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Full Length Research Paper

Preparation of phosphoric acid activated carbons from *Canarium Schweinfurthii* Nutshell and its role in methylene blue adsorption

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Activated carbons were prepared by phosphoric acid activation of *Canarium Schweinfurthii* spent nutshell. The activation conditions for particles with average diameter of 2.36 mm, conducted in nitrogen chamber, were evaluated at 40 and 60% acid concentration, substrate/activating agent (impregnation) ratio of 1:1 to 1:4, activation time of 20 to 60 min and temperatures of 200 and 400°C. The results showed that the yield, BET surface area and adsorption capacities of activated carbon produced increased with impregnation ratio, activation time and temperatures. The activated carbon obtained using 1:4 impregnation ratios at 60 min with 40 wt% acid solution have BET surface area and adsorption capacity of 741 m^2/g and 8.5 gMB/g Carbon while those for 60wt% acid solution were determined as 779 m^2/g and 9.2 gMB/g Carbon, respectively.

Key words: *Canarium schweinfurthii*, activated carbon, phosphoric acid, methylene blue, impregnation ratio, dyes.

INTRODUCTION

Paper, dyeing, plastic, and textile industries use dyes for coloring their products. These industries generate large quantity of waste water containing residual dyes, which are often discharged to the environment with or without treatment (Ehrampoush et al., 2011; Sreedhar and Kotaiah, 2006). There are over 100,000 types of dyes with more than 7×10^5 tons produced annually (Wang et al., 2008). About 2% of dyes produced are discharged in effluent during production, while 10 to 20% remains in textile wastewater (Espulgas et al., 2002; Gregorio, 2006). The release of dyes into waters causes immediate visible pollution aside from contamination due to its organic and toxic nature. The presence of these dyes is objectionable because it interferes with light penetration and therefore reduces photosynthetic activity (Weisburger, 2002). Dyes are not readily biodegradable

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and their removal from wastewater often involves processes such as floatation, chemical oxidation, precipitation, filtration, electrocoagulation, ozonation and photocatalytic. These processes have found industrial applications in meeting the more stringent legislation regarding maximum allowable dye concentration in discharge wastewater (Wang et al., 2008; Bestani et al., 2008).

Activated carbon adsorption is a process that is widely used for removal of waste from effluents. This application relies on the large surface area of the adsorbent, with its micro-porous structure, resulting in high adsorption capacity. The operation is generally simple to implement and gives high removal efficiency (Ramakrishna and Viraraghavan, 1997; Meyer et al., 1992; Natos et al., 2010). Kant (2012), Kanawade and Gaikwad (2011) and Rahman et al. (2012) identified the negative effects of methylene blue on our environment and proposes application activated carbon as adsorbent.

Canarium schweinfurthii is a perennial plant, with oil bearing seeds, which is available abundantly in Nigeria and other parts of the tropics. Its spent nutshell generates a lot of waste that could serve as a reliable feedstock to obtain carbons with good adsorptive properties. Conversion of nutshell from *C. schweinfurthii* to activated carbon would have dual advantages of producing a low cost adsorbent material for environmental protection, while at the same time eliminating the need for land filling, open burning and indiscriminate disposal (Ajayi and Olawale, 2009).

Activated carbon is commonly produced from carbonaceous material via either thermal or chemical activation. In this work, phosphoric acid was chosen as the activating agent in view of its environmental benefits. Chemical activation with phosphoric acid not only reduces tar formation thereby increasing carbon yield (Benadjemia et al., 2011; Shaobih et al., 2005; Lim et al., 2010) it also gives the possibility of developing microporous and/or mesoporous carbon with high specific surface area (Jagtoyen and Derbyshire, 1998).

Accordingly the aim of this work is to study the ability of *C. Schweinfurthii* to serve as a precursor for an effective activated carbon for methylene blue adsorption. The size of methylene blue, would serves as a good probe for the efficiency of the activated carbon developed. (Pelekani and Snoeyink, 2000).The effect of impregnation ratio, activation temperature and time on the characteristic properties of activated carbon developed was also studied.

EXPERIMENTAL

Materials

C. schweinfurthii nutshell was washed with water and then dried in oven at 60°C for 12 h. The seeds were removed from the *C. schweinfurthii* fruit to make the nutshell oil free (Olawale, 2012). The nutshell was then washed repeatedly with water and dried at 110°C for 12 h. The dried nutshell was crushed and sieved to obtain particle size fraction of 2.0 to 2.36 mm, which were later stored in air tight container awaiting further use.

Preparation of activated carbon

Specified mass of the dried nutshell particles were soaked in 100 ml H_3PO_4 solution (40 and 60% concentration) to get the required impregnation ratios of *C. schweinfurthii* nutshell: H_3PO_4 of 1:1, 1:2 and 1:4. Impregnation ratio is defined as the ratio of the weight of precursor, that is, weight of dried crushed *C. schweinfurthii* nutshell to the weight of H_3PO_4. The liquid/solid mixture was stirred continuously at ambient temperature for 2 h and left to soak for 12 h to allow penetration of the H_3PO_4 into the *C. schweinfurthii* nutshell (Montane and Torne-Fernandez, 2005). After the stipulated soaking time, the slurry was oven dried at 110°C for 24 h, so as to achieve adsorption of the H_3PO_4 on to the *C. schweinfurthii* nutshell.

The activation temperature and time for this work was fixed at the lowest possible value, supported by the reported work of Gratuito et al. (2008) and Srinivasakannan and Abu Bakar (2004). They both arrived at optimum activation temperature and time of 416°C and 30 min, respectively, during activation of coconut shell using phosphoric acid, which was also adopted in this work.

The activation of the dried impregnated with phosphoric acid nutshell particles was performed in a batch reactor in nitrogen atmosphere at a heating rate of 10°Cmin^{-1}, set to three different temperatures 200, 300 and 400°C for activation times of 20, 40 and 60 min at each activation temperature. Following activation, the samples were cooled in nitrogen atmosphere for 12 h. The product was washed with cold deionized water until phosphate ions were no longer detected by the lead nitrate test. The product was finally air dried at 105°C for 3 h, after which it was ground and characterized.

Characterization

The products were characterized for yield, BET surface area and adsorptive capacity. The 'yield' of the activated carbon synthesis is defined as the ratio of the mass of activated carbon (after washing and drying) to that of the dried nutshell multiplied by 100. The pH of the samples was determined by placing 1 g of the activated carbon in 20 cm^3 distilled water. The suspension was stirred for 6 h at 250 rpm, after which the clear solution was filtered and its pH was determined using Kent digital pH meter (Model 7055).

The ash, moisture and crude fiber contents and other properties for both the raw material and products were determined as described by AOAC (2010). The BET surface area was determined using water vapor adsorption method described by Adefila et al. (2003). The adsorptive capacities were obtained using methylene blue solution as probe following the method detailed by Raposo et al. (2009).

RESULTS AND DISCUSSION

Physical properties and proximate analysis of *C. scheweinfurthii* nutshell

As could be seen from Table 1, the *C. scheweinfurthii* nutshell could serve as a very good precursor for the production of activated carbon due to its very low value in

Table 1. Proximate analysis of *Canarium scheweinfurthii* nutshell.

Characteristics	Value (%)
Ash	1.16
Moisture	10.3
Crude fiber	40
Protein	2.6
Lipid	3.27
Carbohydrates	37.23

ash content (1.16%) and very high value of carbon containing constituents (88.64%).

Production yield

The carbon yield is relatively high compare to physical activation processes. This is an indication of the ability of H_3PO_4 to retain carbon and to avoid the loss of otherwise volatile materials, on one hand. On the other hand, H_3PO_4 activation promotes dehydration and redistribution of biopolymers and also favors the conversion of aliphatic to aromatic compounds, thus increasing the yield of activated carbon (Yakout and Sharaf-el-Deen, 2012). The carbon yield increases as the impregnation ratio was increase at 40 to 60% for temperatures 200 to 400°C and time varying between 20, 40 and 60 min as shown in Figures 1 and 2.

When increasing quantity of acid, it is expected that mass transfer into and within the substrate will be enhanced, leading to higher rate of reaction which manifests in the reduced yield. This observation was also reported by other researchers (Girgis and Ishak, 1999).

Specific surface area

As depicted in Figure 3, the level of activation and BET surface area increases with acid concentration and activation time at constant temperature (400°C) and impregnation ratio of 1:1, which conforms with the works of Jagtoyen and Derbyshire (1998) and Suarez-Garcia et al. (2004). Based on the result, shown in Figure 3, the activation time period was fixed at 60 min to understudy the effect of activating temperatures, acid concentration and impregnation ratio.

The trend observed in Figure 4 suggested increase in both impregnation ratios and surface area with temperature. The activation temperature was stopped at 400°C following the conclusion made by other researchers on maxima value in specific surface for temperatures ranging from 350 to 500°C for lignocelluloses materials and bituminous coal (Yakout and Sharaf-el-Deen, 2012).

Irrespective of the acid concentration (40 or 60 wt%), products with impregnation ratio of 1:4 gave surface area ranging between 500 and 800 m^2/g which agrees with the works of Girgis and Ishak (1999). Above 200°C, the difference in specific surface area for the same acid ratio was not significantly different. The H_3PO_4 reacting within the internal cellulose structure is assumed to induce a polymerization leading to an enhancement of the pore volume and thus global volume expansion, favoring formation of mesopores (Benadjemia et al., 2011).

Adsorptive capacity

The adsorption of activated carbon using methylene blue was suggested to occur on specific sites forming monolayer coverage. The higher the BET surface area of the activated carbons and impregnation ratio, the higher the adsorption capacity of methylene blue as shown in Figures 5.

The adsorption capacity was observed to increase by about 3 folds for activated carbons with impregnation ratio of 1:4 compared to those with 1:2 and 1:1. This could be explained by the fact that increased in concentrated H_3PO_4 was able to unblock and enlarge the pores of the activated carbon produced. The higher the concentration of H_3PO_4, the better the effect of pore enlargement and unblocking. The large pore volume resulted in surface accommodation of the probing material in this case methylene blue. Additionally activation temperature was seen to improve the adsorption capacity of methylene blue, testify to the role of P_2O_5 resulting from the chemical transformation of H_3PO_4 at elevated temperature.

Conclusion

The present study shows that a viable adsorbent can be prepared from *C. schweinfurthii* nutshell through phosphoric acid activation with significant yield and good surface area. *C. schweinfurthii* is a suitable agro-waste precursor due to its abundance in Nigeria and its present disposal approach is not environmental friendly. The yield, though not strongly influenced by the acid strength has been found to vary between 40 and 60% depending on impregnation ratio and activation temperature. The BET surface area of about 800 m^2/g was obtained at the highest condition of treatment. The adsorption capacity was also found to increase with impregnation time and temperature which peaks at about 8 g of activated carbon per mg of MB.

Conflict of Interest

The authors have not declared any conflict of interest.

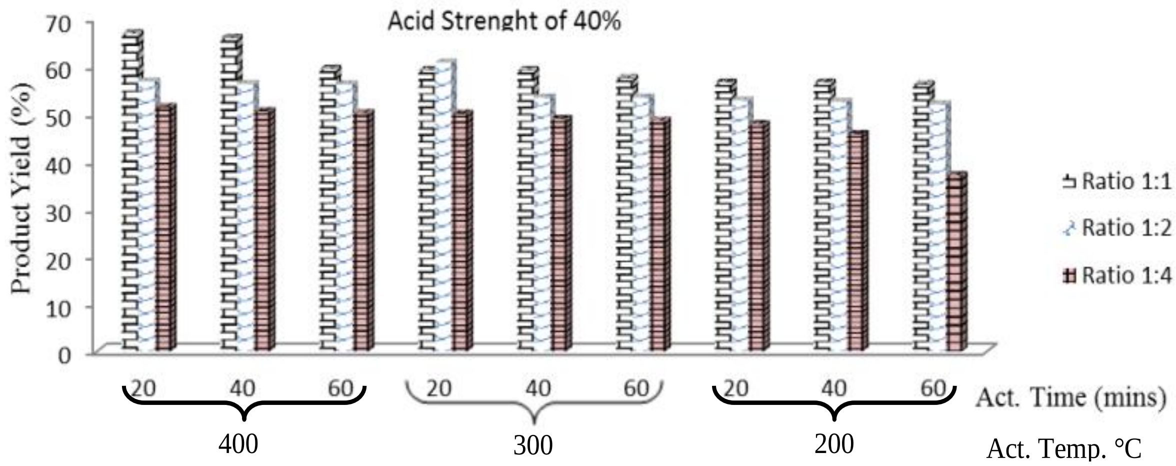

Figure 1. Product yield as a function of activation time, temperature and impregnation ratio for 40% H_3PO_4.

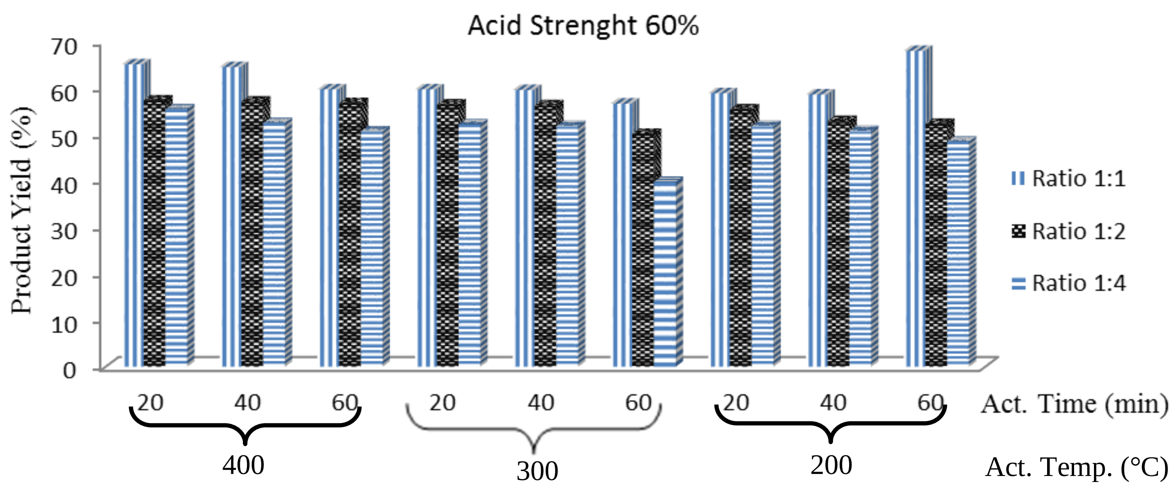

Figure 2. Product yield as a function of activation time, temperature and impregnation ratio for 60% H_3PO_4.

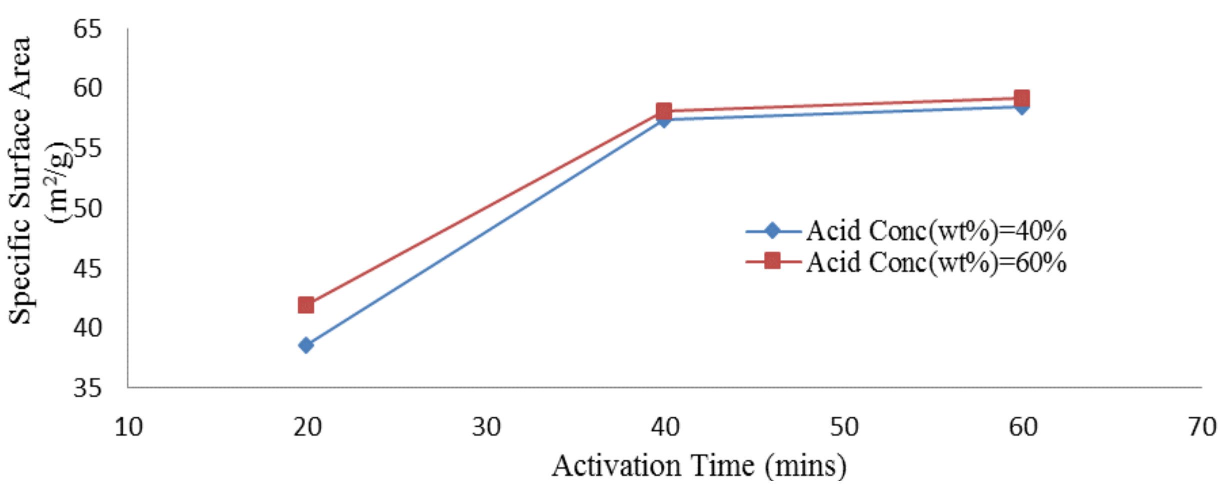

Figure 3. BET surface area as a function acid strength and activation time at 400°C for 1:1 ratio.

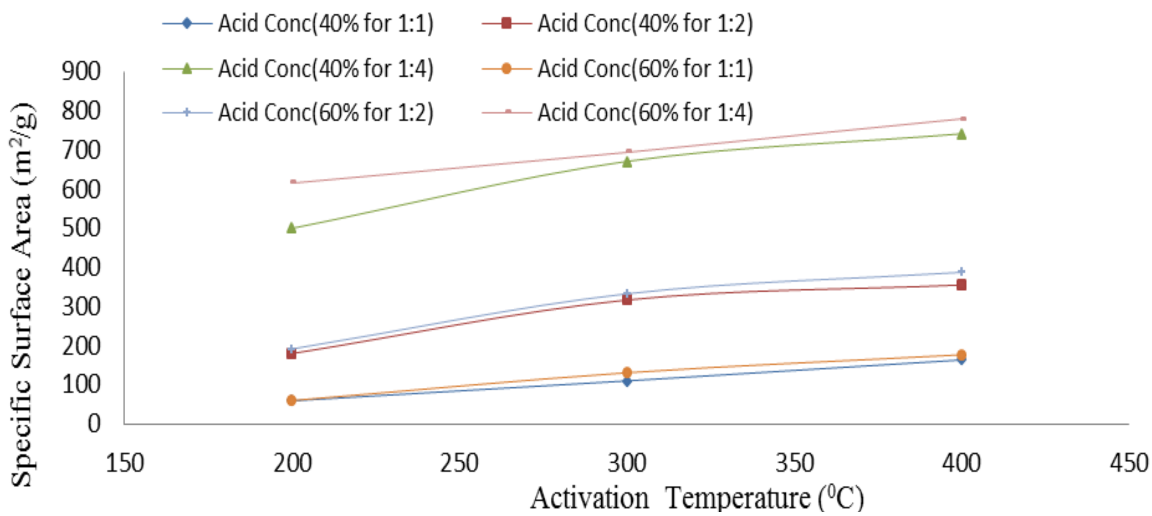

Figure 4. BET surface area as function of acid concentration, temperature at 60 min reaction time.

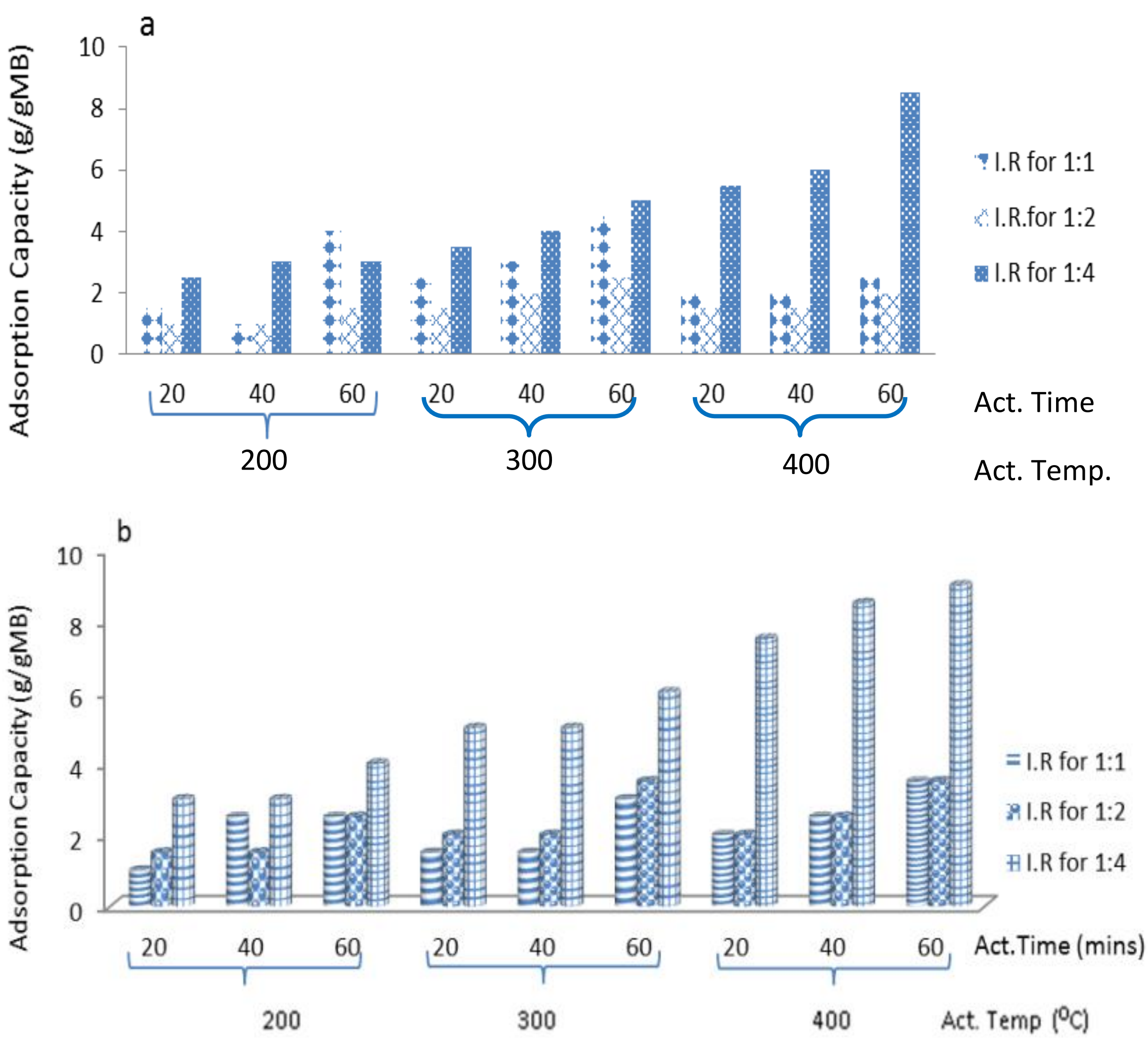

Figure 5. Adsorptive capacity of methylene blue as a function of impregnation ratio, activation time and temperature at acid strength of 40% (a) and 60% (b).

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