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Roles of Impregnation Ratio of K_2CO_3 and NaOH in Chemical Activation of Palm Kernel Shell

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Abstract

The present work was aimed to evaluate the effectiveness of two activating agents, namely potassium carbonate (K_2CO_3) and sodium hydroxide (NaOH) in the chemical activation of palm kernel shell (PKS). The adsorbents were prepared by dried impregnation at different solid mass ratios of activating agent to precursor, followed by thermal treatment at 500°C for 2 h. The adsorbents were characterized for specific surface area, carbon content, ash content and surface functional groups. Results show that the specific surface of K_2CO_3-activated samples are in the range of 5.3 to 53 m^2/g, while that of NaOH-activated samples are between 145 and 458 m^2/g. The removal of methylene blue is in accordance with the development of surface area of adsorbents, with the maximum capacity between 7.8 and 69 mg/g, and fitted well with the Langmuir isotherm. The findings conclude that, under the thermal conditions studied, NaOH is better than K_2CO_3 in the chemical activation of PKS.

Keywords: *Activated carbon, Chemical activation, Palm kernel shell, Potassium carbonate, Sodium hydroxide.*

1. Introduction

Water pollution due to human and industrial activities has become a threat to the ecosystem. Textiles, fabrics and other related industries eventually produce over 700,000 tons of dyes wastewater every year. The presence of dyes in water prevents sunlight from penetrating into the stream, thus hindering the aquatic plants to carry out photosynthesis. Also, a prolong exposure to dyes exceeding the concentration limits can cause harmful effects to the aquatic creatures and human [1].

Technologies for dye removal from wastewater include photochemical and biological degradation, chemical oxidation, coagulation, reverse osmosis and floatation [1]. In general, these treatment strategies are not sustainable because of the production of sludge that requires special handling and disposal. Furthermore, the equipment and facilities involved are expensive and require regular maintenance. On the other hand, adsorption by activated carbon has been a preferable method for dyes removal because of the stability and efficiency of the adsorbent, and the simplicity in the process, design and scale-up [2]. However, the commercial activated carbons produced from coal and petroleum pitch are expensive because the precursors are non-renewable. Moreover, the regeneration

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of spent activated carbon is difficult to restore its pristine properties, and often yields a poor performance for successive use. Therefore, the quest for abundantly available and low-cost precursors mainly from the agricultural by-products has continue to become a topic of interest. In Malaysian context, a promising candidate of activated carbon precursor is palm kernel shell [3,4].

Palm kernel shell-based adsorbents can be prepared by simple chemical treatment, impregnation, carbonization, and physical and/or chemical activation, and have been extensively studied for different types of model pollutants [3-8]. However, water pollutants normally exhibit dissimilar selectivity and affinity of removal, particularly due to the nature of precursor and resultant adsorbent, activating agents and chemicals used in the treatment, and the physicochemical properties of the adsorbate molecules [3,4]. In general, the inherent properties of the adsorbent such as specific surface area, textural properties and surface chemistry exhibit the dominating roles in the adsorption. Yet, it should be noted that the adsorption may not necessarily obeyed these rules [9]. Hence, it is a challenging task to synthesize the adsorbent that performs well for specific water pollutants. To narrow down the gap in the body of knowledge, the present work was aimed at evaluating two chemical agents, namely potassium carbonate (K_2CO_3) and sodium hydroxide (NaOH) in the chemical activation of palm kernel shell. The resultant adsorbents/activated carbons were characterized according to specific surface area, surface chemistry, carbon content and ash content, and methylene blue dye was used as pollutant probe to evaluate the removal capacity of the adsorbents.

2. Materials and Methods

Palm kernel shell (PKS) was obtained from a palm oil factory at Taib Andak in the Johor state of Malaysia. NaOH and K_2CO_3 (activating agents) and hydrochloric acid (HCl) are of analytical-grade reagents, and were supplied by QReC (Malaysia). PKS was washed with distilled water and dried in an oven at 110°C for 24 h. Then, it was ground and sieved to a size of 500 μm. Twenty grams of PKS was mixed with different solid mass ratios (activating agent to precursor) of 1.0, 1.5 and 2.0 for NaOH, and 0.75, 1.25 and 1.75 for K_2CO_3 [10]. The activating agent was dissolved in a beaker containing 200 mL water, and the solid-electrolyte solution mixture was stirred at 90°C for 50 min. After that, the mixture was dried in an oven at 110°C for 24 h for impregnation. Then, the impregnated sample was added in a crucible, by which the crucible opening was wrapped with aluminium foil to limit the contact with air before being subjected to activation in a muffle furnace at 500°C for 2 h. The resultant adsorbents/activated carbons were washed with 0.9 M HCl and then rinsed thoroughly with distilled water to a constant pH. The palm kernel shell char was obtained through pyrolysis of PKS alone at the same heating conditions. The samples were designated as PKS-C, AC-PKSK*x* and AC-PKSN*y* for char, potassium carbonate-activated samples and sodium hydroxide-activated samples, respectively, and x and y represent the impregnation ratio for K_2CO_3 and NaOH activation, respectively.

Moisture content is the percentage of free water in the sample, and was calculated as $(w_i\text{-}w_d) \times 100/w_d$, where w_i (g) is the initial mass of sample, and w_d (g) is the mass of sample after oven-dried at 110°C for 24 h. Ash content is the amount of leftover or minerals when the volatiles and organic matters are liberated from the sample at 800°C for 2 h, and was calculated as $w_f \times 100/ w_d$, where w_f (g) is the mass of ash. Carbon content of the materials was estimated using EDX (X-MaxN 50 mm^2, Oxford Instrument). Fourier transform infrared spectroscopy combined with attenuated total reflectance technique (IRTracer-100, Shimadzu) was used to determine the surface functional groups. Thermogravimetric analysis (TGA) was performed for thermal decomposition profile of PKS. The heating was done under N_2 flow at a heating rate of 10 °C/min from 25°C to 950°C using a TGA4000 (Perkin Elmer). The specific surface area of adsorbents was determined using a Pulse ChemiSorb 2705

(Micrometrics) at a liquid N_2 temperature of 77 K. The surface area was calculated using a single-point Brunauer-Emmett-Teller (BET) method.

Methylene blue (MB) dye was used to evaluate the adsorptive performance of adsorbent. Batch adsorption (bottle-point-technique) was carried out at different initial concentrations of dye solution between 5 mg/L and 300 mg/L. Fifty milligrams of adsorbent was brought into intimate contact with 30 mL of methylene blue solution of varying concentrations. The mixture was allowed to equilibrate on orbital shaker for 72 h at 120 rpm. The residual concentration was measured using a spectrophotometer (Dynamica Halo Vis-10) at a wavelength of 615 nm. Equilibrium uptake, q_e (mg/g) was calculated as, $q_e = (C_o - C_e) \times V/m$ where C_o and C_e (mg/L) are the initial and equilibrium concentrations, respectively, V (mL) is the volume of methylene blue dye solution and m (g) is the mass of dry adsorbent.

3. Results and Discussion

3.1. Characteristics of Materials

Figure 1 shows the thermal analysis of PKS. The peak at temperature lower than 100°C indicates the loss of moisture, while peaks at 250°C and 350°C might be due to the oxidation of chemical functional groups and the degradation of volatile matters [11]. From Figure 1, it is suggested that temperatures ranging from 400°C to 500°C is sufficient for carbonization and activation of PKS because of stable derivative weight loss and about 75% weight loss. However, the interplay amongst the types of activating agent and impregnation ratio with PKS also determine the development of porous structure of the activated carbon produced.

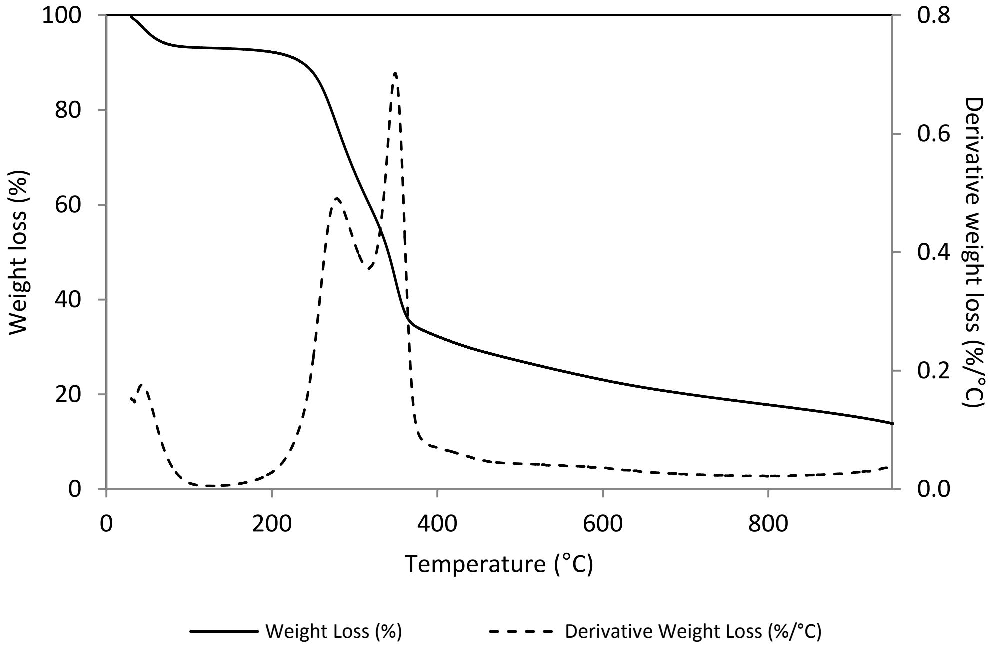

Figure 1. Thermogravimetric analysis of palm kernel shell.

Table 1 shows the characteristics of activated samples derived from palm kernel shell (PKS) using K_2CO_3 and NaOH. AC-PKSN series has the highest moisture content followed by AC-PKSK series and PKS-C. The moisture content of activated carbons increased with increasing impregnation ratio of K_2CO_3 and NaOH. This could be due to the hygroscopic nature of the leftover activating agents (minerals) intercalated with the material matrix that have the ability to absorb moisture from the surrounding. NaOH-activated carbons (AC-PKSN series) showed a higher moisture content compared to K_2CO_3-activated carbons (AC-PKSK series) due to a greater specific surface area of the former. The bigger the pore volume, the more the water vapour that can be readily and physically adsorbed by the activated carbon.

Table 1. Characteristics of activated carbons derived from palm kernel shell

Sample	Moisture content (%)	Ash content (%)	[a] Carbon content (%)	Yield (%)	[b] Surface area (m^2/g)
PKS	5.64	19.6	60.5	-	-
PKS-C	0.36	15.3	84.3	26.0	69.4
AC-PKSK0.75	2.92	12.1	88.2	18.5	5.29
AC-PKSK1.25	3.6	8.41	88.5	21.1	53.0
AC-PKSK1.75	4.04	14.2	87.5	23.7	23.8
AC-PKSN1.0	6.07	33.8	62.2	43.6	145
AC-PKSN1.5	11.8	54.6	52.2	28.9	251
AC-PKSN2.0	17.0	73.4	31.8	20.1	458

[a] surface carbon content by EDX; [b] Single-point BET surface area

NaOH-activated carbons exhibit high ash content compared to K_2CO_3-activated carbons, PKS and PKS-C. The ash content increased as the ratio of NaOH increases. The increase of ash content is attributed to the accumulation of remaining inorganic sodium compounds of high boiling temperature (1388°C) in the material upon activation. The carbon content of K_2CO_3-activated carbons are comparable at 0.2-1.0% difference, while that of NaOH-activated carbons decreased with increasing NaOH ratio. High ash content in AC-PKSN series could be the reason for the low specific surface area of activated carbons as compared with the commercially available activated carbon (surface area = 1000 m^2/g) [12-14].

The yield of K_2CO_3-activated carbons increased as the ratio of K_2CO_3 increases, while that of AC-PKSN series decreased as the ratio of NaOH increases. Also, the carbon content of NaOH-activated carbons decreased with increasing impregnation ratio. In general, K_2CO_3 and NaOH act as dehydrating agents to eliminate the presence of water in PKS during chemical activation, hence producing tar that could clog the pores [15]. It is suggested that NaOH chaotically strips and decomposes the volatiles via oxidation for effective chemical activation, hence decreasing the carbon content. In addition, the boiling point of NaOH is higher than the activation temperature (500°C) and may remained after the activation, thus increasing the ash content and decreasing the carbon content. Nevertheless, the surface area of AC-PKSN series is proportional to the ratio of NaOH. On the other hand, the surface area of PKS-C is higher than that of AC-PKSK series. The specific surface area of K_2CO_3-activated PKS carbons are inferior even with the increase of impregnation ratio. This could be resulted from excessive burning-off due to the presence of potassium salt, that may as well widening the pores and demolish the porous textures during activation.

The FTIR spectra of PKS, char and activated samples are shown in Figure 2. PKS contains carboxylic acids (O—H, 3310 cm^{-1}), alkanes (C—H, 2910 cm^{-1}), alkenes/aromatic rings (C=C, 1580 cm^{-1}), and esters/ethers (C—O, 1031 cm^{-1}; Ar—O, 1237 cm^{-1}). The wavenumber of 3600 – 3200 cm^{-1}

is normally attributed to the moisture content. After carbonization, PKS-C displayed missing peaks of C—O stretch (1031 cm^{-1}) and alkanes stretch (C—H, 2910 cm^{-1}).

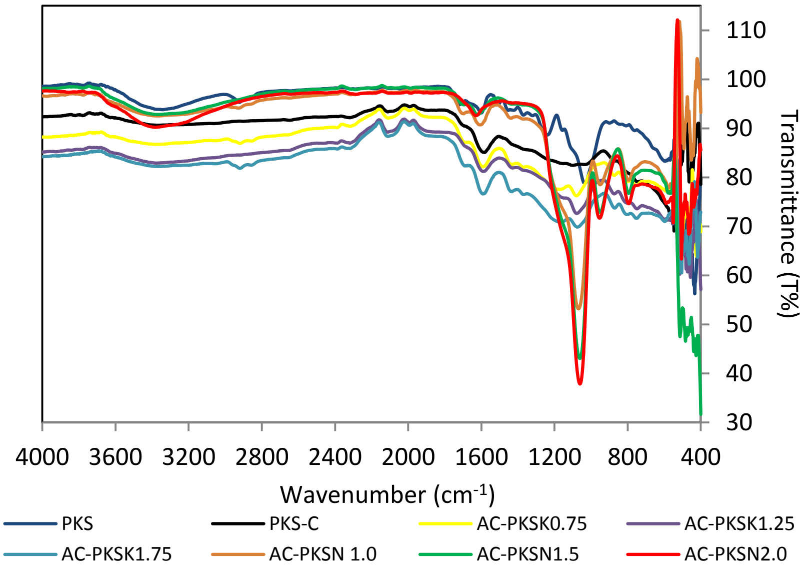

Figure 2. Functional groups of K_2CO_3- and NaOH-activated samples.

However, Alkynes (C≡C, 2081 cm^{-1}) appeared in PKS-C, and K_2CO_3-activated samples. All activated samples showed similar functional groups with varying intensities at different impregnation ratios. K_2CO_3 contributes to the presence of alkanes stretch and amine groups in the activated samples. The assignments of functional groups in AC-PKSK series are alkanes stretch (C—H), alkynes (C≡C, C—H), aromatic rings (C=C) and alcohols, carboxylic acids (C=O, O—H) and amines (C—N). Similarly, the AC-PKSN series showed similar spectra with peaks attributed to carboxylic acid (O—H, C=O), amines (C—N) and aromatics (C—H, C=C), alkynes (C≡C) and alkanes (C—H). The peaks increased intensely as the NaOH ratio increases, while C-X, C=C bending, C≡C and C—H groups diminished upon activation.

3.2. Removal of Methylene Blue

Figure 3 represents the uptake capacity of methylene blue onto adsorbents derived from PKS. In general, the adsorbents exhibit an increasing removal of methylene blue with the increase of initial concentration. The increase of concentration offers the driving force for the methylene blue molecules to overcome the adsorbent-phase mass transfer resistance, which allows more active sites to be filled [12]. This is true until the adsorption sites are fully saturated, at which no increasing methylene blue uptake would be observed with further increase in concentration.

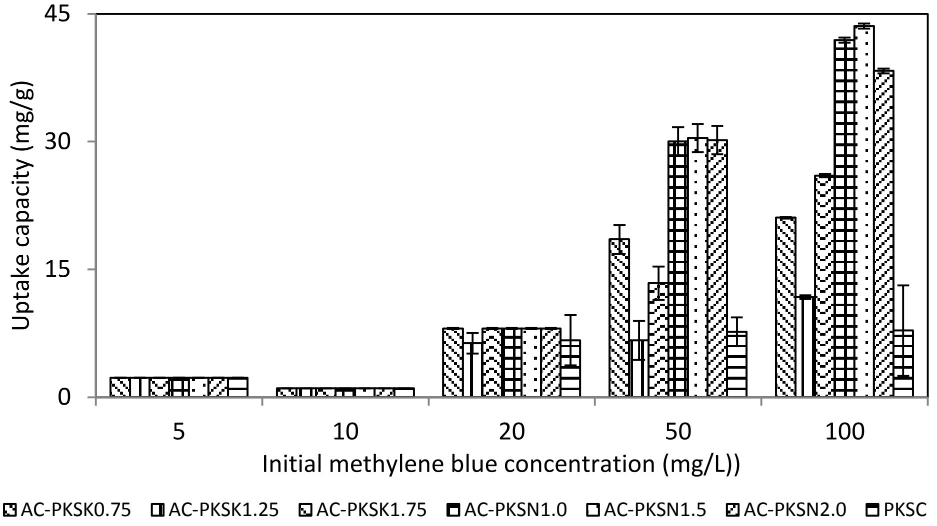

Figure 3. Methylene blue removal by palm kernel shell-based adsorbents.

From Figure 3, it can be seen that at lower initial concentrations (5 to 20 mg/L), all samples exhibit a comparable performance (nearly 100% efficiency) of methylene blue removal. However, when the initial concentration was increased to 50 and 100 mg/L, the NaOH-activated samples demonstrated superior removal capacities than the K_2CO_3-activated samples. This could be due to the abundance of active sites as a result of the high specific surface area, functional groups and ash content. Ash content of more than 25% usually reduces the surface area because of the obstruction in the pore development during activation [2,12]. Nevertheless, these inorganic components can increase the hydrophilic character of the activated carbon in the adsorption of certain target pollutants due to their possible catalytic effects [2]. The increase of surface area of NaOH-activated series as the impregnation ratio increases portrays a direct correlation between the surface area and the methylene blue adsorption by the activated carbons.

Result obviously suggests that the treatment procedures could in some way diminish the important active sites on the surface of activated carbon, thus decreasing the removal capacity. This is supported by the disappearance of functional groups and organic constituents (Figure 2) in activated carbons upon the treatment. However, a greater uptake by NaOH-activated carbons as compared to the other counterparts is possibly due to the use of NaOH that enhances the surface area and affinity for adsorption [9,16].

Figure 4 illustrates the equilibrium uptake and efficiency of methylene blue onto AC-PKSN series. The Langmuir isotherm model was used to describe the adsorptive behaviour of adsorbents, and the isotherm constants are tabulated in Table 2. The efficiency of methylene blue removal decreased as the concentration of methylene blue increased. This signifies that the activated carbons are only efficient at low methylene blue concentration. As the concentration increases, the residual concentration also increases, thus deteriorating the efficiency.

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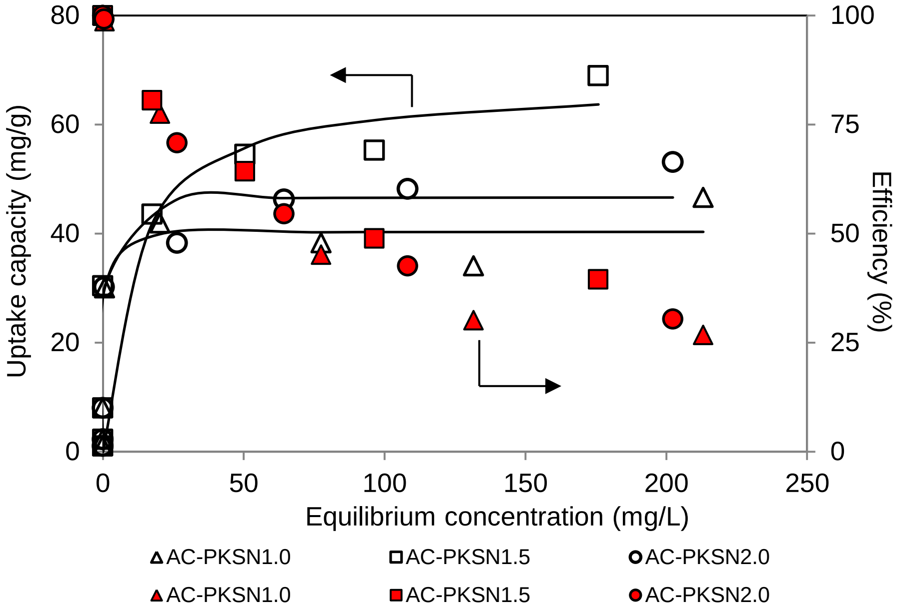

Figure 4. Equilibrium uptake of NaOH-activated palm kernel shell.

Table 2. Langmuir constants

Samples	Q_e (max)	Q_m (mg/g)	b (L/mg)	SSE	R^2
AC-PKSK0.75	21.1	22.1	0.30	71.4	0.92
AC-PKSK1.25	11.7	6.7	42.4	31.7	0.73
AC-PKSK1.75	26.0	19.8	6.97	150	0.74
AC-PKSN1.0	46.6	40.4	4.25	158	0.95
AC-PKSN1.5	69.0	67.6	0.09	1060	0.87
AC-PKSN2.0	53.1	46.7	4.22	180	0.96
PKS-C	7.82	4.66	45.3	29.6	0.96

From Figure 4, the adsorbents studied display a good removal capacity at equilibrium concentration lesser than 10 mg/L, thereafter the uptake gradually increased and levelled-off at different values. The equilibrium uptake with concave downward trend, i.e., increasing uptake with decreasing positive slope, generally indicates a favourable adsorption. The maximum equilibrium uptake of methylene blue was observed to be in the following order: AC-PKSN1.5 > AC-PKSN2.0 > AC-PKSN1.0. Table 2 shows that all samples obeyed Langmuir model as the R^2 is more than 0.85.

Figures 5 and 6 show the effects of carbon content and surface area on the maximum methylene blue uptake by activated carbons. Obviously, there is a decreasing pattern of carbon content on the uptake capacity. This probably due to the properties of the activated carbons such as moisture content, ash content, activating agents and types of the material. In other words, carbon content (probably the graphitic or aromatic structures) is not the sole factor of the material that contributes to the uptake of methylene blue.

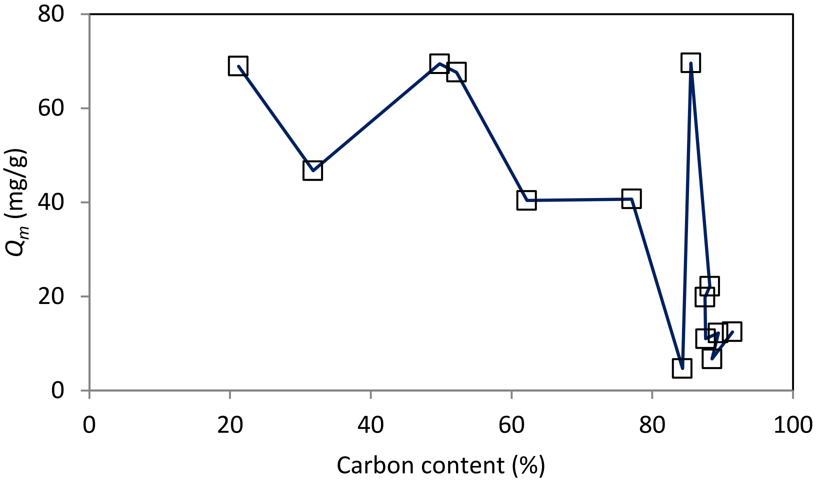

Figure 5. Relationship between sorption capacity (Q_m) and carbon content.

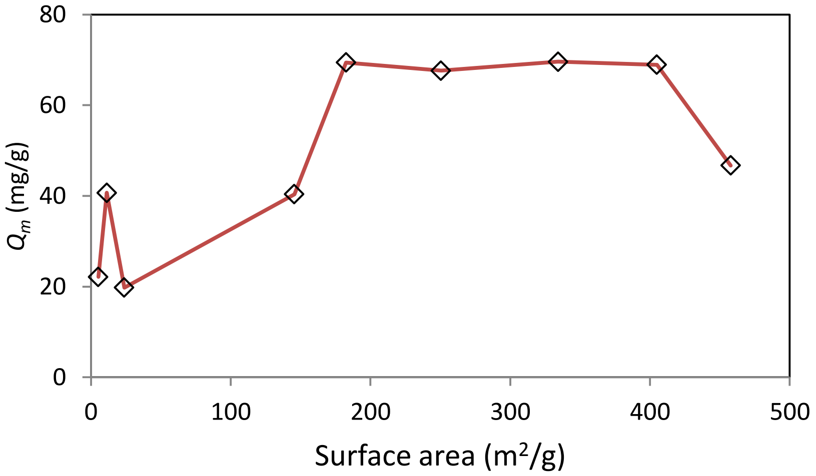

Figure 6. Relationship between sorption capacity and surface area.

It also infers that high carbon content does not necessarily mean that the surface are of activated carbon is high. In this context, char exhibit a high carbon content but poor removal of methylene blue due to the small surface area. The Q_m increases as the surface area of activated carbons increases. This is true for adsorbents synthesized in this work. Nevertheless, other possible characteristics such as ash content and types of activating agent might also influence Q_m.

4. Conclusion

Potassium carbonate and sodium hydroxide were used to activated palm kernel shell into adsorbents/activated carbons. NaOH was effective in developing the surface of PKS-based adsorbents compared to K_2CO_3. Ash-rich adsorbent with surface area of 458 m^2/g was obtained at NaOH impregnation ratio of 2.0. Carbon-rich adsorbents with small yield and low surface area were obtained from K_2CO_3 activation. The removal of methylene blue is directly related to the specific surface area of the adsorbents. However, other associating materials characteristics such as functional groups and ash content may as well enhance the removal performance of certain water pollutants.

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