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Preparation of Activated Carbon from Acacia (*Vachellia seyal*) Tree Branches and Application to Treat Wastewater Containing Methylene Blue Dye

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Abstract

Saudi Arabian desert tree Acacia (Vachellia Seyal) used to produce Activated Carbon (AC) by phosphoric acid mediated chemical activation at low temperature. Characterization of AC done based on proximate and detailed analysis including Moisture content, Total Ash content, pH value, Iodine number, Methylene blue number, pore volume and BET surface area. Results revealed that properties of produced activated carbon (PAC) are comparable to commercial activated carbon (CAC). Low ash content and hardness making it suitable for water and wastewater treatment. Cost of production found to be less than \$0.5/kg. Both AC used to treat wastewater containing Methylene Blue (MB) dye. Initially the removal efficiency of CAC is higher than the PAC however, both AC reached to similar removal (95.3% for PAC and 98.2% for CAC) within one hour. Growing demand of AC in the country can be meet by producing low cost locally available waste materials *Acacia seyal* tree branches.

Keywords: activated carbon, *acacia seyal*, phosphoric acid activation, removal efficiency, MB dye uptake capacity

1. Introduction

Due to high degree of porosity, typically one gram of activated carbon (AC) has a surface area in access of 500 m^2 (Yang et al., 2010). Some researchers also reported the BET surface area from 1494 to 1581 m^2/g which makes it a favorite candidate as an adsorbent (Ahmed et al., 2015). Recently some researchers achieved surface area up to 2939 m^2/g by additional activation with potassium hydroxide (Buczek, 2016).

At present AC is the most extensively used adsorbent in the industries as well as for domestic applications capable of treating diverse type of effluents (Joshi, 2016). Saudi Arabia is one of the countries having wide range industrial setup and AC is being used in various industries such as power, chemical, paper, pharmaceutical, fertilizer, and textile industries. In order to meet the country's demand a substantial amount of foreign exchange spent to import AC. It is reported that during year 1995 to year 2002 about 6507 tons of AC was imported into the Kingdom and spent more than \$23.1 million as foreign exchange (Essa et al., 2004). The high cost of AC has stimulating effect in assessing the feasibility of using cheaper raw materials. In order to cope with the huge requirement, AC should be prepared using locally available raw materials and cost effective production technique. Use of waste material could be an additional benefit (Rehman, 2008). Desert plant Acacia considered as a waste material and available abundantly in many regions of country (Aref et al., 2003). Production of AC from this material seems to be financially more viable since using grain or coal as raw materials for AC will require manufacturers extra amount of money for procurement. Furthermore, carbon produced from this tree is harder and more resistant to attrition (Gratuito et al., 2008). Although there are many studies in the literature relating the preparation and characterization of AC from carbonaceous materials however, there is limited information for the preparation of the AC using Acacia seyal tree branches as the precursor material. The conversion of Acacia seyal tree branches to ACs offers significant potentials for reducing the cost and the environmental damage resulting from decay and disposal of these residues (Shivayogimath et al., 2014).

AC can be produce by physical activation and/or chemical activation. Physical activation is a two steps method in which a raw material is first carbonized and then activated by steam, carbon dioxide, air or their mixtures. The carbonization temperature range between 400 and 1000°C; and activation temperature range between 600 and 900°C (Shoaib and Al-Swaidan, 2016). In the chemical activation the carbonization and activation steps are carried out simultaneously. A raw material is impregnated with a chemical activating agent and heat-treated under inert atmosphere (Li et al., 2016). Phosphoric acid activation of lignocellulosic materials has become an increasingly used method for the large-scale manufacture of ACs in the last 20 years because phosphoric acid activation has environmental benefits and several other advantages, such as ease of recovery as compared to zinc chloride activation, low energy cost, and high char yield (Lim et al., 2010). Thus, investigations have been extensively conducted to elucidate the mechanism of phosphoric acid activation (Olawale at al., 2016; Zuo et al., 2009). Since the surface characteristic and internal pore structure of the AC play an important role in adsorption processes and depend both on the precursor used and the method of preparation, therefore, characterization of these are crucial to the adsorption and separation processes (Anisuzzaman et al., 2015).

2. Materials and Method

In the present study after selection of precursor material Acacia seyal tree branches detailed experimental work performed to 1) produce AC using phosphoric acid mediated chemical activation, 2) characterize the produced AC and 3) find adsorption capacity of PAC and compare with the available CAC (Filtrasorb ®-400) obtained from Calgon Carbon Corporation, Pennsylvania, 15205 USA.

2.1 Production of Activated Carbon

Acacia seyal tree branches were collected from costal area of Jubail Industrial city. Material was thoroughly washed with hot distilled water to remove impurities and dried in an oven at 120 ± 5 °C for 24 hours. Dried pieces were than chopped in pieces using a chopper/cutting mill. The final particle size of the material achieved was 0.4 to 0.5 mm.

Chemical activation with phosphoric acid was used to produce AC as it is relatively easy and does not require skilled and trained personnel. Method requires less heat and it has less complex operating conditions as compared to physical or steam activation techniques and a simple laboratory set up is sufficient. One kilogram of the prepared precursor material was mixed with 40% V/V phosphoric acid having actual concentration of 85.5 wt% (Rehman, 2008). A slurry was formed which was left overnight in the oven at 120 ± 5 °C. After 24 hours slurry was transferred into specially fabricated stainless steel hollow cylinders having 50 mm dia and 140 mm length. Two narrow ports of 4 mm diameter (for flue gases exhaust) and two removable end caps were provided at both ends of each tube. After preparation cylinders were placed inside a muffle furnace and were heated at a slow rate, to allow free evolution of volatiles up to a hold temperature of 600°C. Soaked material was kept at final temperature for 2 hours. Later cooled material was repeatedly washed with hot water until the washings showed pH > 6.5; the washed sample was then again dried at 120 ± 5 °C for 2 hours and kept in air-tight bottles ready for characterization and use. The percentage yield of PAC was found to be 62.7%.

2.2 Characterization and Application of PAC to Remove MB Dye from Wastewater

In order to characterize PAC as a first step elemental analysis of selected precursor material was done. Characterization of PAC was done on the basis of proximate and detailed analysis by adopting the standard procedures (Schaeffer, 2002). The specific surface area, pore volume, iodine number (ASTM D4607-94), bulk density (ASTM D2395), volatile matter content (ASTM D5832-98), moisture content (ASTM D4933-99, 2010), pH value (ASTM D3838-05), hardness (ASTM D3802, using Gilson SS-30 Ro-Tap Sieve Shaker), and ash content (ASTM D2866-94, 2004) were determined. Surface area of the AC was characterized by a physical technique involving nitrogen adsorption at 195.6ºC (Brunauer–Emmett–Teller, BET surface area).The total pore volume was determined from the amount of liquid N2 held at $P/P_o = 0.98$. Freshly boiled water was digested with the dried carbon and the pH was determined for the clear solution using a pH meter. Bulk densities for the 0.4-0.5 mm particle size material were also determined. All the results of characterization analysis are discussed in the next section.

As methylene Blue (MB) dye is one of the common dye in the textile effluent removal of MB dye from synthetic wastewater was tested by using PAC (Shah et al., 2016; Li et al., 2016). During adsorption study stock solution of MB by dissolving 100 mg in one liter of distilled water was prepared and consequently various dilutions were prepared according to need.

The efficiency of MB dye (E) removal from synthetic wastewater was investigated using following relationship (Kamil et al., 2014).

$$E = (C_0 - C_f)/C_0 \times 100 \quad (1)$$

Where, C_0 is the initial concentration of MB dye and C_f is the concentration of MB dye in aqueous phase by the end of study time. Same procedure was repeated with the CAC (Filtrasorb ®-400) to make comparative study.

2.3 Adsorption Capacity of the PAC

In order to check the adsorption capacity of PAC and simulate treatment of textile wastewater synthetic textile wastewater containing Methylene Blue (MB) dye was used. A stock solution of MB (40 mg/l) was prepared and dispensed in two sets of 100-ml bottles. Each bottle containing 5 gm of respective AC (PAC and CAC). These stoppered bottles were placed in a mechanical shaker and left to equilibrate for a period of 48 hours. At the end of equilibration period mixture was centrifuges three times to separate the small AC particles. Samples were withdrawn from each bottle, filtered through 0.45 µm filter (Millipore), and analyzed for the MB residual concentrations using the UV-spectrophotometer, Shimadzu UV-160IPC at a wavelength of 664 nm. A calibration curve (Absorbance vs concentration) was prepared by using standard MB solutions between 10 to 50 mg/l. In order to compare the adsorption capacity of PAC samples of CAC (Filtrasorb ®-400) was also used in parallel and adsorption capacity of both AC was determined.

3. Results and Discussion

Details of the results obtained in the present study along with discussion on results presented in the following sections.

3.1 ***Production of Activated Carbon***

Generally, to prepare a good quality AC the precursor materials selected as it has higher carbon content with low sulfur and ash content (Sánchez-Polo et al., 2006). A comparison of elemental analysis results of Acacia seyal tree branches with values reported in the literature is presented in table 1. Result shows that Acacia seyal tree wood has higher carbon content which is a favorable component to produce good quality AC (Shivayogimath et al., 2014). Other elements such as nitrogen, hydrogen and oxygen are similar to the composition of Acacia nilotica and pine bark reported in literature for production of AC. Furthermore, sulfur content is only 0.03 % which is making this precursor material more environmental friendly to use (Shahid, 2011). Hence, results shows that Acacia seyal tree branches are suitable precursor material to produce good quality AC.

Table 1. Comparison of elemental analysis results of precursor *Acacia seyal* tree branches with values reported in literature

Constituent (%)	Acacia seyal	[1]Shisham wood	[2]Acacia nilotica	[3]Pine Bark
C	51.3	41.2	48	54.9
K	1.82	1.2	--	--
Al	0.17	0.2	--	--
N	0.33	--	0.4	0.2
H	5.8	--	6	5.8
Zn	0.01	ND	--	--
S	0.03	0.04	--	0.1
P	0.09	5.4	--	--
O	32.9	39.7	44	39.0
Ash	5.9	4.9	5.8	--

ND: Not Detected

[1] Shahid (2011)

[2] Shivayogimath et al., (2014)

[3] Ragland et al., (1991); Saarela et al., (2005

Some of the properties/characteristics of PAC with the properties of two commercially available AC (Filtrasorb ®-400 and QAC-400) and information available in literature (Shisham wood and Acacia nilotica) are presented in table 2. Results show that PAC has a comparable BET-surface area. Higher the surface area means more sites are available for adsorption and AC will has higher adsorption capacity (Buczek, 2006). BET-surface area obtained is about 80.7% of CAC (Filtrasorb ®-400) and higher than all other AC reported here. Similar trend was found in iodine number (82.7%). It shows that produced AC is a feasible adsorbent while considering the availability of raw material and cost. The value of pore volume and iodine number (4.92 m^3/g and 827) are in good agreement with values reported in literature and commercially available ACs. Furthermore, produced AC has relatively higher hardness and making it suitable for continues flow type setups. In addition to that, the low ash content of the produced AC (5.9%) is making it suitable in mixed flow/batch type of reactors. A basic cost analysis including material acquisition, chemical, labor and lab analysis cost was performed. It was found that the cost of AC produced from Acacia seyal tree branches is less than $0.5/kg. As low cost waste material will be used for AC production this strategy will results in economic production of AC and reduction in solid waste in the country.

Table 2. Comparison for the characteristics of PAC and CAC

Property	Acacia seyal	[1]Shisham wood	[2]Acacia nilotica	*Filtrasorb® 400	#QAC-400
Ball Point Hardness	91	Low	Low	High	95
Ash (%)	5.9	4.9	5.8	5-6	6
Bulk Density (g/cc)	0.3	0.23	--	0.44	0.55
Moisture Content (%)	4.2	--	4.1	--	5
pH	6.5	5.7	7.0	6.2	9-10
BET-Surface Area (m^2/g)	762	695	590	944	400
Pore Volume (m^3/g)	4.92	5.17	4.4	0.6	--
Iodine Number	827	813	480	1000	400

* Calgon Carbon Corporation, Pennsylvania, 15205 USA.

Quantum Active Carbon Pvt Limited (2016)

[1] Shahid (2011)

[2] Shivayogimath et al., (2014)

3.2 **Removal Efficiency of PAC**

Removal efficiency of PAC along with CAC (Filtrasorb ®-400) was determined by suspension of both AC in 100 ml of MB solution having concentration of 40 mg/l.

The removal efficiency of PAC and CAC with time is shown in figure 1which shows that the removal efficiency of AC can be divided in three zones initially the rate of MB dye removal is high and in second zone rate of removal is relatively low which is following by equilibrium zone showing insignificant removal. By comparing PAC with CAC, initially the uptake of CAC is higher than the PAC however, both AC reached to similar removal (95.3% for PAC and 98.2% for CAC). The impregnation of phosphoric acid before carbonization showed a good effect on the precursor material on BET surface area and porosity development which produced AC of good removal efficiency (95.3%).

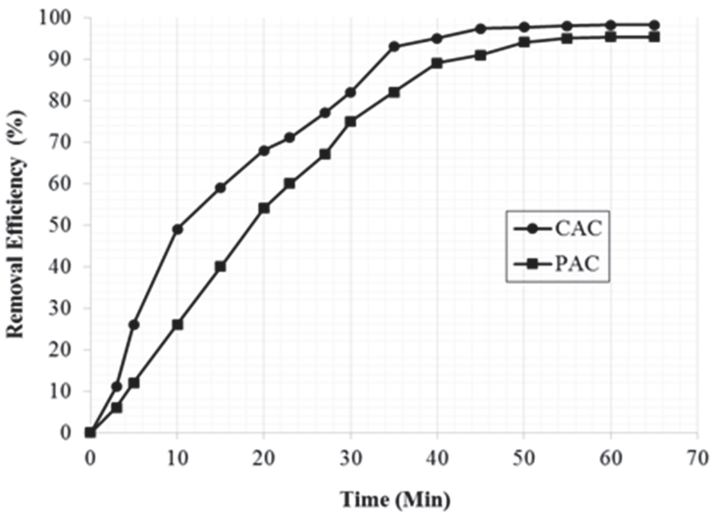

Figure 1. Comparison of removal efficiency of PAC and CAC for MB dye removal

3.3 MB Dye Uptake Capacity of PAC

MB dye uptake capacity of PAC and CAC was studied by following the adsorption of MB from aqueous solution. Study shows that the MB uptake capacity for PAC and CAC are 194.3 mg/g and 241.3 mg/g respectively.

It means that the adsorption capacity of PAC is about 80.52% of CAC. This value is comparable to the BET-Surface area value which is about 80.7% of CAC. This shows a relationship between BET-Surface area and the adsorption capacity of AC. Furthermore, the pore volume of PAC is 4.92 m^3/g while for CAC (Filtrasorb ®-400) is only 0.6 m^3/g which means that the adsorption capacity is not only controlled by pore volume and dominating factor for PAC is BET-Surface area. This result is in contrast of Hussein et al., findings which is reporting the dependency of adsorption capacity mainly on the pore structure and volume (Hussein et al., 2015). This difference may be attributed to the difference in the precursor material as they used date palm in their study and AC from date palm may has dependency on pore volume due to different pore structure of said material (Saleem et al., 2010).

These differences in behavior necessitate the further investigation of various precursor materials for their adsorption capacities to relate them with their pore structure, pore volume and BET-Surface area.

4. Conclusions

Desert tree Acacia seyal is abundant in Saudi Arabia and tree branches are common waste material to dispose in environment friendly manner. It has potential as a precursor material to be used for the production of AC by means of chemical activation with phosphoric acid. PAC can be used to remove color dye (MB-dye) from wastewater. Following conclusions are drawn from the results of this study:

- The chemical activation of *Acacia seyal* tree branches with phosphoric acid showed that it could be a preferred method to produce low cost and good quality AC at low carbonization temperature of 600°C having adsorption capacity of 194.3 mg/g.
- AC produced from tree branches has comparable surface area (762 m^2/g) which is about 80.7% of the CAC Filtrasorb ®-400.
- Removal efficiency of PAC with time was investigated and found that initially the uptake of CAC is higher than the PAC however, both AC reached to similar removal (95.3% for PAC and 98.2% for CAC).
- Low ash content and higher hardness making it suitable for mixed flow/batch type as well as for continues flow reactors in water and wastewater treatment.
- The basic cost analysis of the PAC shows that it is a low cost adsorbent and cost is less than $0.5/kg which is far cheaper than available costly commercial ACs.
- Growing demand of AC in the country can be meet by producing low cost locally available waste materials such as Acacia seyal tree branches. This strategy will not only provide the low cost AC but also help in reducing worth less solid waste.

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