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Production and characterization of activated carbon from petroleum coke

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ABSTRACT
Activated carbons (AC) were prepared from petroleum coke of Khartoum Refinery Company Delayed Coke Unit (KRC-DCU) by chemicalactivation methods with KOH as an active agent. The porous carbons were characterized by iodine value and methylene blue value, Fourier transform infrared spectroscopy and heavy metal content for petroleum cokeand AC. Two samples of porous AC obtained from KRC coke, by KOH activation with 1:4 and 1:5 (Coke: KOH) at 800 °C for 60 min. The iodine number and methylene blue values of these samples were found to be 1248 and 1242 mg g^{-1}, 43 and 51 mg g^{-1},respectively.The carbon yields of the two samples were registered to be 68 and 61%.It has been found that Coke to KOH ratio and activation time is effective for preparing high quality porous carbons

KEYWORDS: Petroleum coke activated carbon, iodine number, methylene blue.

المستخلص

تم تحضير الفحم المنشط من الفحم البترولي المنتج بوحده التفحيم في شركه مصفاة الخرطوم بإستخدام التنشيط الكيميائي بهيدوكسيد البوتاسيوم كعامل تنشيط. الكربون المسامي المنتج تم تشخيصه بواسطة إختباري الرقم الأيودي والأزرق الميثلي ومطيافية الاشعه تحت الحمراء. عينتان من الكربون المنشط من مصفاة الخرطوم تم الحصول عليها بواسطه هيدروكسيد البوتاسيوم بنسبه 1:4 و 1:5 (فحم : هيدوكسيد البوتاسيوم) عند درجة حراره 800 درجه مئويه لمدة 60 دقيقة. الرقم الأيودي و الرقمالميثيلي لهذه العينات وجد ليكون 1248 و 1242 مج/جم ، 43 و 51 مج /جم علي التوالي. ونسبه مئويه بلغت 68 و61 % أيضا تم الحصول عليها.ولقد وجد أن كل من النسبه بين الفحم وهيدوكسيد البوتاسيوم وزمن التنشيط هي عوامل مؤثره في جوده الفحم المنشط المنتج.

INTRODUCTION
Activated carbon AC is a common term used to describe carbon based materials which contains well developed internal pore structure. AC is produced from a variety of carbonaceous rich materials such as wood, coal, lignite and coconut shell[(1)]. The high surface area, large porosity, well developed internal pore structure consisting of micro-, meso- and macropores as well as a wide spectrum of functional groups present on the surface of AC make it a versatile material which has numerous applications in many areas, but mainly in the environmental field[(2)]. The efficiency of ACs as adsorbents for diverse types of pollutants is well reported[(3)]. It is well known that

activated carbon has been found much efficient for removing organic compounds than metals and other inorganic pollutants. Efforts are ongoing to substantially improve the potential of carbon surface by using different chemicals or suitable treatment methods [(4)] which will enableAC to enhance its potential for the removal of specificcontaminants from aqueous phase. The physical and chemicalstructure of carbon could be changed by various methods, i.e. activationconditions (different agents, temperature and time of the process), precursor, additives, etc[(5)].

Petroleum coke is produced in crude oil refineries using delayed Coker unit, which is a type of Coker whose process consists of heating a residual oil feed to its thermal cracking temperature in a furnace with multiple parallel passes. This cracking process converts the heavy, long chain hydrocarbon molecules of the residual oil into cokergas oil and petroleum coke. A fired heater with horizontal tubes is used in the process to reach thermal cracking temperatures of 485 to 505°C[(6)].

The preparation of AC generally involves physical or chemical activation methods. In physical activation techniques, the raw material is first subjected to a carbonization process under an inert atmosphere followed by activation of the resulting char in the presence of activating agents such as CO_2 or steam. The main drawbacks of this method are the requirement of high working temperature, usually above 1000 °C, and the production of activated carbon with relatively low surface area[(7)]. In chemical activation method, the raw material is physically mixed or impregnated with activating agents such as $ZnCl_2$, H_3PO_4, KOH, and K_2CO_3 followed by thermal activation at 400-900°Cto create the pore structure. Chemical activation is preferred over physical activation owing to the lower temperatures and shorter time needed for activating material [(8)].

The aim of this study is to find the optimum operating conditions for the preparation of high quality activated carbon from petroleum coke by simultaneously considering the activating agent (KOH) concentration and activation time.

MATERIALS and METHODS

2.1 Materials and chemicals

Three Petroleum coke samples from Delayed Coker of Khartoum Refinery Company were randomly collected in a polyethylene bags and taken to the laboratory. They were grinded and sieved. The obtained samples were used as precursors for the chemical activationprocess

All chemicals used were of Analytical grade except where stated.

- De-Ionized water, Techno-pharmachem- India.
- Methylene blue, Scharlau - Germany
- Nickel standard solution, Merck-KGAA Germany
- Nitric acid 65 %, SDFL Chemicals Mumbi-india
- potassium bromide, Scharlau - Germany
- potassium hydroxide, Scharlau -Germany
- potassium iodide, Scotte Science –UK.
- sodium thiosulphate, Scotte Science –UK.
- Starch solution. Scharlau - Germany
- Sulfuric acid 98 %, SDFL Chemicals, Mumbi-india
- Zinc standard solution, Merck-Kga-Germany

Experimental Methods

Activated carbon production

The chemical activation experiments were carried out by impregnating 1.0 g of petroleum coke with an aqueous solution (100 ml H_2O) of potassium hydroxide (KOH) according to the required impregnation ratio, w/w, 1:1 to 1:5, as in Table 1. The resultant mixture was evaporated at 150 °C for 2 hours, heated up to 800 °C by an electric furnace (Labtech- LEF TYPE P, Daihan- India) with heating rate of 25°C/ min and temperature control,for different activation times starting from 30, 45 and 60 min. The Produced samples were washed with 500 ml hydrochloric acid 10%, washed with hot and cold distilled water to remove the alkali metal and washes until the filtrate isneutral.

Table 1: parameters and conditions used in the activation experiments

Ratio in g (Coke:KOH)	Activation temp./C°	Activation time/minute
1:1	800	30
1:1	800	45
1:1	800	60
1:2	800	30
1:2	800	45
1:2	800	60
1:3	800	30
1:3	800	45
1:3	800	60
1:4	800	60
1:5	800	60

Determination of heavy metals

5.0 g of either raw petroleum coke or AC were accurately weighed. The solution of Tri-acid was prepared by adding asolution of 10%HNO_3, 1%H_2SO_4 and4% $HClO_4$, 15 ml of these solutions were added to each sample and were cooled to room temperature, filtered through a filter paper and diluted to 100 ml, heated on a hot plate at 200 °C for 3 hrs then diluted to 100 ml.

Atomic adsorption spectroscopy (Thermo Scientific-ICE 3000, USA) was used to determine the heavy metals, using hallow cathode lambs for each element. A series of standard solutions of Zinc (0.5, 1.0 and 1.5 ppm), nickel (2.0, 4.0 and 6.0 ppm) and chrome (3.0, 6.0 and 9.0 ppm) were prepared using standard solution stock of 1000 ppm, then theabsorbance of each solution was measured at specific wavelength according to standard analytical method using a SOLAAR software.

Fourier Transform Infrared Spectroscopy

FTIR analysis using FTIR-84005 (SHIMADZU Corporation Kyoto, Japan), 0.10 g was mixed with 1.0 g of KBr in a mortar. The fine powder was pressed to a solid disc which was placed in an oven at 105°Cfor 4 hours to prevent any interference with any existing water vapor or carbon dioxide molecules, transferred to the FTIR analyzer and a corresponding chromatogram was obtained in the

wave numbers range of 400 -4000 cm^{-1}.

Iodine Number (IN)

2 drops of starch solution were added to 10 ml of 0.10 N Iodine solution, the pale yellow color of Iodine solution turned blue. The solution was titrated against 0.050 N sodium thiosulphate until it became colorless (B). A quantity of 0.2 g of ACwas added to 40 mL of 0.10 N Iodine solution, the flask was shaken for 4 minutes and then filtered, the filtrate was collected in a dry flask and 10 mL of the filtrate were titrated against standard solution of sodium thiosulphate using starch as indicator (A), normality of iodine filtrate was calculated[9].

Methylene blue (MB):

5.0 g of MB were dried in an oven at 110 C° for 2 hours before use. All of the MB solutions were prepared with distilled water, stock solution of 1000 mg/L was prepared by dissolving 1.0 g of MB in 1000 ml distilled water[10], experimental solution was prepared by diluting the stock solution with distilled water, the absorbance of 10 and 50 mg/L. Concentrations of MB were determined at 660 nm by the UV–visible spectrophotometer (LivoPond-Tintometer, GmbH, Germany), a calibration curve of optical densities against methylene blue concentrations were obtained by using standard MB solutions of known concentrations at pH values between 3 and 4.A quantity of 0.1 g of AC was added to 100mLof57 mgL^{-1}, the flask was shaken for 4 minutes and then kept for 24 hrs., the filtrate was collected in a dry flask and 10 ml of the filtrate absorbance were measured [11].

RESULTS and DISCUSSION

3.1 Activated carbon yields

The results in Table 2 and Fig. 1 show thatAC yield mainly depends on the amount of activating agent added to the coke.It is obvious when the amount of activating agent was increased the yield increased too. This could be assigned to sufficiency of the activation agent loaded on the coke during impregnation which prevents volatilization of carbon during activation.

Table 2: AC yield at various temperatures and ratio at 800 C°

Coke:KOH	Yield % (30 min)	Yield % (45 min)	Yield % (60 min)
1:1	58.20	21.20	28.40
1:2	45.10	25.30	22.00
1:3	45.00	52.10	50.00
1:4	N/D	N/D	68.70
1:5	N/D	N/D	61.00

N/D= Not determined.

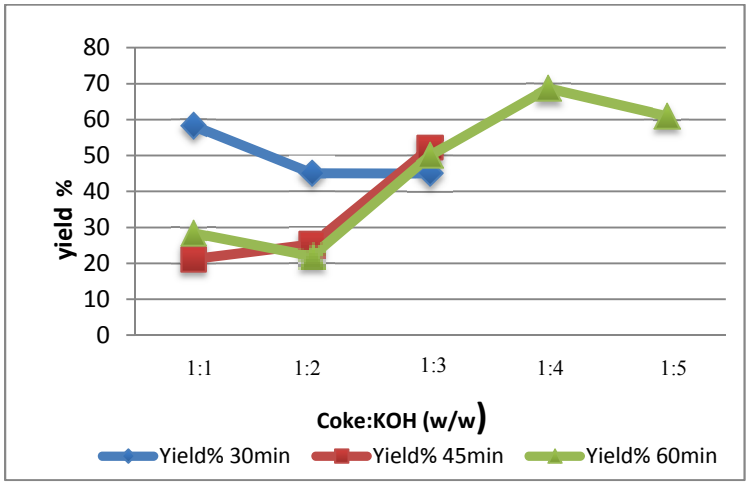

Fig. 1: The Effect of activation time and different ratios AC yield at 800 C°.

3.2 Activated carbon characterization

3.2.1 Determination of heavy metals

Table 3 shows the result of heavy metals present in petroleum coke, Zinc, Nickel and Chromium, were measured in both raw coke and produced AC. This measurement was performed to know their concentration limits, since these metals are considered as a harmful pollutant, therefore its presence in AC is not recommended. It has been found that the concentration of these metals is relatively low, and their concentration is always less in the produced AC, mainly due to the washing of these metals during production.

Table 3: Heavy metals in petroleum coke and AC.

Heavy metal	Petroleum coke-mg/L	AC -mg/L
Zinc	0.0668	0.0546
Nickel	1.8863	0.2089
Chrome	0.1400	0.0980

3.2.2 Fourier transform infrared spectroscopy (FT-IR)

The FT-IR spectroscopic study of the produced carbon is shown in Figure2. The sample showed four major absorption bands at 2900-3500 cm^{-1}, 1300-1750 cm^{-1}, 1000-1250 cm^{-1} and 450-900 cm^{-1}[12]. A wide band with two maximum peaks can be noticed at 2930 and 3450 cm^{-1}. The band at 3452 cm^{-1} is due to the absorption of water molecules as result of an O-H stretching mode of hydroxyl groups and adsorbed water, while the band at 3037 cm^{-1} is attributed to C-H interaction with the surface of the carbon. However, it must be indicated that the bands in the range of 3200-3650 cm^{-1} have also been attributed to the hydrogen-bonded OH group of alcohols and phenols[12][13].

In the region 1300-1750 cm^{-1}, amides can be distinguished on surface of AC

which has two peaks at 1640 and 1450 cm^{-1}. The band at 1525 cm^{-1} may be attributed to the aromatic carbon–carbon stretching vibration. The two peaks at 1143-1193 cm^{-1} yield the fingerprint of this carbon. The sharp absorption band at 1087 cm^{-1} is ascribed to either Si-O or C-O stretching in alcohol, ether or hydroxyl groups[14].

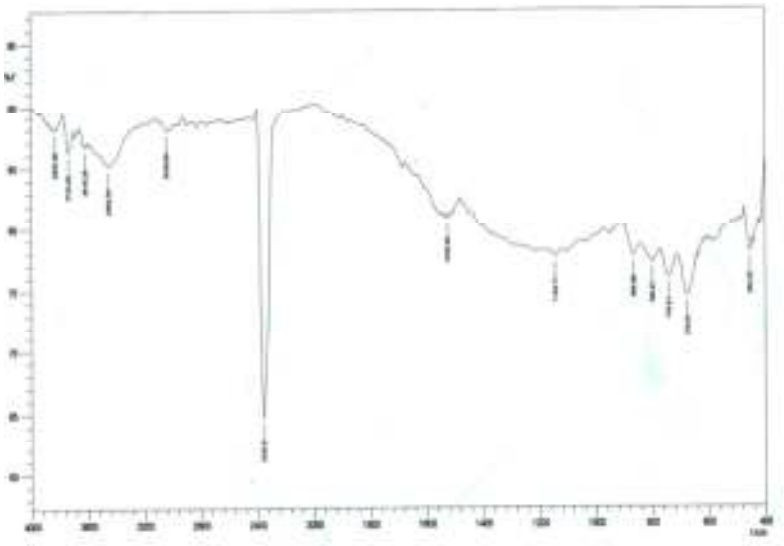

Fig. 2: FT-IR spectrum of AC (1: 5, Coke: KOH).

The band at 1143 cm^{-1} can also be associated with ether C-O symmetric and asymmetric stretching vibration (-C-O-C- ring), Si-O-Si stretching mode as a result of existing alumina and silica containing minerals.The region 450-750 cm^{-1} show two bands in the 480 and 485 cm^{-1} which are associated with the inplane and out-of-plane aromatic ring deformation vibrations Peaks at 598 and 671 cm^{-1} are assigned to the out-of-plane C-H bending mode. These spectra were also suggested to be due to alkaline groups of cyclic ketons and their derivatives added during activation[15].

3.2.3 The effect of Coke: KOHratio

Calculations involved in iodine value estimation:

Iodine value: **C** x Conversion factor; mg/g.

Factor:Mol wt. of iodine (127) x normality of iodine x 40 / Wt. of carbon x B.

C=B – A.

The MB is calculated by the following equation:

$$Q_{eq}(mgg^{-1}) = \frac{(C_0 - C_e)XV}{M}$$

Where:

C_0(mg /L) = concentration of the MB solution at starting time (t = 0).

C_e(mg/L) = concentration of the MB solution at equilibrium time.

V (L) = volume of the solution treated and

M (g) is the mass of the adsorbent

The activating agent/precursor ratio is known to be an important parameter in a chemical activation process[16] and hence it was one of the variables which was investigated with iodine number and methylene blue (MB)in the present study. Figures3 and 4show the increase in IN and MB values with increase of the coke : KOH ratio, due to sufficient KOH to react with the coke to efficiently create the internal pores and deterioration of micropores structure to form mesopores according to the global reaction[17].

$6KOH + 2C \rightarrow 2K + 3H_2 + 2K_2CO_3$.

Yamashita and Ouchi studied the interactions of alkaline hydroxides with

carbonaceous material and proposed an activation process as follows:

$$4KOH + =CH_2 \longrightarrow K_2CO_3 + K_2O + 3H_2 \quad (1)$$
$$K_2O + C \longrightarrow 2K + CO \quad (2)$$
$$K_2CO_3 + 2C \longrightarrow 2K + 3CO \quad (3)$$

Clearly, $=CH_2$ species is necessarily required to react with KOH to produce K_2CO_3 and K_2O[18].

3.2.4 The effect of activation time

As can be observed in Figures3 and 4, by changing the activation time from 30 to 45 minthe IN and MB increased. This can be attributed to more diffusion of active agent during the activation. It can be noticed that the suitable activation time is 60 min in terms of IN and MB and this is much shorter than the time reported in literature that is normally around 2h [19].

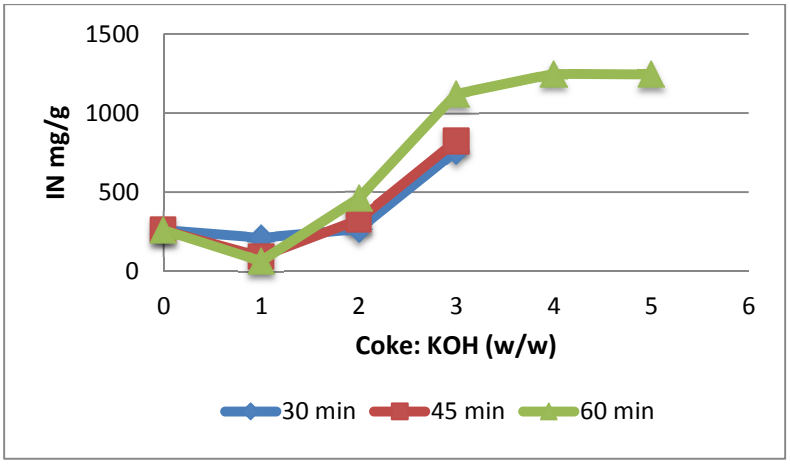

Fig 3 the effect of Cake: KOHratioon IN at 800 °C

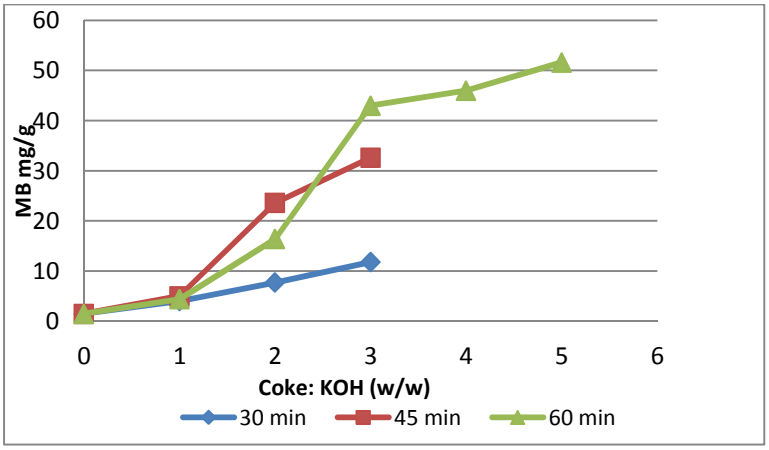

Fig.4: The effect of Coke: KOHratio on MB at 800 °C.

CONCLUSION

This study aimed to investigate the preparation of activated carbon AC from petroleum coke using KOH as activating agent, namely, the effect of Coke to KOH (w/w) ratio and activa-

tion time. This has been done by using different ratios starting from 1: 1 to 1: 5 (w/w) and 30, 45 and 60 minutes as activation time. The results showed that it is feasible to prepare activated carbons (AC) with relatively high IN and MB petroleum coke by direct chemical activation using potassium hydroxide as activation agent. The IN and MB of the activated carbons (AC) increase with the increasing of the activation ratio up to 1:5 and reaching a maximum value of 1242.10 and 51.60 mg/g of IN and MB were reached, respectively. The optimal conditions were found to be, Coke: KOH 1:5 (w/w) activating ratio for 1 hr at 800 °C.

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