The Sorption Studies of Waste Cooking Oil using Raw and Treated Pineapple Crown Leaf

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ABSTRACT

The unregulated discharge of pollutants into water bodies has become an issue that led to pollution. Fiber derived from various forms of agricultural wastes as the sorbent is widely used as it has a high sorption capacity and efficiency. It is environmentally friendly and could be cost-effective as it only utilizes the unwanted parts of plants, which usually would otherwise be discarded. The pineapple crown leaf (PCL) and other plants with high cellulose content have the potential for environmental applications. Oil pollutants, particularly waste cooking oil (WCO) from the food and beverage industry, often contaminate water bodies due to poor waste management. Using cellulose-rich plants like PCL could offer an effective solution for absorbing these pollutants. This study examines the characteristics and sorption capacities of raw, NaOH-treatment PCL, and carbonized PCL to develop an effective, eco-friendly method for oil spill remediation. The methodology involves washing, drying, grinding, and sieving PCL to obtain a powdered PCL. Then, raw PCL (RPCL) undergoes chemical treatment with 10% sodium hydroxide, NaOH and thermal treatment at 300 °C. The raw and treated PCL were characterized using Fourier Transform Infrared Spectroscopy (FTIR). The elimination of some non-cellulosic components in NaOH-treatment PCL (CPCL) and carbonized PCL (TPCL) observed in the FTIR spectrum would contribute to higher sorption efficiency and capacity of WCO. In agreement with the results from FTIR analysis, the highest sorption efficiency in pure oil was shown by TPCL at 33% and CPCL in slick oil at 16.33%. The highest value for pure and slick oil recorded for sorption capacity was 9.23 g g^{-1} from TPCL samples and 4.3 g g^{-1} from CPCL samples. This

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study supports sustainable waste management and green technology for environmental remediation, highlighting PCL's potential in mitigating oil pollution and the value of agricultural waste in creating eco-friendly solutions for oil disposal challenges.

1   INTRODUCTION

Pineapple or *Ananas Comosus* has one of the highest cultivated land areas in Malaysia[1]. Malaysia produced over 400,000 to 600,000 metric tons of pineapple fruits annually in 2021, with total revenue of RM 675.7 million, according to the Malaysia Pineapple Industry Board (MPIB). Sarawak, the second largest pineapple producer in Malaysia, has an area of 8,429 hectares, with Samarahan being the largest producer, covering 37% of the total planted areas[2]. The increasing demand for pineapple generates a large amount of waste. Studies have shown that almost 40-80% of pineapple fruit is discarded as waste[3]. On the other hand, the Solid Waste and Public Cleansing Management Corporation (SWCorp) reports that one household in Malaysia discards 0.9 kg of leftover cooking oil improperly on average. Malaysia has about 5.8 million residences, which translates to 5.22 million kg of cooking oil disposed of per year. Global vegetable oil production was estimated to be more than 200 million tons in 2019 and 2020 and is expected to continue to increase in the coming years[4]. Without awareness among the community, the oil production would also increase the amount of WCO released into the water bodies, which would worsen the environmental issues.

In Malaysia, the cuisine is known for its rich and diverse flavors, which often rely heavily on cooking oil especially for some local snacks such as fritters, which need to be deep fried using a lot of oil. This frequently leads to environmental issues related to the disposal of large quantities of used oil. This is not only in households but also in food and beverage industries, which pose significant environmental challenges. Common disposal methods, such as dumping oil down the drains or in landfills, contribute to water pollution, disrupting aquatic ecosystems and endangering wildlife[5]. Improper disposal can also contaminate groundwater and soil, which is harmful to human health and plant growth, and the breakdown of discarded oil releases unpleasant smells that worsen local air pollution.

Traditional cleanup methods often involve synthetic materials such as chemical dispersants, synthetic absorbents, and bioremediation[6]. While effective in the short term, these materials present significant challenges due to their limited biodegradability and potential environmental impact[7]. Therefore, there is a need to explore sustainable and effective alternatives for oil sorption. For this, the waste of PCL was used as a natural sorbent to investigate the effectiveness of these alternatives, considering factors such as the modification of PCL samples. By measuring the removal efficiency of waste cooking oil (WCO) and the sorption capacities of raw, chemically, and thermally modified samples helps determine which treatment of pineapple crown leaves is most effective. This understanding contributes to reducing the environmental impact caused by improper oil disposal and addresses the issue of pineapple waste. It focuses on PCL for oil removal and explores their potential as an effective and sustainable method for oil spill remediation.

2   MATERIALS AND METHODS

The materials and chemicals used include pineapple crowns, waste cooking oil, water, a beaker, sodium hydroxide (10% NaOH) solution, and deionized water.

2.1   Preparation of PCL

PCL was derived from a pineapple species found in Sarawak and obtained from a local pineapple farm in Samarahan. The first step was to split the crowns into a single set of leaves. The leaves were oven-dried for 18 hours at 70°C to eliminate moisture and contaminants. Next, the leaves were ground into a

powder and put through a British Standard Sieve (BSS Sieve) with a 125-850 µm (20-120 mesh) size range. This sample is known as raw PCL (RPCL). Then, the samples were further treated to obtain chemically treated (CPCL) and thermally treated (TPCL) samples.

2.2   Treatment of PCL

Chemically treated PCL was prepared using 50 g of washed dried ground PCL and was treated for 1 hour with 500 mL of a 10% NaOH solution at 100 °C with stirring. The mixture was allowed to cool down at room temperature and then washed with deionized water until the pH was neutral[8]. This chemically treated PCL is then labelled as NaOH-treatment PCL (CPCL). While the thermally treated PCL was prepared by carbonizing the dried ground PCL in a muffle furnace at 300°C for an hour[9].

2.3   Characterisation of PCL

Raw and treated PCL were characterized using Fourier Transform InfraRed (FTIR) spectroscopic method. FTIR spectra was obtained within the wavenumber range 4,000-600 cm^{-1} using the ATR method on a Perkin-Elmer Frontier FTIR.

2.4   Sorption studies

To simulate a cooking oil spillage, two different conditions of oil pollutants were used, which are pure and slick oil. No additive is added to the pure oil, while the slick oil is prepared by mixing WCO with water[8]. WCO was mixed with water in a beaker and stirred thoroughly at room temperature to ensure the oil dispersed throughout the water, emulating the conditions of an actual spill. 0.1 g, 0.15 g, 0.2 g, 0.25 g, and 0.3 g of RPCL, CPCL, and TPCL were added to a mixture of oil spillage consisting of 10 mL WCO and 90 mL water for 30 minutes. At the end of the process, the mixture was filtered with a netting, and a mixture of oil and water was centrifuged at 2600 rpm for 5 minutes. Then, oil was obtained using a micropipette, and its mass was measured. These steps were repeated by replacing slick oil with 100 mL of pure oil. The formula below was used to determine the sorption efficiency and capacity towards WCO[9].

Sorption Efficiency (%) = (mass of oil removed (g) / initial mass of oil (g)) × 100   (1)

Sorption Capacity = (mass of oil removed (g) / mass of adsorbent (g))   (2)

3   RESULTS AND DISCUSSION

3.1   Characterisation of raw and treated PCL

Based on the IR spectrum in Fig.1 and Table 1, the O-H stretching vibrations, which are indicative of carbohydrates and phenolic compounds as well as hydrogen bonds appear at 3,334 cm^{-1} for RPCL, 3,328 cm^{-1} for CPCL, and 3,337 cm^{-1} for TPCL. The C-H stretching and bending vibrations, associated with the saturated alkanes are observed at 2,916 cm^{-1} and 2,850 cm^{-1} for RPCL and show minimal shift upon chemical treatment and thermal processing. The C=O stretching, attributed to hemicellulose and pectin, is noted at 1,732 cm^{-1} for both RPCL and CPCL. The C=C stretching vibrations, indicating the presence of aliphatic and unsaturated aromatic compounds in lignin, appear at 1,603 cm^{-1} for RPCL and slightly shift to 1,590 cm^{-1} for CPCL. Furthermore, the C-O stretching of lignin and hemicellulose is identified at 1,247 cm^{-1} for RPCL and 1,242 for TPCL. The elimination of non-cellulosic components in CPCL and TPCL was observed in the FTIR spectrum, as shown in Fig. 1 and Table 1. Finally, the C-O vibrations in cellulose are consistently present around 1,319-1,375 cm^{-1} and 1,032-1,034 cm^{-1} across all treatments.
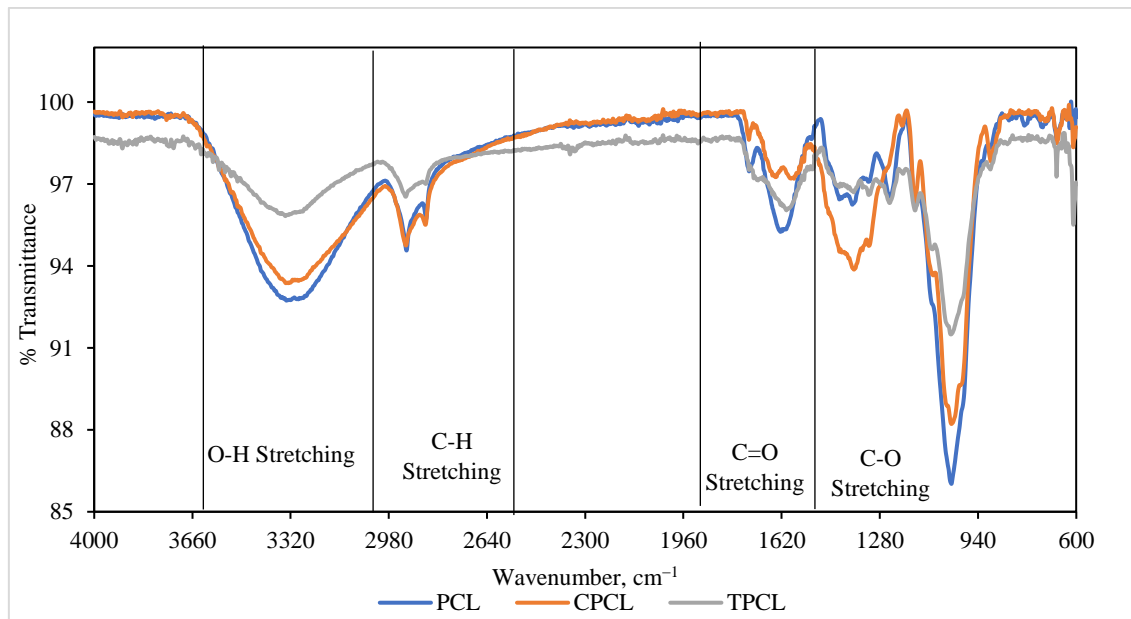
Fig. 1. IR spectrum of raw and treated PCL.

Table 1. FTIR spectral data of raw and treated PCL

Functional Group	Frequency for RPCL, cm^{-1}	Frequency for CPCL, cm^{-1} (10% NaOH)	Frequency for TPCL, cm^{-1} (300°C)
O-H stretching	3,334	3,328	3,337
C-H stretching	2,916, 2,850	2,920, 2,852	2,920, 2,853
C-H bending (plant wax)	1,419	n.d	1,422
C=O (pectin)	1,734	1,734	n.d
C=O (pectin)	1,624	1,643	n.d
C=C	1,603	1,590	1,602
C-O (lignin)	1,247	n.d	1,242
C-O	1,319, 1,375, 1,032	1,319, 1,367, 1,032	1,316, 1,375, 1,034

3.2   Sorption Studies of Raw and Treated PCL

The results indicate a negative correlation between the sorption capacity and dosage of sorbent in pure and slick oil, as depicted in Tables 2 and 3. When the sorption capacity decreases, the dosage of the sorbent increases. It is proven that the value of sorption capacity obtained from all the types of sample shows the highest value at 0.1 g at 6.73 g g^{-1} for raw sample, 8.57 g g^{-1} for chemically treated, and 9.23 g g^{-1} for thermally treated sample. The modified sample shows higher capacity compared to the raw sample with the thermally treated sample consistently showing the highest capacity at different dosages compared to the chemically treated and raw samples. However, both modified samples show a higher capacity compared to the raw sample due to the hydrophilic properties possessed by the hydroxyl group which had been eliminated during the modification which gives more surface area for oil sorption to be done as shown in the FTIR spectrum[10,11]. This made the modified sorbent more hydrophobic and efficient for the sorption of WCO. Besides that, the thermally modified sample has a more porous surface and overall porosity, while the chemically treated sample has an additional functional group of carbonyl, which made these samples more oleophilic than the raw sample[12].

Besides that, the results on sorption of slick oil are also negatively correlated but the capacity is much lower than that of pure oil. This is because the concentration of oil is lower since it is mixed with water. This reduces the amount of oil molecules which makes the sorption limited[13]. The highest capacity shown by each sample is at 0.1 g which includes 2.83 g g^{-1}for the raw sample, 4.3 g g^{-1} for the chemically treated samples, and 3.83 g g^{-1} for the thermally treated sample with raw samples showing the lowest capacity at all dosages same as in pure oil. Overall, the negative correlation that occurs between the sorption capacity and the sorbent dosage is caused by the unsaturation of the sorbent site, which would likely to occur during the sorption process[14]. A previous study done by AbdulWahab et al.[15], used polymer coated partially esterified sugarcane bagasse for the separation of oil from seawater. Their finding on oil sorption capacity is 11.7 g g^{-1} for vegetable oil, which is slightly higher than this study. Most of the studies on agricultural wastes are more focused on the removal of crude oil from seawater.

For sorption efficiency, it shows a different pattern of reading which is inconsistent compared to the capacity. It is because the capacity was calculated based on the dosage used while the efficiency was based on the initial mass of oil used. The highest sorption efficiency for pure oil as presented in Table 2 was recorded at 0.25 g which was around 30.93% and 33.00% for chemical and thermal treated samples, respectively while the highest efficiency for raw samples was at 0.3 g with a value of 25.73%. A one-way analysis of variance (ANOVA) was conducted to assess the sorption efficiency of the untreated and treated PCL. The p-value obtained from the ANOVA test was 0.0003. The significant p-value suggests that the treatment method (raw, chemical, or thermal) significantly affects the sorption efficiency of pure oil. The chemically and thermally treated samples have higher sorption efficiencies than the raw samples, with the thermally treated samples having the highest efficiency overall.

Table 2. Sorption capacity and efficiency of raw and treated PCL samples with different dosages in pure oil

Dosage, g	Sorption Capacity, g g^{-1}			Sorption Efficiency, %		
	PCL	CPCL	TPCL	PCL	CPCL	TPCL
0.10	6.73	8.57	9.23	20.30	17.13	18.47
0.15	6.43	6.73	7.05	12.73	20.20	21.13
0.20	4.67	5.47	6.60	18.13	21.87	22.73
0.25	4.29	5.16	5.50	21.47	30.93	33.00
0.30	4.28	4.51	5.29	25.73	22.53	26.47

Besides that, the efficiency of sorption in slick oil as shown in Table 3 also shows that the modified samples were higher at most of the dosages with the highest efficiency for the raw sample and thermally treated sample at 0.25 g with a value of 10.53% and 16.00%, respectively while the highest efficiency for the chemically treated sample is at 0.3 g with a value of 16.33%. However, it also shows a lower efficiency compared to the sorption efficiency in pure oil due to the same reason stated before in sorption capacity. A one-way ANOVA showed a 0.38 *p*-value. Therefore, there is no significant difference in data obtained from raw, chemical, and thermal treatment of slick oil. Overall, the efficiency increases as the dosage increases due to an additional amount of adsorbent active sites available on its surface. Still, it would start to decrease due to existing unsaturated adsorption sites during the adsorption process[15].

4   CONCLUSION

This study used PCL as a sorbent to remove WCO in both pure and slick oil. It was discovered that the sorption capabilities and surface characteristics of PCL were significantly changed by each treatment. Treated PCL exhibited higher oil sorption capacities and efficiency due to the elimination of some non-cellulosic components as compared to raw samples. The study highlights the potential of PCL as a sustainable and cost-effective natural sorbent for oil spill clean-up, emphasizing the importance of utilizing agricultural waste for environmental remediation. Future studies should explore optimizing PCL treatments for enhanced sorption efficiency and capacity.

Table 3. Sorption capacity and efficiency of raw and treated PCL samples with different dosages in slick oil

Dosage, g	Sorption Capacity, g g^{-1}			Sorption Efficiency, %		
	PCL	CPCL	TPCL	PCL	CPCL	TPCL
0.10	2.83	4.30	3.85	5.67	8.93	12.53
0.15	2.45	3.72	3.83	9.67	11.33	7.67
0.20	2.44	3.02	3.56	7.33	12.07	10.67
0.25	2.04	2.84	2.90	10.53	14.20	16.00
0.30	1.53	2.72	1.78	9.20	16.33	10.67

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CONFLICT OF INTEREST

The authors agree that this research was conducted in the absence of any self-benefits, commercial or financial conflicts and declare the absence of conflicting interests with the funders.

AUTHORS' CONTRIBUTIONS

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