 800°C [16]. Besides that, chemical activation reduces time, uses less energy since it uses lower activation temperature and generates more noticeable activated carbon [17].

2.4 Pre-treatment of Leaves waste

2.4.1 Tea

The waste from the processing of tea leaves must first be ground, sieved, and cleaned before itcan be utilized as an adsorbent. Washing is critical in the pre- treatment process since tea-based wastesinclude significant levels of hydrolyzable tannins, polysaccharides, and proteins, other components thatmust be removed before being utilized to avoid contamination [18]. Wash the raw material many times with hot distilled water until the solution remained colorless [19] and using hot dilute NaOH solutions to wash the raw material decreased the number of washing cycles necessary [20].

1.4.2 Oil Palm

The oil palm leave (OPL) has been removed from the petiole and sifted manually to eliminate undesirable elements, such as sand and dirt. The OPL was chopped into large pieces about10 cm in long, cleaned with water tap and rinsed with distilled water. The cleaned OPL was dried for 72 hours in an oven at 80 °C. The dried OPL was crushed into powder and separated into two samples.It was decided to utilize one of the samples that had not been changed and the other sample that had been exposed to acid treatment [21].

2.4.2 Pineapple

The pineapple was cut in smaller pieces 1 cm tall, rinsed with distilled water,and dried at 105°C for 24 hours before any treatment. The dry material was further pulverized to the powder and sieved for less than 150 μm of a consistent size [12].

3. Results

3.1 Data Collection

The second phase of the study was to analyze the keywords used by writers in the selected 67 publications. A map based on bibliographical data may be used with the assistance of Vos Viewer software to visualize bibliographic metric data based on visualization approach.

The result of the software data network is as shown in Figure 4. The thickness of the lines therefore relates to the association between the keywords (thicker means higher correlation). Good resemblance indicates high correlation. For example, for blue coloured including activated carbon, adsorption and water pollutants chemical are significantly connected.

It can be seen those studies on leaves waste as activated carbon to remove heavy metal are focusingon adsorption, activated carbon, heavy metal and waste pollutants chemical. It was observed that the activated carbon produced from agricultural waste that can give benefit towards people and industry

3.2 Heavy Metals Removal

A good activated carbon must be regenerative, such as those from agricultural waste, have highcarbon content, have better potential for activation and be cheaper to provide. As a result, manufacturingof activated carbon from agricultural waste can also be less expensive. Table 4 shows the removal efficiency and adsorption capacity of heavy metals from leaves waste

Table 4: Removal efficiency and adsorption capacity of heavy metals from leaves waste

Leaves waste	Heavy Metal	Removal Efficiency (%)	Adsorption Capacity (mg/g)	Reference
Tea	Arsenic Manganese	99.8	-	[18]
		99.8	- 0.1579	[18]
		99.5	- 14.2	[25]
	Aluminium Zinc	99.8	8.9	[18]
		72	0.2789	[19]
		- 99.5		[26]

				[25]
Pineapple	Aluminium	-	97.88	[27]
		-	93.73	[27]
		-	95.39	[27]
Oil Palm	Manganese	71	-	[28]
	Zinc	93	-	[28]

3.3 Properties and Characterization of Leaves Waste

3.3.1 Tea

From the previous study, the tea waste has a BET surface area of 1.3196 m2/g and a carbon content of 46.74 percent on a dry basis [18]. In the meantime, [29] have described tea waste occupying a surface area of 54.59 m2/g before adsorption, whereas 24.09 m2/gafter adsorption. It is vital to study the influence of the contact time necessary for each batch adsorption experiment to achieve balance [25]. The longer the length of retention, the greater the adsorption.The adsorption of heavy metal, Zn (II), and Mn (II), is examined throughout different periods (20, 40, 60, 80, 100, and 120 minutes). The balance time was 60 minutes at 3.0g tea leaves with 95% removal time Mn (II). With Zn (II), the balance time is 80 minutes with 3.0g TW and 99.5 percent elimination.

It has been discovered that FTIR analysis is a helpful technique for identifying the presence of functional groups in the bio adsorbent [30]. The FTIR spectra of tea leaves is shown in Figure 5 and covers the wavenumber range of 500– 4000 cm1 (wavenumber range). Meanwhile, the TGA profile in

Figure 6 reveals the usual weight loss trend for the adsorbent, and full adsorbent breakdown begins at 300°C. The weight loss occurs only as a result of the elimination of moisture from the atmosphere between 40 and 90°C [9].

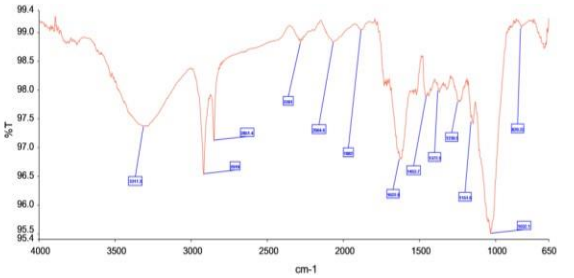

Figure 5: FTIR Spectra Result

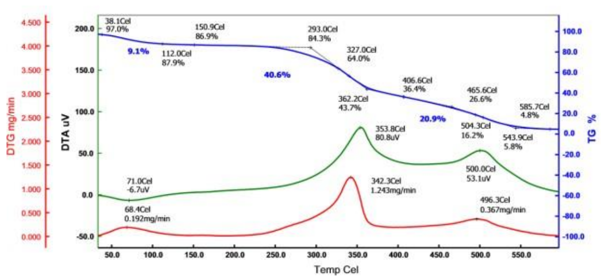

Figure 6: TGA result

3.3.2 Oil Palm

On the basis of effectiveness of removals progressively increased to pH4 for metal ions of Zn (II), and to virtually constant after pH6 for ions of Zn (II). More elimination of Zn (II) metal ions witha removal efficiency of more than 71% was obtained using OPFAC. However, OPFACMP has showed good performance in attaining high Zn (II) ion removal up to 93%. For these metal ions, OPFAC-MP has shown a good removal with a modest adsorbent dose of 0.1g. The surface area, pore volume, and pore diameter measurements are presented in Table 5. Activated carbons have a large surface area and a high concentration of micropores and mesopores. TheOPFAC is made up of a total area of 440 m^2/g with a microporous surface of 368 m^2/g and mesopores of 72 m^2/g. In contrast, the surface area of OPF was low (1.91 m^2/g) and activation of OPF in preparationof OPFAC enhanced their surface space considerably.

Table 5: Surface area, volume of pore and OPF pore diameter

Sample	Surface Area			Volume (cm^3/mg)		Diameter (mm)	
	Total	Micro	Meso	Micro	Meso	Micro	Meso
OPF	1.91	n.a368	1.91	n.a 0.15	0.005	n.a 0.60	8.77
OPFAC	440		72		0.05		4.21

Figure 7 and 8 show the surface images of OPF and OPFAC through FESEM images. The surface of OPF-AC shows the differences of morphology structure compared to OPF sample. The porous structure was formed on the surface affected by chemical activation process.

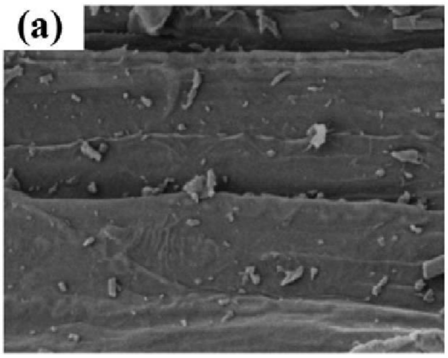

Figure 7: OPF (a) FESEM pictures

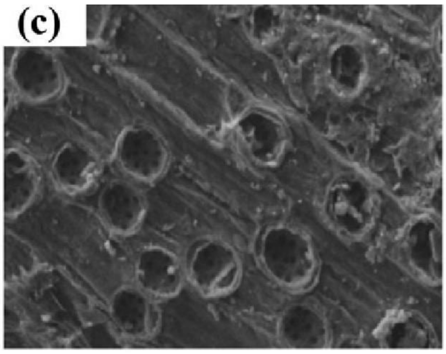

Figure 8: OPF-AC (C) FESEM pictures

3.3.3 Pineapple

A Surface Area Analyzer was used to determine the activated carbon using (ASAP 2020, V3.04H; Micrometrics). To determine the surface area, the BET model was employed. The activated carbon generated from pineapple leaf from the BET surface area was (1002 m2/g) [31].

Three samples are done to activate carbon using pineapple leaves [31]. The investigation showsthat the PLAC- B sample has a maximum total area of 915 m^2/g, followed by PLAC-C, 522 m^2/g and PLAC-A, 23 m^2/g as shown in Table 6. The previous study reports on all samples showing the existence of microporous and mesoporous material [32].

Table 6: Results of pineapple leaves on pore characteristics by (Mahamad et al., 2015)

Activated Carbon	Total surface area BET (m^2/g)	Micropore Surface area (m^2/g)	Mesopore Surface area (m^2/g)
PLAC-A	22.99	5.87	17.12
PLAC-B	914.67	289.09	652.58
PLAC-C	521.88	252.99	268.88

Scanning Electron Microscopy (SEM) was used to study the morphology of active carbon. Figure 9 shows the biomass of the SEM micrographs and the resulting activated carbons of pineappleleaves. Pineapple leaves surface appears to be covered with thick external covering with minimally apparent porous features.

Results in Table 7 shows the percentage for heavy metals removal by pineapple parts wastes activated carbon using different chemical activation. The results indicate that Al has the highest adsorption percentage by the pineapple parts activated carbon when compare to Pb, Cu and Fe in the batik wastewater. Pineapple crown with KOH activation has the highest adsorption of Al which is 97.88%. While pineapple core activated carbon with ZnCl2 activation has the highest adsorption of Alwhich is 93.73%. For $ZnCl_2$ activation, the highest adsorption percentage is 95.39% (Al).

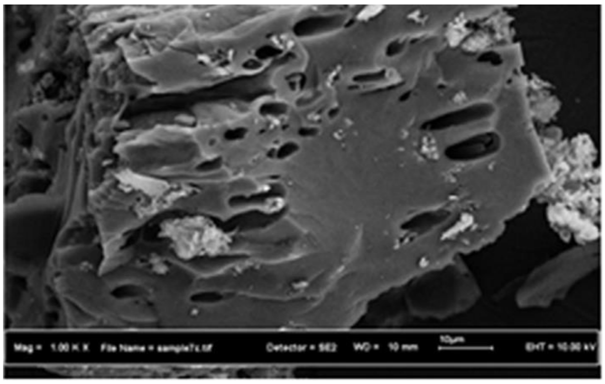

Figure 9: SEM of pineapple leaves activated carbon

Table 7: Heavy metals removal from Batik Wastewater by (Subki et al., 2019)

Sample	Crown		Peel		Core	
	KOH	$ZnCl_2$	KOH	$ZnCl_2$	KOH	$ZnCl_2$
Pb	85.78	84.80	91.76	66.42	51.47	64.71
Cu	95.60	50.60	88.89	79.22	87.65	74.28
Al	97.88	94.61	97.96	95.39	87.83	93.73
Fe	96.52	90.88	80.41	91.97	87.65	90.88

With its high removal ability for heavy metals, pineapple leaves activated carbon shownpotential as a sustainable option for the removal of heavy metals from wastewater [31].

4. Conclusion

The review paper presented the results of a literature review of the previous study. The aim of the research was to provide an overview of the characteristics and the potential oil palm, pineapple and tea leaves as adsorbent for arsenic, zinc, aluminium and manganese removal from wastewater. Leaf-based materials have attracted greater attention from the tested adsorbents, partly as they are affordable and accessible in large numbers in practically all parts of the world.

Tea leaves is one of the wastes that suitable to be precursor. Hussain et al., (2018) stated the tea waste has a BET surface area of 1.3196 m2/g and a carbon content of 46.74 % on a dry basis. meanwhile Kabir et al., (2021) have described tea waste occupying a surface area of 54.59 m2/g before adsorption, whereas 24.09 m2/g after adsorption. Badrealam et al., (2019) stated the balance time was 60 minutes at 3.0 g tea leaves with 95% removal time Mn (II). With Zn (II), the balance time is 80 minutes with 3.0 g tea waste and 99.5 % elimination.

The broad ability, easiness and appealing physiochemical properties to collect discarded tea leaves make them a viable substitute for commercially utilized absorbers. The use of physicochemical techniques to modify the surface of oil palm waste-based adsorbents leads to a new way for improving pollutant absorption from wastewater. According to Zainol et al., (2017), more elimination of Zn (II) metal ions with a removal efficiency of more than 71% was obtained using OPFAC meanwhile OPFACMP Zn (II) ion removal up to 93%.

The utilization of pineapple leaf in composite material is a new source of materials which can be economic, eco-friendly, and recyclable. Because of its excellent removal efficiency and adsorption capacity, pineapple leaves activated carbon demonstrated potential as a sustainable alternative adsorbent option for the removal of heavy metals from wastewater. results by Astuti et al., (2019) shows that Al has the highest adsorption percentage by the pineapple parts activated carbon in the batik wastewater. Pineapple crown leaves with KOH activation has the highest adsorption of Al which is 97.88%. While pineapple core activated carbon with ZnCl2 activation has the highest adsorption of Al which is 93.73%. For ZnCl2 activation, the highest adsorption percentage is 95.39% (Al).

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