

Study on the Comprehensive Utilization of Bitter Almond Shell

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A comprehensive process was developed to make full use of the solid and liquid products during the production of activated carbon. Almond shell waste was modified with phosphoric acid and thermally treated to give activated carbon. Wood vinegar was generated and collected within the temperature range of 90 to 500 °C, and the maximum amount of the wood vinegar was in the range of 170 to 370 °C, which also gave the strongest anti-pathogens activities with the lowest pH and the highest organic acid content. The remaining residue after wood vinegar generation was further calcined in inert atmosphere to obtain high surface area activated carbon. The pre-treatment of almond shell with H₃PO₄ leads to the higher surface area, but H₃PO₄ solution with concentration more than 40% does not increase the surface area further. The impregnation of H₃PO₄ helps the formation of pores in the almond shell during the calcination, and gives higher iodine number and methylene blue sorption capacity of the resultant activated carbon materials.

Keywords: Almond shell; Activated carbon; Wood vinegar; Comprehensive utilization

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INTRODUCTION

Almond is the general name of *Prunus dulcis* or *Prunus amygdalus* L. Almond fruit consists of the hull, shell, and kernel (nut). The almond tree can grow to a height of seven to ten meters, and it has been a main source of almond fruit worldwide (Schirra 1997; Choudhari *et al.* 2013). It has been estimated that the annual output in north China is up to 40 thousand tons, and the amount has tended to increase due to a strong demand for the fruit (Wang *et al.* 2010). During the harvest period, the hull and kernel are the desirable products; the almond shell consists of 70% of the dry mass of a whole almond fruit. These nutshells can be collected on a community basis for reuse (Rodriguez-Reinoso *et al.* 1984; Ruiz Bevia *et al.* 1984; Gonzalez *et al.* 2005; Izquierdo *et al.* 2011; Meenakshi Sundaram and Sivakumar 2012; Pirayesh and Khazaeian 2012; Tiryaki *et al.* 2014). Almond nutshells are abundant, inexpensive and readily available lignocellulosic materials, which contain a high content of carbon and other renewable chemicals. There have been many studies on converting almond shell into activated carbons (Gonzalez-Vilchez *et al.* 1979; Rodriguez-Reinoso *et al.* 1982; Linares-Solano *et al.* 1984; Rodriguez-Reinoso *et al.* 1984; Ruiz Bevia *et al.* 1984; Torregrosa and Martin-Martinez 1991; Hayashi *et al.* 2002; Toles and Marshall 2002; Gonzalez *et al.* 2005; Pajooeshfar and Saeedi 2009; Meenakshi Sundaram and Sivakumar 2012; Yagmur 2012; Omri and Benzina 2013; Omri *et al.* 2013; Martinez de

Yuso *et al.* 2014).

Gonzalez *et al.* (2009) carried out a study of the pyrolysis of various biomass residues including almond shell for the production of activated carbons. It was shown that the four biomass residues used are versatile precursors that allow the preparation of adsorbent materials with different textural characteristics. However, they did not describe how to deal with the resultant liquid.

Tiryaki *et al.* (2014) compared the activated carbons produced from almond shell and equivalent chemical compositions using concentrated phosphoric acid as the activation agent. The activated carbon produced from each natural biomass was characterized in terms of its surface area and pore volume. The phosphoric acid activating agent is effective for the pore and surface area formation, while it does not lead to the formation of chloride-containing volatile compounds.

Uchimiya *et al.* (2013) studied the pyrolysis temperature-dependent release of dissolved organic carbon from plant, manure, and biorefinery wastes for soil alternation. There have been also some studies on the utilization of the almond shell as an energy source; in such studies the almond shell material was either gasified or burned directly. However, no report has considered the emission of the volatile compounds in the early stage of thermal treatment.

To date, most research has focused on the conversion of the almond shell to activated carbon. Little attention has been paid to the volatile compounds or liquid compounds, which are mostly wood vinegar during the pyrolysis or thermal treatment. However, these volatile compounds, which are relatively high in amount, may become pollutants if not properly disposed or collected. The present work describes development of a novel way to comprehensively utilize the almond shell. In activated carbon generation, H_3PO_4 was chosen as the active agent, so as to prevent the reaction of the volatile organic compound with the chloride residue emitted from ZnCl_2 , thus avoiding the formation of organic chlorides, which are considered to be toxic. Liquid collected during the process was shown to be useful as wood vinegar, which has anti-bacteria effect due to its organic acid content. The high temperature treated residue was converted into activated carbon, which showed a high iodine number and methylene blue adsorption capacity.

EXPERIMENTAL

Raw Material Collection

Bitter almond shell was collected from Linyou County, Shaanxi Province, China. The shell was broken for kernel collection, and the broken shell was naturally dried under sunshine at 20 to 35 °C, after the kernel was removed. The moisture in the shell is about 8.5 wt%. The broken shell was ground and sieved into 10 to 20 mesh particles. The images of the collected almond nut shell is shown in Fig. 1a.

The conversion of almond shell into active carbon normally employed different activators. There have been quite a lot of technologies using ZnCl_2 as the activator (Ruiz Bevia *et al.* 1984; Torregrosa and Martin-Martinez 1991; Rodriguez-Reinoso and Molina-Sabio 1992; Aygun *et al.* 2004). Such work has shown that such processing may result in the emission of organic chlorides and also in the production of wood vinegar. Thus to eliminate the organic chlorides during the activated carbon production, H_3PO_4 was chosen as the activator. In this work, 300.6 g of the almond shell particles were impregnated with 150.2 g of different H_3PO_4 solutions, *e.g.*, 20, 40, 60, and 85 wt% H_3PO_4 . The mixture was

placed in air under ambient conditions for 20 h, then dried in static air at 120 °C for 4 h to give the active carbon precursor. The activated carbon and wood vinegar were produced according to the following steps.

For each test, 200.5 g of the H₃PO₄ containing almond shell was placed into a tubular 40 mm quartz tube, which was plugged with quartz wool with the two ends. The quartz reactor was placed into an electrical furnace under flowing nitrogen at 20 mL/min, and the temperature was raised at 5 °C /min to different target temperatures, held at the temperature, and wood vinegar was collected. After reaching 500 °C, the remaining carbon residue was heated at 10 °C /min to 950 °C and held for 2 h. The exit gas was monitored using on-line GC (HP5890, equipped with DB—WAX capillary column with an oven temperature of 60 °C). The choice of final activation temperature of 950 °C was to remove the phosphate from the resultant activated carbon during the process and also to obtain highly thermally stable activated carbon for use as catalyst support. There were some white residues in the reactor wall, which was from the high temperature stage, but only a very small amount.

The calcined samples were cooled down to room temperature in flowing N₂ and unloaded. The resultant carbon material residues were water washed in a Soxhlet apparatus until 6 < pH < 7, then dried at 120 °C until constant weight was reached. The solids were stored in a vacuum package.

The activated carbon yield was calculated according to the following equation,

$$P = m/M \times 100\% \quad (1)$$

in which P is the activated carbon yield (%), m refers to the washed and dried carbon amount (g), and M is the total weight of the almond shell particles amount (g, excluding the impregnated H₃PO₄) loaded into the quartz reactor.

The measurement of the iodine number of the resultant activated carbon was carried out according to the GB/T12496.8-1999 (Chinese National Standards for the Iodine Number), and the methylene blue sorption value of the active carbon was measured according to GB/T12496.10-1999 (Chinese National Standards for the Methylene Blue adsorption), and expressed as mg/g for both.



Fig. 1. a: Bitter almond shell powder; b: the resultant activated carbon

Collection of the Wood Vinegar

During the carbonization of the dried almond shell, the gas flows down through the almond shell bed and some exit gas is passed through a wash bottle where the volatile liquid is cooled down to liquid. The liquid is measured every 20 °C, and the amount is weighed and the composition is analyzed. The crude wood vinegar in the end is collectively divided into 3 stages, and is refined with filtration through activated carbon to obtain the desirable wood vinegar.

The composition of the wood vinegar samples was analyzed using a Shimadzu GC-MS 2010SE equipped with a DB-WAX capillary column (30 m x 0.25 mm x 0.25 µm). The sampling injection temperature was 220 °C, and the initial oven temperature was 60 °C, held for 2 min after sampling. The temperature was then increased to 240 °C at 60 °C/min and held at 240 °C for 8 min. The flow rate of the He carrier gas was 1.0 mL/min. The ionization temperature of the MS was 250 °C and the scanning range was 35 to 400 amu. The compounds were identified according to the NIST database.

The Anti-Bacteria Test

The bacteria for the test included: *Escherichia coli*, *Aerobacter aerogenes*, *Staphylococcus aureus*, *Bacillus prodigiosus*, *Trichoderma viride*, *Trichoderma koningii*, *Penicillium glaucum*, *Aspergillus niger*, *Colletotrichum lagenarium*, *Plasmopara viticola*, *Verticillium dahlia*, *Phytophthora capsici*, *Fusarium graminearum*, and *Valsa mali*, which were supplied by the Micro-organism lab of the Resources and Environmental College, Northwestern University of Agriculture and Forests.

The culture media was beef extract peptone base for bacteria growth, which was composed of beef extract 3.0 g, peptone 10.1 g, agar 18.9, deionized water 1000 mL, at a pH of 7.2 to 7.4. Plant pathogen and moulds were grown in the media of sweet potato, glucose and agar-agar, and DI water 1000 mL.

In this work, the zone of inhibition method was employed to study the inhibition effect of the wood vinegar on various bacteria. The wood vinegar's inhibition to the hyphal growth rate was monitored by measuring pathogens in colony diameter. The experimental details have been given in an earlier publication (Looa *et al.* 2008). Briefly speaking, prior to the test, the plant pathogens bacteria were inoculated onto a potato dextrose agar (PDA) growth plate and grown for 1 week at 28 °C, then cut as a 6-cm circle from the bacterial plate for the test.

The wood vinegar was diluted to a series of liquid concentrations and used for the anti-bacterial test using sterile water as the control condition. The PDA culture media was first melted and cooled down to 50 °C, then 100 mL culture media flask was added by 2 mL of the wood vinegar with shaking to mix it, then diverted into a culture dish, with measurement of the concentration. The culture dish was cooled to condense and embed the bacteria plate. The process was repeated 3 times. The petri dish was then placed into a 28 °C incubator for 72 h, and the diameter of the bacteria region was measured.

RESULTS AND DISCUSSION

Analysis of the Raw Almond Shell

The almond shell was analyzed relative to its components and elemental composition, and the results are shown in Table 1.

Table 1. Pyrolysis and Elemental Composition of the Raw Materials

Component analysis	Content (wt%)	Industrial analysis by pyrolysis	Content (wt%)	CHNOS analysis	Content (wt%)
Cellulose	50.7	Fixed carbon	21.54	C	51.94
Hemicellulose	26.4	Volatile fraction	76.83	H	5.39
Lignin	20.4	Ash content	1.63	N	0.66
Extract	2.5			O	41.9
				S	0.11

The almond shell had a high content of cellulose and hemicellulose, and the extract accounted for 2.5 wt% of the total mass, more or less in agreement with the literature results (Rodriguez-Reinoso and Molina-Sabio 1992; Marcilla *et al.* 2000; Hayashi *et al.* 2002). However, when pyrolyzing the almond shell, the sample yielded 21.54 wt% of fixed carbon, and the volatile fraction generated during the pyrolysis was more than 76.83 wt%, while the ash content was 1.63 wt%. In terms of the elemental composition, carbon and oxygen were the dominant elements at 51.94 wt % and 41.9 wt% with hydrogen content of 5.39 wt% in the almond shell, which echoed the main composition of cellulose and hemicellulose. It is interesting to see that the almond shell had much higher N content (0.66 wt%) than the sulfur (0.11wt%), suggesting that the almond shell contains more nitrogen compounds (Table 1).

Thermal Treatment of the Impregnated Almond Shell Powder

The various H₃PO₄ impregnated almond shells was heated in a quartz reactor under a flowing N₂ atmosphere, and the temperature was increased at 5 °C/min and held at different stages until no liquid came out. Then the temperature was raised to another range. The liquid was collected at three temperature ranges, which were 90 to 170 °C, marked as WN- A, at 170 to 370 °C marked as WV- B, and that at 370 to 500 °C marked as WV-C. After 500 °C, almost no liquid was condensed while the flowing gas was being analyzed. The total amount of the wood vinegar sample was in the range of 44 to 48 wt% of the total almond shell. The weight ratio of the WV-A to WV-B to WV-C is 10:86:4, and almost all the same in all almond shell samples, suggesting that the H₃PO₄ pre-treatment did not have significant effect on the relative amount of the wood vinegar. When the temperature reached 950 °C, it was held at this temperature for 2 h. The liquid product was collected over a balance so as to monitor the quantity. The feed amount and the resultant carbon, wood vinegar, and gas products *e.g.*, the mass balance of the process is shown in Table 2.

Table 2. Results of the Activated Carbon and Wood Vinegar

Sample treated with H ₃ PO ₄ concentration	Total feed/g	Wood vinegar %	Activated carbon /%	gas+moisture calculated /%
0	230.1	43.8	30.5	
20	196.4	47.9	33.4	18.7
40	208.9	45.8	34.7	19.5
60	213.4	44.6	35.1	20.2
85	202.4	45.7	35.4	18.9

It can be seen that the modification of the almond shell with H_3PO_4 slightly increased the wood vinegar yield. The unmodified almond shell gave about 43.8% of wood vinegar. The amount of activated carbon was 30.5% under the same experimental conditions, along with the highest yield of gas, including some moisture (uncondensed). When the almond shell was modified with 20% of H_3PO_4 solution, the wood vinegar yield was increased to 47.9, and the activated carbon yield also increased to 33.4%, with the least gas generated about 18.7%. The pre-treatment of the almond shell with 40%, 60%, and 85% H_3PO_4 solution yielded almost the same percentage of wood vinegar, accounting for about 45.8, 44.6, and 45.7 wt%, respectively, and the activated carbon yield was about 35 wt% in the 3 samples. The gas yield in the concentrated H_3PO_4 solution treated almond shell samples was around 19 wt%. These results showed that the H_3PO_4 solution impregnation did not have a significant effect on the carbonization of the almond shell samples under the experimental conditions.

Characterization of the Activated Carbon Materials

An image of the resultant activated carbon powder (from sample 3 in Table 3, and sieved to less than 30 mesh size) is shown in Fig. 1b. The product can be described as a mixture of black powder and particles, with 65% as particles more than 200 μm in diameter. The powder was judged to be less dusty, which may be due to the effect of H_3PO_4 addition. The properties of the various activated carbon samples were characterized using BET surface area measurement, iodine, and methylene blue adsorption, and the results are summarized in Table 3.

Table 3. Properties of the Resultant Activated Carbon

Sample No.	Sample impregnated with H_3PO_4 solution	BET Surface area (m^2/g)	Iodine number (mg/g)	Methylene blue sorption mg/g)
1	0	696	566	122
2	20	836	796	215
3	40	843	839	311
4	60	839	864	326
5	85	825	950	319

Although the activated carbon yield was increased from 30.5 wt% for the H_3PO_4 non-treated almond shell sample, when treated with 20% H_3PO_4 solution or higher concentrated H_3PO_4 solution, the almond shell gave higher activated carbon yield, around 33.3 to 35wt% in the four samples. This suggests that impregnation with H_3PO_4 solution can give a little more activated carbon. The surface area of the different resultant activated carbon showed that the sample containing no H_3PO_4 had the lowest surface area, about 696 m^2/g . The treatment of H_3PO_4 of the almond shell increased the surface areas to 836, or 843 m^2/g and no further increase with increasing H_3PO_4 concentration. This is in agreement with the literature results, showing that the modification of the almond shell with H_3PO_4 can induce higher surface of the resultant carbon materials (Arjmand *et al.* 2006; Yeganeh *et al.* 2006; Soleimani and Kaghazchi 2007), although the yield of the present system was higher than the literature results (Soleimani and Kaghazchi 2007), which is probably due

to the fact that higher H_3PO_4 soaking ratios were employed in the present work.

In terms of the absorption performance, the iodine sorption number also increased with the pre-treatment H_3PO_4 concentration. The non- H_3PO_4 treated almond derived carbon had an iodine number of 566 mg/g, whereas the pre-treatment of 20% H_3PO_4 on the almond shell led to the iodine number of the activated carbon increasing to 796 mg/g, and further increasing with the concentration of H_3PO_4 treatment. The sample treated with 85% H_3PO_4 had the highest iodine number, about 950 mg/g. This shows that the sample with the highest surface area (sample 4) did not have the highest iodine number.

For methylene blue, which reflects the bigger pore sorption of the activated carbon properties, the impregnation of H_3PO_4 almost doubled the methylene blue sorption capacity in the resultant activated carbon. With the further increase the pre-treatment H_3PO_4 concentration of the almond shell, the methylene blue sorption capacity further rose to 311 mg/g and increased to 326 mg/g in the 40% H_3PO_4 treated sample. This suggests that the H_3PO_4 pre-treatment of the almond shell can significantly increase the larger pore (mesopore) generation for the almond shell, thus leading to the formation of more of the larger pores in the resultant activated carbon.

The resultant activated carbons from the various pre-treated almond shells were observed using SEM, and the images of the samples are shown in Fig. 2. The untreated almond shell gave an image of some framework-like twisting, but less pores. When the almond shell was treated with 20% H_3PO_4 solution, the images of the carbon were changed, but the pores still were not clearly formed. The 40% H_3PO_4 solution treatment gave rise to holes and pores in the shell after calcination.

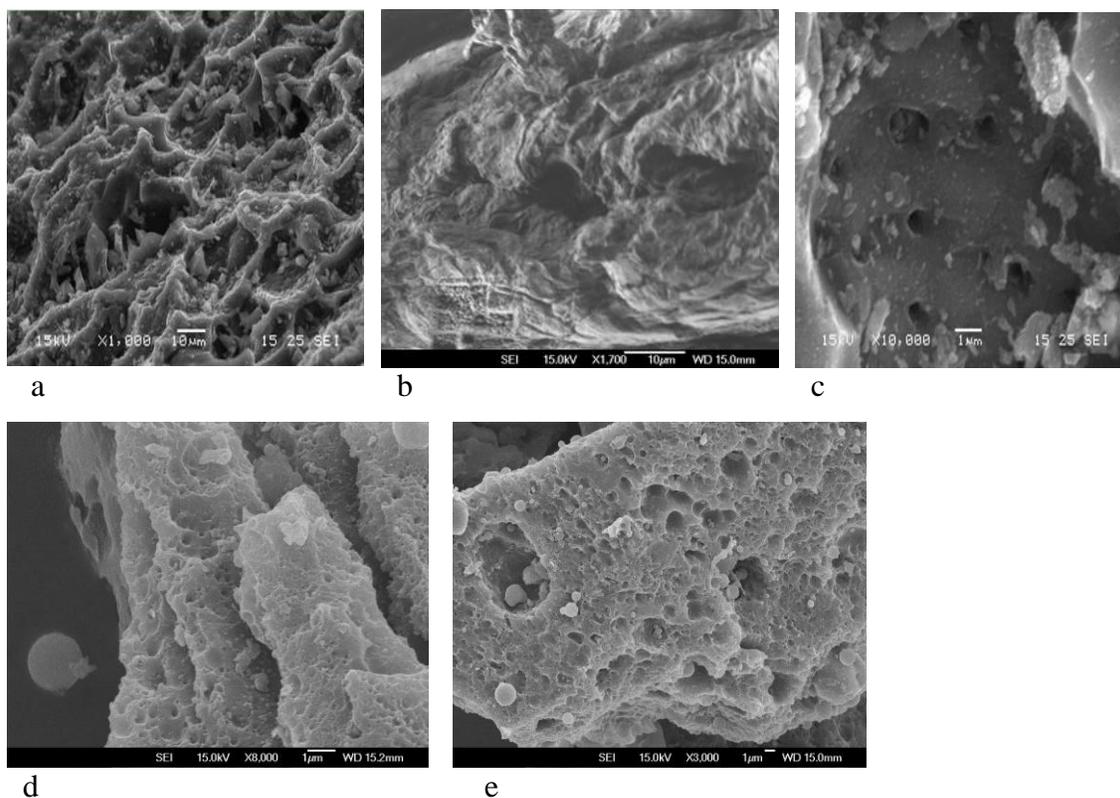


Fig. 2. SEM images of the activated carbon obtained from differently-treated almond shell samples: a) from the 0% H_3PO_4 solution, b) 20% H_3PO_4 , c) 40% H_3PO_4 , d) 60 wt% H_3PO_4 , and e) 85 wt% H_3PO_4

It is interesting to see that the 60% of the H_3PO_4 treatment resulted in much more pores distributed more evenly. The increase of H_3PO_4 concentration treatment yielded more holes and big pores, although the BET surface area measurement exhibited little difference, as shown in Table 3. The big pores and holes in the active carbon may be relevant to the possible formation of residue phosphate compounds in the activated carbon. However, the amount of the phosphate was too small to be detected using XRD.

Analysis of the Wood Vinegar and its Anti-bacterial Performance

The wood vinegar samples were collected within the temperature ranges of 90 to 170 °C, 170 to 370 °C, and 370 to 500 °C, respectively. The sample collected within the first temperature range had a pH of 3.4, and it contained an organic acid content of 3.7%. The refined product yield was 92.3%, which suggests that it contained a significant amount of organics. The wood vinegar in the 170 to 370 °C sample had the lowest pH of 2.9, which is more acidic than the WV-A; thus it contained more organic acid, accounting for 6.4 wt% of the total vinegar. However, the refined product yield was only 72.6% because it may have contained more condensed water. The pH of the wood vinegar collected at 370 to 500 °C was 3.3, while the organic acid content was 2.9% and the refined product yield was 60.2%, which means it contained more non-acid organic compounds, and maybe more moisture.

The density of the wood vinegar collected from the three temperature ranges was almost identical, about 1.02 to 1.05g/L, suggesting that it contained more soluble organics.

The overall wood vinegar was analyzed using GC-MS, and the results showed that phenols accounted for 30.13% of the organic phase (some water was also condensed in the sample which can be easily separated from GC-MS), in which phenol was 5.54 wt%. The organic acids accounted for about 40.89 wt% of the organic phases, in which acetic acid was 32.18 wt% of the acid phase. The furan derivative content was about 7.43wt%, with 2.88 wt% being furfural. Ketone group compounds accounted for 15.85 wt% of the organic liquid mixture. In addition, there existed a small amount of alcohol, benzene, and furan. The total amount of phenols, acid, aldehyde, and ketone was about 84.6% of the organic phase of the wood vinegar.

From the above analysis, it can be seen that acetic acid accounted for 32.18 wt% in the organic phase, which was much more than the other organic acid, and also the other organic compounds in the wood vinegar. Also the pKa of acetic acid is 4.75, lower than other longer organic acids identified by the GC-MS, and with its absolutely high content, it is therefore inferred that the strong acidity of the wood vinegar sample results from the acetic acid components.

The identification of the each compound using GC-MS in the wood vinegar is summarized in Table 4. The ketone family showed 16 compounds with 3-methyl-1,2-cyclopentanedione, the highest content among them. There were seven different compounds in the organic acid class with the acetic acid the dominant compounds in the system, accounting for 32.18 wt% of the total organic acid. The furan derivatives in the wood vinegar had seven different compounds, with furan the main compound in this class. The others were minor. The phenol family had 20 different phenol compounds, with the phenol itself being the dominant one. Only one nitrogen-containing compound was identified in the wood vinegar, which was 3-pyridinol, and its content in the wood vinegar was 0.27%, and this was lower compared to the N content in the almond shell. This may be due to some nitrogen being emitted as ammonia in the gaseous products.

Table 4. GC-MS Analysis of the Wood Vinegar

Retention time /min	Compounds	Relative content in the organic phase (%)
	Ketone	15.85
5.57	Cyclopentanone	0.74
7.59	3-Hydroxy-2-butanone	0.58
7.94	1-Hydroxy-2-propanone	2.83
9.10	2-Cyclopenten-1-one	1.96
9.35	2-Methyl-2-cyclopenten-1-one	1.02
9.49	1-hydroxy-2-butanone	1.02
12.47	3-methyl-2-cyclopenten-1-one	1.16
12.74	2,3-Pentanedione	0.30
15.71	3-Ethyl-2-hydroxy-3-cyclopenten-1-one	0.27
17.35	1,2-Cyclopentanedione	0.30
17.77	3-Ethyl-1,2-cyclopentanedione	1.12
18.04	Tetrahydro-2 <i>H</i> -Pyran-2-one	0.31
18.41	3-Methyl-1,2-cyclopentanedione	3.27
19.94	2,4-Dimethyl-1,3-Cyclopentanedione	0.28
30.99	1-(4-Hydroxy-3-methoxyphenyl)- 2-propanone	0.69
	Organic acid	40.89
10.69	Acetic acid	32.18
12.31	Butanoic acid anhydride	1.19
12.81	Propanoic acid	4.39
14.64	Butanoic acid	1.52
15.45	2-Methyl-hexanoic acid	0.27
17.41	Isocrotonic acid	0.28
24.10	2-Methyl-propanoic acid anhydride	1.06
	Furan derivatives	7.43
11.43	Furfural	2.88
11.76	Tetrahydro -2-furanol	0.73
12.25	1-(2-Furanyl)-ethanone,	0.95
13.64	5-methyl-2-furancarboxaldehyde	0.54
15.33	3-Furanmethanol	2.04
18.76	3,5-Dimethyl -2,5-dihydro-2-furanone	0.29
	Ester	1.89
14.75	Butyrolactone	1.13
15.11	2,5-Dihydro-3,5-dimethyl- 2-furanone	0.34
28.54	Ethyl oleate	0.32
	Phenols and their derivatives	30.13
19.00	2-Methoxyphenol	2.16
20.65	2-Methoxy-4-methylphenol	1.15
21.47	Phenol	5.54
21.87	4-Ethyl -2-methoxyphenol	0.49
22.72	4-Methylphenol	3.85
24.17	3,4-Dimethylphenol	0.80
25.55	2,6-Dimethoxyphenol	3.86
26.80	1,2,4-Trimethoxybenzene	1.40
27.61	1,2,3-Trimethoxy-5-methyl-benzene	0.73
28.47	2-Methoxy-1,4-benzenediol	1.13
31.56	1,2-Benzenediol	3.97
32.45	3-Methyl-1,2-benzenediol	2.57
36.13	2-Methyl-1,4-benzenediol	0.86
36.34	Desaspidinol	0.96
36.70	Hydroquinone	1.56
	Alcohol and sugar compounds	1.66
20.77	maltol	0.53
27.48	1,4:3,6-Dianhydro- α -D-glucopyranose	0.82
30.17	isosorbide	0.31
	N-containing compounds	0.27
27.74	3-Pyridinol	0.27

Study on the Bacteriostasis Activity of the Wood Vinegar Samples

The wood vinegar samples *e.g.*, WV-A, WV-B, and WV-C collected from the three temperature ranges were used for the tests so marked. The as-received wood vinegar samples were used directly. The bacteriostasis activities of each wood vinegar to the different kind of bacteria are shown in Table 5. Generally, all the wood vinegar raw liquids exhibited activity to depress the bacterial growth, but the WV-B achieved greater depressing diameters than that of WV-C, whereas wood WV-C showed higher activity than the WV-A. The highest bacteriostasis activity was associated with the WV-B and *Bacillus prodigiosus*, for which the diameter of the bacteria killing area was 3.07 ± 0.60 cm, and WV-C depressed 1.88 ± 0.20 of *Bacillus prodigiosus* growth. This can be correlated to the more acidic nature of WV-B and its high organic acid content.

For comparison, ciprofloxacin, a typical anti-inflammatory drug, has also been tested for the bacteriostasis, and its activity was almost identical for *Enterobacter aerogenes*, *Escherichia coli*, and *Bacillus subtilis*, but weakest for *Staphylococcus aureus* and next to *Bacillus prodigiosus*. This suggests that the wood vinegar samples even have higher activity for killing the bacteria, in addition to their being natural products.

Table 5. Results of Bacteriostasis Activity of Wood Vinegar to Bacteria (unit: cm)

Wood vinegar sample	<i>Enterobacter aerogenes</i>	<i>Escherichia coli</i>	<i>Bacillus subtilis</i>	<i>Staphylococcus aureus</i>	<i>Bacillus prodigiosus</i>
WV-A	0.81 ± 0.06	0.60 ± 0.00	0.60 ± 0.00	0.68 ± 0.06	0.89 ± 0.09
WV-B	2.49 ± 0.09	2.29 ± 0.17	2.82 ± 0.20	2.69 ± 0.19	3.07 ± 0.60
WV-C	1.10 ± 0.11	0.95 ± 0.21	1.03 ± 0.29	1.79 ± 0.19	1.88 ± 0.20
CK	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
Ciprofloxacin	2.45	2.55	2.45	1.65	2.20

Note: Data in the table is the diameter of the killed bacteria in cm, which is the average value of the 3-times measurement. WV-A, WV-B, and WV-C are the symbols of wood vinegar collected within the temperature ranges of 90 °C to 170 °C, 170 °C to 370 °C, and 370 °C to 500 °C.

Table 6A. Anti-Plant Pathogenic Fungi Performance and Anti-Mould Performance of the Wood Vinegar Samples Collected at Different Temperature Stages (unit: cm)

Wood vinegar	Cucumber Anthracnose	Grape downy mildew	Verticillium wilt of cotton	Pepper phytophthora blight	Wheat Fusarium head blight	Apple canker
WV-A	2.77 ± 0.51	3.92 ± 0.19	3.40 ± 0.07	3.85 ± 0.10	4.93 ± 0.18	2.97 ± 0.47
WV-B	0.10 ± 0.06	1.17 ± 0.11	0.94 ± 0.04	1.45 ± 0.14	0.66 ± 0.06	0.99 ± 0.11
WV-C	2.22 ± 0.07	2.66 ± 0.12	2.83 ± 0.09	3.30 ± 0.14	4.04 ± 1.01	2.37 ± 0.19
CK	$3.37\pm 0.04a$	3.78 ± 0.15	3.71 ± 0.19	6.31 ± 0.19	5.05 ± 0.05	3.83 ± 0.05

Table 6B. Anti-Plant Pathogenic Fungi Performance and Anti-Mould Performance of the Wood Vinegar Samples Collected at Different Temperature Stages (unit: cm)

Wood vinegar Anti-mould performance	<i>T. koningii</i>	<i>Penicilliosis</i>	<i>Trichoderma viride</i>	<i>Aspergillus niger</i>
WV-A	0.14±0.25	0.41±0.03	0.00±0.00	0.00±0.00
WV-B	1.53±0.13	1.23±0.42	1.14±0.33	0.96±0.00
WV-C	0.86±0.64	0.37±0.32	0.00±0.00	0.28±0.00
CK	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
ciprofloxacin	0.60	0.60	0.60	0.60

The wood vinegar samples were also used to depress the plant pathogenic fungi, and the results are shown in Table 6. It is interesting to see that that WV-A displayed higher activity for depressing the plant pathogenic fungi; the biggest fungal depressing diameter was 4.93±0.18 cm for wheat fusarium head blight, while WV-B only had the activity of 0.66±0.06 cm for the fungi depression, which showed the lowest activity, although its acidity was the highest. The WV-A generally had higher anti-fungi activity than WV-C, and the later had higher activity than WV-C. However, they all showed lower activity than the benchmark sample, CK.

This set of results showed that the anti-fungal activity followed a different mechanism from the anti-bacterial performance. Thus, a lower acidity may favour the fungi-killing process, as suggested by the results from Table 6. Also, fungi from various plants showed a different response to the wood vinegar sample.

The performances of the wood vinegar samples for depressing mould are shown in Table 6. The diameter of the mould disappearance area from the WV-B was about 1 cm for all the 4 mould samples, which was much bigger than WV-C and WV-A. As shown in Table 4, the pH of WV-A was the lowest, *e.g.* highest acidity, and WV-C showed slightly higher pH, and the WV-A has the weakest acidity. This result shows that the anti-mould performance was related to the acidity of the wood vinegar, where the higher acidity favoured the mould-depressing performance.

CONCLUSIONS

1. Almond shell was collected and analyzed. Analysis showed that the bitter almond shell contains high cellulose and also high N content, but little sulfur. It is a proper feed for activated carbon generation.
2. Wood vinegar was collected at three temperature ranges and was analyzed using GC-MS. The main components in the wood vinegar are acetic acid and phenols. The wood vinegar collected from 170 to 370 °C had the lowest pH value.

3. The wood vinegar samples mainly contained acetic acid, phenols, ketones, and some furfurals. Those samples with the highest acidity displayed the highest activity for anti-bacteria and anti-moulding. However, for the inhibition of plant fungi, wood vinegar with highest pH showed better performance. In summary, the wood vinegar is an effective anti-bacteria substance.

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