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Rice Straw as an Adsorbent for Reducing the Peroxide and Acid Values of Used Cooking Oil

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Rice straw is an abundant by-product of rice harvest, which can be developed into an adsorbent to remove contaminants from liquid and gaseous substances. The objectives of this study were to develop an adsorbent from rice straw, determine its characteristics, and test its performance in improving the quality of used cooking oil. Rice straw was collected and developed into an adsorbent based on its ability to reduce the peroxide value (PV) of used cooking oil (UCO). The particle size, adsorption capacity, functional groups on adsorbent surface, surface morphology, and pore size of the adsorbent were determined, and its performance on improving the quality of used cooking oil in terms of peroxide value, acid value (AV), and color were tested. Results showed that the best preparation of rice straw adsorbent (RSA) was through activation with 0.5 M NaOH at a particle size of 355 µm. The RSA had an adsorption capacity of 5% by weight for PV reduction in used cooking oil. The FTIR analysis showed the presence of O-H and C-O functional groups, while SEM analysis revealed porous structure and pointy nodules, at the surface of RSA. The RSA improved the quality parameters of used cooking oil through reducing PV and AV by 5.05 – 5.37% and 40.78%, respectively, and improving the lightness of the oil.

1. Introduction

Agricultural and industrial developments are increasing in order to keep up with economic growth and the rising demand for goods and services brought on by an expanding human population. An important consequence of these developments is the generation of increased amounts of waste. Several approaches to waste disposal in underdeveloped and developing countries have negative effects on human health and the environment. Therefore, research is needed to develop alternative treatment techniques and technologies so that agricultural waste can be transformed into goods with added value and minimize the impact on the environment (Saleh, 2021).The growing population in the Philippines results in a huge amount of used cooking oils (UCOs) from frying and cooking that are improperly disposed of in sinks, syphons, or within solid residues. The mismanagement of UCOs generates an array of problems, including pollution and public health issues (Go et al., 2019). The major changes that occur when vegetable oils are exposed to high heat and light during cooking include hydrolysis and oxidation that cause the degradation of used oils. Some products of these degradation reactions are fatty acids and peroxides which alter the properties of cooking oil, and are mainly the reason why used cooking oils cannot be reutilized in preparing food because of their harmful and negative effects on human health (Cardenas et al., 2021). Thus, there is the need to monitor and maintain the quality of the edible oil to ensure the safety of the oil product for consumption. Although there is no official standard set for evaluation, color, PV, and AV are commonly used in the industry to report edible oil quality. The PV measures the primary oil products formed during the initial stages of oxidation which leads to rancidity, while the AV is one of the significant indicators of free fatty acids in oil (Dunford, 2016).

One of the treatment alternatives for the reduction or removal of peroxides and colored compounds is the adsorption process (Cardenas et al., 2021). The adsorption capacity of an adsorbent is the quantity of adsorbate that binds to the adsorbent per unit mass or volume of adsorbent (Knaebel, 2016), and is dependent upon the chemical composition, existence of functional groups on the surface, and the nature and distribution of pores

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that make up the overall porosity (Wang et al., 2022). A variety of adsorbents were utilized in the purification of used cooking oils, including activated carbon, aluminum oxide and silicon gel (Cardenas et al., 2021).

In the Philippines, rice husks and straw are abundant agricultural wastes from rice production (Briefing, 2021). For every 15.20 million tons of rice produced in the Philippines, there are about 11.30 million tons of rice straw left spread out in the field (Team, 2022). The potential of these lignocellulosic biomasses as low-cost adsorbents for the removal of various contaminants in water and for the reduction of acidity and undesirable peroxides from waste cooking oil has been conceptualized as a viable alternative to narrow the growing number of solid and liquid wastes induced by economization (Goodman, 2020).

Thus, this study aimed at exploring the potential of rice straw waste as an adsorbent to improve the quality of used cooking oils. Specifically, this study developed an adsorbent from rice straw biomass waste, and determined the following characteristics of the rice straw adsorbent (RSA): particle size, adsorption capacity, functional groups on adsorbent surface, surface morphology and pore size. The RSA was tested according to its performance on improving the quality of used cooking oil in terms of PV, AV, and color. Results from this study will help in the management of agricultural biomass and used cooking oil wastes, by converting them into useful products which can be used for income generation for communities, and preservation of the environment. The results of the study uphold the United Nations Sustainable Development Goals for good health and well-being (SDG 3), sustainable cities and communities (SDG 11), and responsible consumption and production (SDG 12).

2. Methodology

2.1 Collection and Preparation of Rice Straw

Rice straw was obtained from a freshly harvested rice variety available in Brgy. Pagsanga-an, Pavia, Iloilo, on November 15, 2023. These were cut into smaller pieces, oven-dried at 90℃ for 3 h, cooled and stored in plastic zip bags for further experimental use.

2.2 Collection of Used Cooking Oil

The UCO in this study was obtained from the Dining Hall of CPU on December 5 - 7, 2023. It was generated as follows: 5 kg chicken was fried in about 12 L coconut oil. The oil was cooled, transferred to a clean container and sealed for overnight storage. The following day, this oil was used to fry another 5 kg chicken. The oil was cooled, filtered through several layers of cheese cloth, and filled into clean, plastic bottles of 2-L capacity. The bottles containing UCO were then stored in a -40ºC freezer until use.

2.3 Adsorbent Preparation

The RSA was prepared based on Baharim et al. (2023) with modifications. Dried rice straw samples were pulverized and sieved to achieve particle sizes 201 and 355 µm. About 30 g sample was added with 300 mL 0.5 M NaOH, and shaken at 200 rpm for 3 h. The residue was washed with distilled H_2O until the pH was between 7 and 8, then dried at 90 ºC for 6-10 h, cooled, and passed through the corresponding sieve. It was then dried at 90 ºC for another 12 h and kept in a desiccator until further use.

2.4 Treatment of Used Cooking Oil with Rice Straw Adsorbent

The treatment of UCO with RSA was carried out in triplicates according to Kishimoto (2021), with modifications. About 7.5 g RSA was weighed into 250 mL flasks and added with 50 mL UCO to make 15% wt mixture. The flasks were covered and agitated at 200 rpm for 1 h. The mixture was then filtered while being protected from light. The filtration of UCO for the batch of adsorbent treatment was carried out within one hour or less. The filtered UCO was immediately subjected to analysis of quality parameters.

2.5 Analyses of Characteristics of Rice Straw Adsorbent

2.5.1 Particle Size

UCO was treated with the adsorbents at particle sizes of 355 and 201 µm, and the particle size that gave the greatest PV reduction was used in the determination of the following characteristics of the RSA:

2.5.2 Adsorption capacity

UCO was treated with varying amounts of RSA in triplicates at 5%, 10%, 15%, and 20% by weight. The adsorption capacity of RSA was determined to be the amount that gave the highest reduction in PV.

2.5.3 Functional groups on adsorbent surface

A small amount of RSA was analyzed using the PerkinElmer Spectrum Two Fourier Transform-Infrared (FTIR) spectrometer with ATR function. The functional groups were determined from the FTIR spectrum generated.

2.5.4 Surface morphology and pore size

A small amount of sample was pretreated by sputter coating with gold to enhance the conductivity, then viewed under the JCM-7000 NeoScope™ Benchtop Scanning Electron Microscopy (SEM). The images were obtained at resolutions from 200-2000x. The pore size of the RSA was determined from the SEM images using the ImageJ program based on Saraf et al. (2019).

2.6 Analyses of the Quality Parameters of Used Cooking Oil

The RSA at particle size and adsorption capacity that gave the highest PV reduction was used.

2.6.1 Peroxide value

The PV was determined in triplicates according to Nuru & Getachew (2021), with modifications. About 5 g oil was added with 30 mL acetic acid-$CHCl_3$, and 0.5 mL saturated KI. The mixture was incubated in the dark for 1 min, added with 30 mL ultrapure H_2O, and 2 mL 1% starch, followed by titration with standardized 0.005 M $Na_2S_2O_3$ until the ivory white endpoint. The PV was expressed in milliequivalents of oxygen per kilogram of oil, according to the equation:

$$PV = \frac{(V_{Total} - V_{Blank})(M\ Na_2S_2O_3\ used)(1000)}{g\ cooking\ oil}$$

2.6.2 Acid value

The AV was determined in triplicates according to Ahmed et al. (2022), with modifications. About 5 g oil was added with 50 mL 97% ethanol, and titrated with the standardized 0.01 M KOH until the faint pink endpoint. The acid value, expressed in milligrams of KOH per gram of oil, was calculated using the equation:

$$AV = \frac{(V_{Total} - V_{Blank})(M\ KOH\ used)(56.1)}{g\ cooking\ oil}$$

2.6.3 Color

The color analysis test was carried out based on Peamaroon et al. (2021) and Gao et al. (2023) with modifications. Four test tubes were filled with oil and images were taken using three different Samsung smart phones under the same conditions. The pictures were analyzed using the Color Grab version 3.9.2 by Loomatix using the L* a* b* color space.

2.7 Statistical analysis

Significant differences between treatment means were determined using one-way ANOVA and LSD using IBM SPSS version 26.

3. Results and Discussion

3.1 Characterization of Rice Straw Adsorbent

3.1.1 Particle size

The RSA at 355 μm reduced the PV of UCO by 5.37% which was higher than that of 201 μm (Table 1). Amer et al. (2017) observed that the rice straw adsorbent with smaller particle size had increased the overall adsorption capacity for the removal of lead (II) from aqueous solutions. However, the data shown in Table 1 indicates that the reduction of peroxides in UCO was greater at bigger particle size. This may be explained by the needle like shape of the RSA at 355 μm, which is not observed with the 201 μm RSA (Fig. 1). This needle-like shape of the 355 μm adsorbent allows more pores and nodulations due to the surface's coarseness (Fig. 3) which may provide more efficiency in adsorbing peroxides (Huang et al., 2021).

Table 1. Effect of particle size on peroxide value of the used cooking oil. The RSA was activated with 0.5 M NaOH and mixed with UCO at 15% by weight.

Particle size	PV (meq O_2/kg) ± SEM	% Reduction ± SEM
Used cooking oil	10.43 ± 0.04	
201 μm	10.11 ± 0.07	3.02 ± 0.36 [b]
355 μm	9.87 ± 0.09	5.37 ± 0.51 [a]

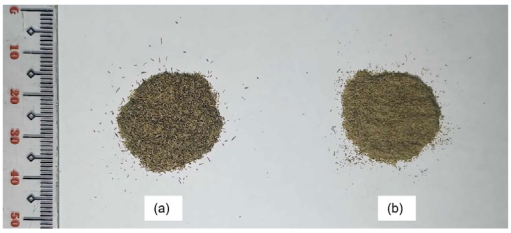

Figure 1. Images of the rice straw adsorbent at particle sizes: (a) 355 µm; (b) 201 µm

3.1.2 Adsorption Capacity

The highest PV reduction (Table 2) was achieved at 5% wt RSA, and shows that the adsorption capacity decreases with increasing adsorbent weight. According to Padmavathy et al. (2016), the number of adsorption sites is higher at lower adsorbent concentrations because an increase in adsorbent dose causes aggregation of adsorbent, and as a consequence, the adsorbate uptake decreases. Adsorbent aggregation influences the adsorption capacity as it leads to a reduction of the adsorbent's surface area (Wang et al., 2010).

Table 2. Effect of the amount of RSA on PV of used cooking oil. The RSA was activated with 0.5 M NaOH at a particle size of 355 µm. $^{a-b}$Mean values with unlike letters were significantly different ($p < 0.5$).

Amount of RSA	PV (meq O_2/kg) ± SEM	% Reduction ± SEM
Used cooking oil	11.45 ± 0.09	
5%	10.87 ± 0.03	5.05 ± 0.26 ^{a}
10%	10.91 ± 0.10	4.69 ± 0.85 ^{a}
15%	11.16 ± 0.00	2.54 ± 0.00 ^{b}
20%	11.28 ± 0.00	1.47 ± 0.00 ^{b}

3.1.3 Functional groups on adsorbent surface

Figure 2 shows the FTIR spectrum of the RSA, with the characteristic peaks of O-H and C-O observed at around 3300 cm^{-1} and 1100 cm^{-1}. This is typical of the cellulosic component of RSA (Phitsuwan et al., 2017). Rice straw cellulose is linked with glucose units that consist of three reactive O-H groups at C-2, C-3, and C-6 atoms (Ramos et al., 2023), which is favorable for rice straw as a potential adsorbent (Chakraborty et al., 2011). These hydroxyl groups contained in rice straw cellulose have a certain degree of adsorption capacity to bind peroxides and free fatty acids in oil (Jiang & Hu, 2019).

3.1.4 Surface morphology and pore size

The surface morphology of the RSA is rough with porous structures (Fig. 3a) and pointy nodules (Fig. 3b). According to Fathy et al. (2013), these structures are the exposed pores present on the surface of the cellulose after the removal of lignin. The average pore size of RSA is 11.2 ± 0.6 µm. The porosity and pore size of is directly proportional to adsorption capacity since the diffusion of adsorbates to the adsorbent is not limited (Hsieh & Teng, 2000).

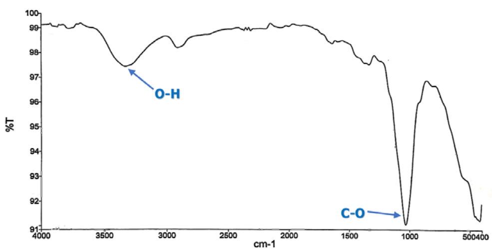

Figure 2. FTIR spectrum of the RSA

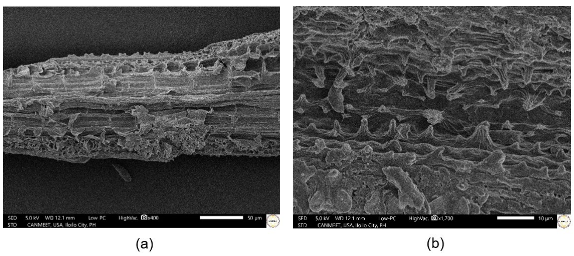

Figure 3. *SEM images of RSA at resolution of (a) 400x; and (b) 1700x.*

3.2 Effect of RSA treatment on used cooking oil

3.2.1 Acid value

Table 3 shows the effects of RSA on the AV of cooking oil. Heating the new cooking oil led to an increase in AV from 0.03 to 0.17 mg KOH/g, which indicates hydrolysis of the oil. The RSA-treated used cooking oil has reduced AV from 0.17 to 0.11 mg KOH/g, which indicates the adsorbent's potential to lower the acidity of UCO. This is due to the fact that cellulose fiber is good for maintaining the low acid values of cooking oils (Rahayu et al., 2018). Also, the porosity of the RSA (Fig. 3) provides an ample site for the adsorption of fatty acids and the presence of O-H groups at the RSA surface made the interaction and adsorption of fatty acids easier (Onn et al., 2023).

Table 3. Effect of rice straw adsorbent on the acid value of cooking oil. [a-c]Mean values with unlike letters were significantly different ($p < 0.5$).

Cooking oil	AV (mg KOH/g) ± SEM	% Reduction ± SEM
New	0.03 ± 0.01 [c]	
Used	0.17 ± 0.01 [a]	
After treatment with RSA	0.11 ± 0.02 [b]	40.78 ± 1.77

3.2.2 Color

Results in Table 4 showed that the new oil has a light and yellow color, while that of used oil had a darker yellow color. Treatment of RSA has significantly improved the lightness of the oil color, but added a very light greenish color to the yellow color of the used oil. The darkening of the UCO that was observed may be caused by colored impurities generated from the Maillard reaction during heating (Nayak et al., 2015). These colored impurities are adsorbed by the pores of the adsorbent (Sari et al., 2022). The greenish hint of RSA-treated UCO may have been due to residual chlorophyll from RSA (Hu et al., 2013).

Table 4. Effect of RSA on the color of cooking oil. a-zMean values with unlike letters were significantly different ($p < 0.5$).

Cooking oil	L*	a*	b*
New	76.37 ± 0.18 [a]	-2.73 ± 0.20 [z]	12.40 ± 0.60 [i]
Used	70.53 ± 0.30 [b]	-5.74 ± 0.32 [y]	27.83 ± 1.03 [h]
After treatment with RSA	76.05 ± 0.17 [a]	-6.48 ± 0.42 [x]	27.67± 0.25 [h]

4. Conclusions

Rice straw waste, which is an abundant by-product from rice harvest, has been developed as an absorbent for the treatment of waste cooking oil. The RSA prepared was characterized to have a particle size of 355 µm and adsorption capacity for PV at 5% wt/vol of used oil. The surface of the RSA had porous structures with average pore size of 11.2 µm, pointy nodules, and O-H and C-O functional groups. Treatment of used cooking oil with RSA reduced PV by 5.05 – 5.37%, AV by 40.78% and improved the lightness of the oil color. Thus, rice straw waste biomass can be valorized as an adsorbent for the improvement of quality parameters of used cooking oil.

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