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Activated carbon synthesis from palmyra seed shell via physical and chemical activation methods

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Abstract
Activated carbon is generally used as absorbing and purifying agent due to its porous nature. Recently, agro-residues are considered as precursor for activated carbon production. Palmyra seed shell is one of the unexploited lignocellulosic feedstock and resource to produce multiple bioproducts for energy and environmental applications. Present study focused with the specific objective on activated carbon synthesis from palmyra seed shell using physical and chemical activation methods. Further, their relationship among the precursor characteristics, its microstructure, such as chemical and iodine adsorption properties were analyzed. The results inferred that the maximum iodine number of 840 mg g^{-1} was attained under optimal conditions of 800 °C and 60 min. or physical activation. Whereas, through sequential physical and chemical activation method, the maximum iodine number of 948 mg g^{-1} was obtained at the impregnation ratio of 1:2 at the activation temperature and activation time of 800 °C and 60 minutes.

Keywords: Activated carbon, adsorbent, biochar, impregnation, pyrolyzer

Introduction
Agro-residues are wastes generated from important agricultural practices such as harvesting and processing and there are lot of scope for energy generation through any thermal energy conversion technology (Ali *et al*. (2012) [1]. However, these residues are burnt in the agricultural fields and thereby, results in more environmental pollutions. There will be lot of agro-residues generated from different farm produce processing operations and each of them has unique nature (Anupama *et al*. (2023) [2]. Instead of in-situ burning, agro-residues may be used effectively to enhance their quality by converting into bioproducts by suitable biomass conversion processes. On the other side, coal and wood are the costliest precursors used for activated carbon production. Recently, activated carbon has vast applications in different fields *viz*., medicine, filtration, gaseous media, gas (methane & hydrogen gas) storage, purification, solvent recovery, decaffeination, gold purification, metal extraction, water purification, medicine, sewage treatment, air filters in respirators, filters in compressed air, teeth whitening, production of hydrogen chloride, catalyst support, and super capacitors (Cardoen *et al*. (2015) [3]. For these applications, activated carbon mostly used due to its added advantages such as powdered, granular, pellet form applications, porous structure, higher porosity and larger surface area (Chandrasekaran *et al*. (2017) [4]. The estimated global demand of activated carbon is ca. 40 times higher than its current production (>0.3 million tonnes/year) (Daniel *et al*. (2023) [5]. There is a wide gap between supply and demand, which may be fulfilled by low cost precursor derived from untapped and plenty available biomass resources (Qian *et al*. (2015) [6]. Therefore, activated carbon derived from lignocellulosic materials has considered for wide scope and significant potential as a low-cost resource to produce the carbon precursor for activated carbon (ElMekawy *et al*. (2014) [7]. Thus, results in low cost production and also safer disposal for agro wastes (Nuradila *et al*. (2022) [8].

Palmyra tree is most commonly found in the tropical countries like India, Srilanka, Indonesia and Thailand. Generally, the palmyra seed shell is a byproduct generated of palm fruits processing units, which is discarded as wastes into the environment (Feroldi *et al*. (2018) [9]. Among the residues, palmyra seed shell is an unexplored resource and to our best of knowledge, only few researches were done for energy aspects for this waste (Gil *et al*. (2015) [10].

Since, palmyra seed shell contains less moisture and rigid structure, drying step may not be required for carbonization process. In the case of biomass feedstock, the activated carbon can be synthesized by two steps (i) carbonization (ii) activation method. In carbonization process, the biomass is converted into biochar by heating in an inert atmosphere. Biochar produced is further subjected to activation to obtain the activated carbon. For activation, either physical or chemical methods can be adopted. For physical activation, biochar is subjected to higher reaction temperatures along with oxidizing gases; whereas, the chemical activation uses oxidizing chemicals for activation process (González-García, 2017) [11]. The properties and compositions of palmyra seed shells may vary as compared to other agrarian wastes. Similarly, the properties of activated carbon synthesised from the seed shells are also different. Therefore, the present study focused on optimization of process conditions for activated carbon synthesis from the palmyra seed shell biochar.

Materials and Methods

The materials and methods for the synthesis of activated carbon from palmyra seed are presented in this section.

Biomass Characterization

The physical, chemical, and thermal properties of Palmyra seed shell is performed in triplicate by employing the following methods. Moisture content (ASTM D 3173-87) is determined by placing 5g of finely powdered sample in a dried container in an electric hot air oven with a temperature setting of 103 °C until the weight of the shell becomes constant and observing the loss in weight. Volatile content (ASTM-D3175:2017) is found by placing the known quantity of moisture-free sample in a crucible with a lid placed in a muffle furnace at 650 °C for 6 min. and 750 °C for 6 min. then loss in weight is accounted. The ash content (ASTM-E1755:1995) is found by taking a known quantity of moisture-free sample in an open crucible and keeping in a muffle furnace at 750 ºC for 3 h till constant weight was reached. The quantity of residue left yields the ash content. Fixed carbon is calculated by the difference, in the sum of ash content and volatile matter (%) from 100. The chemical constituents of biomass *viz*., cellulose, hemicellulose, and lignin are determined as per NREL protocol.

Activated carbon production

Carbonization

A carbonization reactor (1 kg capacity) consist of pyrolytic chamber, electrical heating coil, insulation, valves for nitrogen gas supply and expel pyrolytic gas, steam generator and accessories (Fig.1). During the experiments, a quantity of 0.6 kg of palmyra seed shell was placed in the pyrolytic chamber and heat was supplied to attain reaction temperature of 700 °C in an inert condition by purging Nitrogen gas to get biochar.

Fig 1: Carbonisation cum activation reactor

Activation

In physical activation process, biochar is subjected to partial and controlled gasification using steam as physical agent at high temperatures usually between 600 to 1000 °C. After allowing steam, the sample is kept for nearly 30 to 90 min. inside the reactor. Chemical activation involves the KOH as an activating (impregnating) agent with a ratio of 1:1, 1:2, and 1:3 with an activation time of 2 h for the optimized physical activation methods (Jarosław *et al*. (2023) [12]. After drying the sample under oven conditions, neutralization of pH was done by washing the sample with hot and cold distilled water. After pH neutralization, the sample is kept again in hot air oven for drying and then the sample is activated at the temperature of 800 °C with an activation time of 60 min. in an activated carbon reactor.

Activated carbon characterization

The iodine number is determined according to ASTM D4607-14 (1999) method. The amount of iodine adsorbed by activated biochar is calculated from the following equation. The iodine number is determined according to ASTM D4607-14 (1999) method. The amount of iodine adsorbed by activated biochar is calculated from the following equation.

$$\text{Iodine number, mg g}^{-1} = \frac{\left\{126.93 N_1 V_1 - \left[\frac{V_1 + V_{HCl}}{V_F}\right] \times 126.93 N_{Na_2S_2O_3} V_{Na_2S_2O_3}\right\}}{M_c}$$

Where, N_1 = Iodine solution normality, N; V_1 = Added volume of iodine solution, ml; V_{HCl} = Added volume of 5% HCl, ml; VF = Filtrate volume used in titration, ml; $N_{Na2S2O3}$ = Sodium thiosulfate solution normality, N; $V_{Na2S2O3}$= Consumed volume of sodium thiosulfate solution, ml; M_c = Mass of sample, g.

Results and Discussion

The results obtained in the palmyra characterization and the results of activated carbon synthesis and adsorption tests are discussed for better understanding of effect of process parameters on the resultant products.

Characterization of Palmyra seed shell and biochar

Studying the properties of biomass is an important factor to assess the suitability of biomass for activated carbon production. Moisture Content of palmyra seed shell varied from 16 to 17%. Lower moisture content eliminates the need of drying before any thermochemical conversion process. Volatile matter of palmyra seed shell varies from 73 to 74%. Ash content of the palmyra seed shell varied from 4.3 to 5.1%.

The biomass with lower ash content could be used for activated biochar production. Fixed carbon content of palmyra seed shell ranged from 20.9 to 22.7%. The biomass with fixed carbon content above 25% is suitable for producing activated biochar with good surface properties (Sashikesh *et al*. (2023) [23]. The palmyra seed shell offered higher fixed carbon, and lower ash content which is the decisive factors for getting higher yield and good quality activated biochar (Jung *et al*. (2014) [14]. The chemical constituents namely cellulose, hemicellulose, and lignin of palmyra seed shell are found to be 32.96, 24.57 and 40.23% respectively.

Delignification occurs during the thermal treatment so enhances the activated carbon production. The palmyra seed shell is pyrolyzed in an activated carbon production unit at 700ºC at a residence time of 2 h with a Nitrogen flow rate of 200 ml min^{-1} (Karthyani *et al*. (2017) [15]. The volatile content, ash content, and fixed carbon content of palmyra seed shell char are found to be 7.51, 13.99, and 78.5% respectively. It is estimated that the fixed carbon of biochar is enriched in comparison with the biomass (Maulina and Iriansyah, 2018) [16]. The mass loss during the pyrolysis is estimated with the loss of volatiles from the biomass (Nahiln and Williams, 2012) [17].

Activated carbon production

Dimensions of the reactor used for activated carbon production are 12 cm dia, 34 cm high, and 0.4 cm thick. The system is equipped with electric heating with a 3.5 kW coil and preheater setup for steam production. The effect of activation temperature and activation time on activated biochar yield (%) and iodine number (mg g^{-1}) are studied. Optimization is done to select the best operating conditions to obtain maximum iodine adsorption. In physical activation process, the palmyra seed shell is carbonized to produce biochar under an oxygen-free atmosphere. The resulted biochar was subjected to partial and controlled gasification by physical agents such as steam at high temperatures usually between 600 to 1000 °C. The char material of 100 g is fed into the reactor column where it is heated by the surrounding coil. When the temperature reaches the required activation temperature (600 to 1000 °C), steam is supplied (produced at a water flow of 2 ml min^{-1}) along with nitrogen subsequently. After the activation time (30 to 90 min), the steam flow is arrested and the reactor temperature is set to room temperature to cool under nitrogen flow. The yield of activated carbon at different temperature is represented in Table 1.

Table 1: Activated carbon yield at various reaction conditions

Temperature, (°C)	Time, (min)	Yield, (%)
600	30	28.9
	60	32.8
	90	28.0
700	30	26.3
	60	27.5
	90	26.4
800	30	29.6
	60	31.2
	90	26.4
900	30	21.2
	60	20.2
	90	19.8
1000	30	8.3
	60	6.7
	90	9.5

The optimized temperature is found to be 800 °C. 25 g of activated carbon produced at the optimized conditions is impregnated with 25 g of KOH and 250 ml of distilled water in the same proportion. Accordingly, the same amount of sample is also impregnated with the ratio of KOH as 1:1, 1:2, and 1:3 and the activated carbon yield is found to be 22.3, 25.1 and 207% respectively. The prepared solution is kept in a magnetic stirrer for 2 h at room temperature. Then the sample is subjected to drying and washing to attain a neutral pH.

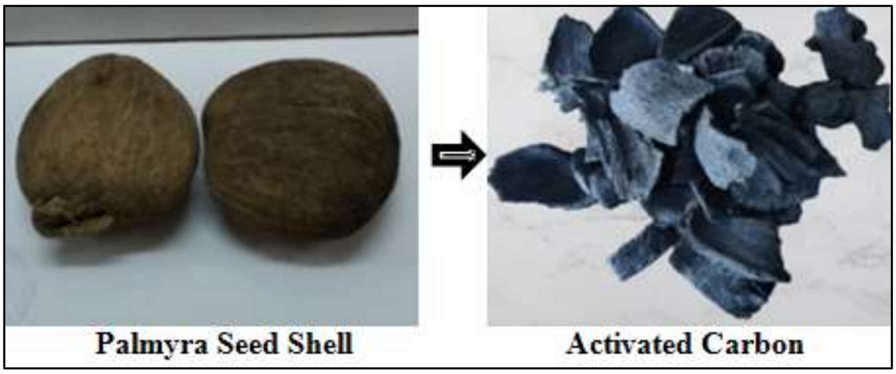

Fig 2: Activated carbon from palmyra seed sheel

Characterization of Activated carbon

Iodine number is a measure of the adsorption capability of activated carbon for low molecular weight compounds and is used for the characterization of activated carbon produced from Palmyra seed shell. The results of the iodine number at the experimental points are presented in Table 2. Iodine number varied from 254 to 840 mg g^{-1} for the activated carbon. At lower temperatures (<900 °C) and lower activation time (60 min), the iodine number is increased with temperature and time (Ogungbenro *et al*. (2017) [18]. This could potentially be due to the removal of volatiles and tar by oxidation reactions by steam. Steam activation enhanced the surface carbon burn-off at higher activation temperatures, leading to the development of micropores. Higher value of iodine number 840 mg g^{-1} is obtained at 800 °C with 60 min.activation time. At the higher temperature range (900 to 1000 °C), the quality of the activated carbon is deteriorated. This might be due to the collapse of micropores, which became more significant than the rate of increase at higher temperatures, resulting in the reduction of the iodine number (Peredo-Mancilla *et al*. (2018) [19].

Table 2: Iodine number of activated carbon produced through physical activation

Temperature (°C)	Time (min)	Iodine Number (mg. g^{-1})
600	30	254
	60	428
	90	498
700	30	356
	60	428
	90	549
800	30	752
	60	840
	90	798
900	30	528
	60	675
	90	790
1000	30	487
	60	465
	90	320

The activated carbon produced through chemical activation is also characterized for iodine adsorption and the results are depicted in Table 3.

Table 3: Iodine number of activated carbon produced through sequential physical and chemical activation

Impregnated ratio	Temperature (°C)	Time (min)	Iodine number (mg g^{-1})
1:1	800	60	487
1:2	800	60	948
1:3	800	60	152

From the above results, it is found that the maximum iodine number is obtained at the ratio of 1:2 at the activation temperature and activation time of 800 °C and 60 minutes.

Conclusion

Palmyra shell pyrolyzed at 700 °C at a residence time of 2 h with a nitrogen flow of 200 ml min^{-1} is used as a precursor for activated carbon synthesis. From the characterization of biochar, it is found that the volatile matter and ash content ranged from 7.48 to 7.56% and 13.4 to 14.6%. The fixed carbon varied from 79.2 to 79.04%. It is estimated that the fixed carbon of biochar is enriched in comparison with the biomass. The mass loss during the pyrolysis is estimated with the loss of volatiles from the biomass. The charred material is fed into the reactor column and heated until the temperature reaches the required activation temperature (600 to 1000 °C). Then steam is supplied (produced at a water flow of 2 ml min^{-1}) along with nitrogen subsequently. After the activation time (30 to 90 min), the steam flow is arrested and the reactor temperature is set to room temperature to cool under nitrogen flow. The produced activated carbon from the Palmyra shell is characterized by Iodine adsorption. For activated carbon from palmyra seed shell, higher value of iodine number 840 mg g^{-1} is obtained at 800 °C with 60 min.activation time. The Palmyra seed shell biochar sample was chemically treated with KOH and distilled water at different impregnate ratios. The impregnated biochar samples are activated at 800 °C with an activation time of 60 min. The obtained activated carbon is characterized for its iodine adsorption. The maximum iodine number is obtained at the ratio of 1:2 at the activation temperature and activation time of 800 °C and 60 min. Activated carbon produced from agricultural biomass is cost-effective as it is easily available. It can also be easily produced by the combination of physical and chemical activation. The production of activated carbon agricultural biomass can greatly reduce the production of activated carbon from non-renewable resources.

Future Perspective

Activated carbon can also be tested for cleaning gases like biogas, producer gas, and flue gases through adsorption (Song *et al*. (2018) [20]. Apart from adsorption studies, this activated carbon can also be used as a replacement for energy storage materials (Lu *et al*. (2022) [21]. The regeneration studies of activated carbon can also be studied for a detailed understanding of thermodynamic principles and cycles for reusing it for continuous operation.

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