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Preparation of Activated Carbon from Carbonaceous Industrial Wastes

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تحضير كربون منشّط من مخلفات صناعية كربونية

لطيف حميد علي وعبد الرزاق بلقاسم الشبلي

تم في هذا البحث تحضير كربون منشّط من مخلفات صناعية يمتلك بعضها قيمة اقتصادية متدنية ويعد البعض الآخر مصدراً ملوثاً للبيئة وتركزت الدراسة حول الآتي:

1 – مخلّفات التقطير الفراغي للنفط فوق 500°م.
2 – أسفلتين مفصول من الترسّبات النفطية لخاميْ السدرة والحمادة.
3 – مخلفات مطاطية من الإطارات المستهلكة لوسائل النقل.
4 – مزيج من الأسفلتين والمطاط المستهلك.

تمت عملية الكربنة بمزج المصدر الكربوني مع عنصر الكبريت بنسبة واحد إلى واحد وزناً وأجريت بمراحل حرارية ثلاث:

- مرحلة أولى عند 250°م وفي ظروف جوية عادية.
- مرحلة ثانية عند 500°م في جو من غاز النيتروجين.
- مرحلة تنشيط حراري أخيرة عند 900°م في جو من غاز النيتروجين.

تم تجميع غاز كبريتيد الهيدروجين (H_2S) الناتج من المراحل الثلاثة في مصائد كيميائية وفي التطبيق الصناعي للطريقة فإن هذا الغاز يحوّل مرة أخرى إلى عنصر الكبريت بطريقة كلاوس المعروفة ويدور الكبريت الناتج إلى مفاعل الكربنة في طريقة صناعية مستمرة.

جرى تقييم فعاليّة أنواع الكربون المنشّط التي تم تحضيرها باستخدام طرق معروفة تضمنت تقييم قابليّة الكربون على امتزاز المواد التالية من محاليلها المائية المخففة:

1 – مادة عضوية (حمض الخليك).
2 – مادة غير عضوية (اليود).
3 – مادة عضوية ملونة كبيرة الوزن الجزيئي (صبغة الميثلين الزرقاء).

وتمت مقارنة النتائج مع فعالية كربون منشط تجاري جيد النوعية في ظروف تجريبية متطابقة.

Abstract *Activated carbon (AC) was obtained by carbonizing the following low value sources and industrial wastes:*

- $500^{+\circ}$ *C vaccum residue (VR)*
- *Asphaltenes separated from crude oil sludge deposits (SA)*
- *Waste rubber from used tires (WR)*
- *A blend of asphaltenes and waste rubber (AWR)*

A mixture of the carbon source with elemental sulfur in a 1:1 ratio was first carbonized under atmospheric conditions at 250°C followed by a second stage carbonization at 500°C under nitrogen atmosphere in an electrically heated tubular furnace. Carbon was finally thermally activated at 900°C under N_2 *gas atmosphere in the same heater.*

Evaluation of the activity of the prepared carbon types was achieved by measurements on adsorption of acetic acid, iodine, and methylene blue dye from their aqueous solutions.

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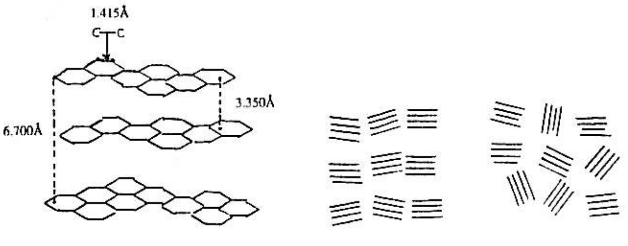
INTRODUCTION

The importance and world wide recognition of activated carbon as an essential material was through its use in poisonous gas masks during World War 1. Nowadays activated carbon finds an ever expanding uses in the fields of purification of materials, control of environmental pollution and catalysis.

Activated carbon (AC) represents a form of non-crystalline, amorphous material. Its basic unit resembles that of pure crystalline graphite, except that the layers (sheets) of the fused hexagonal carbon rings are not stacked uniformly in a parallel manner on each other:



(a) Graphite (b)Graphitizing AC (c) Non-graphitizing AC

X-ray examination of graphite (a) and activated carbon shows two types of the latter [1]. One type (b) is a semi-crystalline (graphitized structure), having parallel layers of hexagonal rings but not stacked on each other in a complete uniformity. The other type (c) has no parallel layer connections with a complete randomness in the net formation, thus having pores of vast size and distribution. Thermal activation increases the formation of carbon type (c) resulting in an increased surface area and a diversity of pore formation. The size, shape, and surface area of pores depend on carbonizing and activating temperatures, as well as on the nature of carbonaceous material (CM) [2].

Activated carbon is usually prepared from high carbon content CM such as wood coal, bones, coconut shells, organic waste, petroleum residues, etc. Several methods are available in the literature for the preparation of AC [3, 4, 5, 6, 7].

In this paper, accounts on the preparation, activation and assessment of activated carbon obtained by reacting petroleum carbonaceous materials and waste rubber, with elemental sulfur, will be given.

EXPERIMENTAL

1. Separation of Asphaltenes from Sludge Bitumen (SA)

3g of bituminous material; which was previously extracted from Hamada crude oil sludge with toluene; was mixed with 100 ml of normal heptane (n-C_7) in a 200 ml conical flask. The mixture was shaken 2 h at room temperature, followed by filtration and separation of asphaltenes using a suitable Buchner funnel under water pump suction. Asphaltenes were dried 1 h at 105°C.

The extraction of organics (bituminous like material) from inorganics and water was performed in a modified soxhlet system using toluene as the refluxing solvent which effected the separation of water by azeotropic distillation (see Fig. 1).

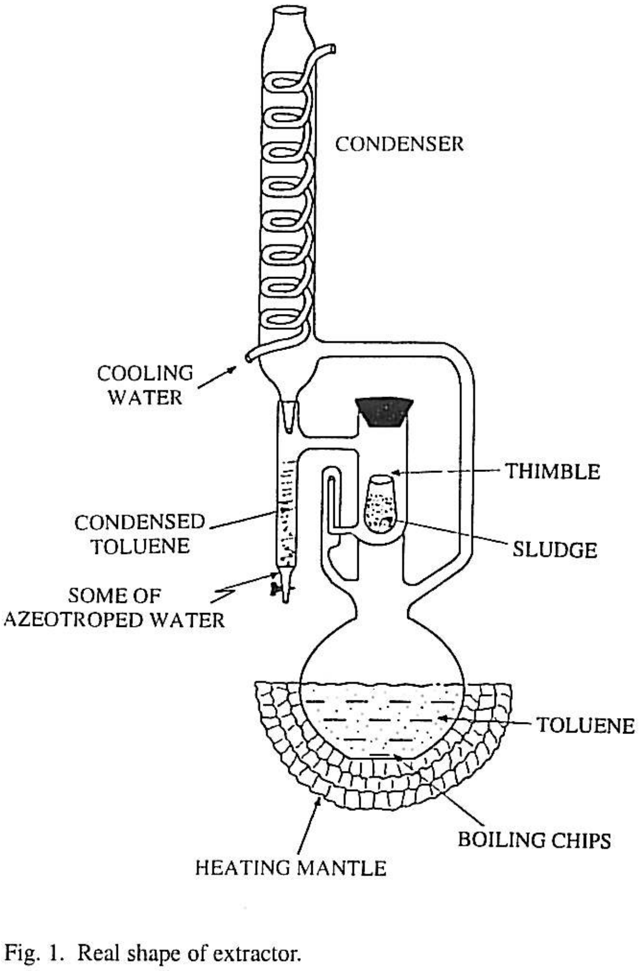


Fig. 1. Real shape of extractor.

2. Preparation of Waste Rubber (WR) as a Feed for Carbonization

Pieces of waste rubber from a used tire were further granulated either by using an electric blender, or by immersing into liquid nitrogen followed by quick hammering in a mortar. WR granules of particle size of 1–3 mm diameter were screened by a suitable sieve.

3. Vacuum Residue (VR), 500^+ °C As a Feed for Carbonization

VR was directly obtained as such from crude oil evaluation laboratory at Petroleum Research Centre.

4. Carbonization and Activation Operations

10 g samples of CM (VR, WR or SA) were mixed with 10 g of elemental sulfur (i.e. 1:1; wt/wt ratio), in a 250 ml round bottom (RB) flask connected to a condenser. The condenser was connected to a cold trap of salt and ice mixture and the latter was connected to solution traps containing 10% aqueous NaOH for the purpose of trapping H_2S gas produced from the carbonization operation (Fig. 2).

The partially carbonized material in the RB flask was crushed and placed in porcelain boats and was further carbonized 1 h at 500°C, under N_2-gas atmosphere in an electrically heated tubular furnace.

Activation was achieved in the same tubular furnace by raising the temperature to 900°C and maintaining a 30 cc/min. flow of N_2-gas for a period of 1 h.

H_2S gas evolved in the second stage carbonization at 500°C and during activation was trapped in 10% aq. NaOH solution in a series of traps connected to the heater (Fig. 3). Final yield of activated carbon is about 60% based on CM.

5. Activated Carbon from a Blend of SA and WR

To 5 g of fully carbonized WR (at 500°C/N_2-atmosphere), 5 g SA was added to form a new carbonization feed AWR. 5 g of elemental sulfur was added to the latter feed and was thoroughly mixed. The mixture was carbonized and activated in exactly the same manner as described in 4 above to yield a new activated carbon denoted AWR-AC.

6. Assessment of Carbon Activity by Acetic Acid Adsorption

To 50 ml samples of 0.1 M acetic acid solution, was added 0.1 and 0.3 g of each activated carbon prepared in the course of this work and to a commercial powdered activated carbon obtained from Merk. The mixture was shaken 30 min., filtered and the first 5 ml discarded. 20 ml of the filtrate was titrated against 0.1 N NaOH using phenolphthalein as indicator. The titration was repeated twice

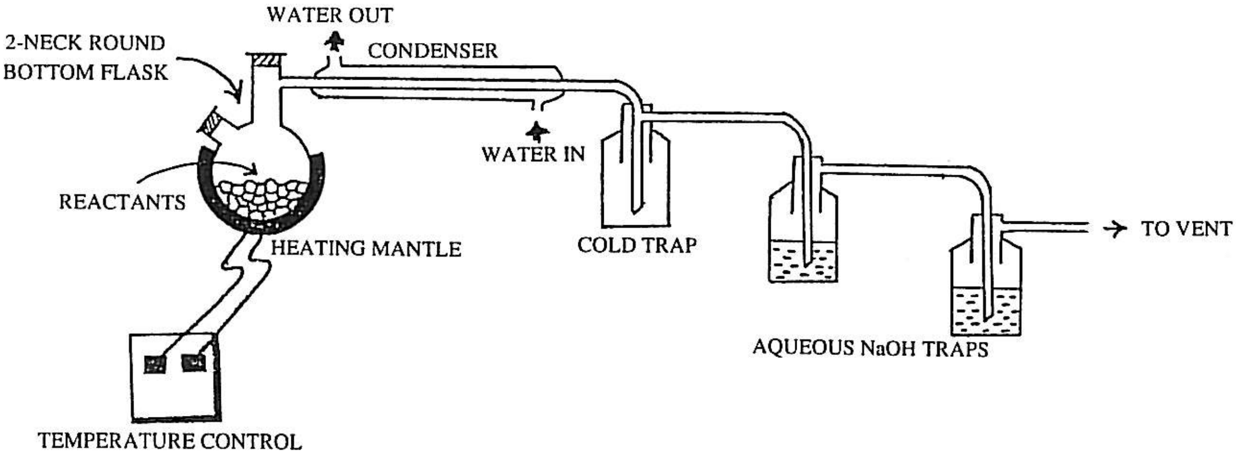


Fig. 2. First stage atmospheric carbonization.

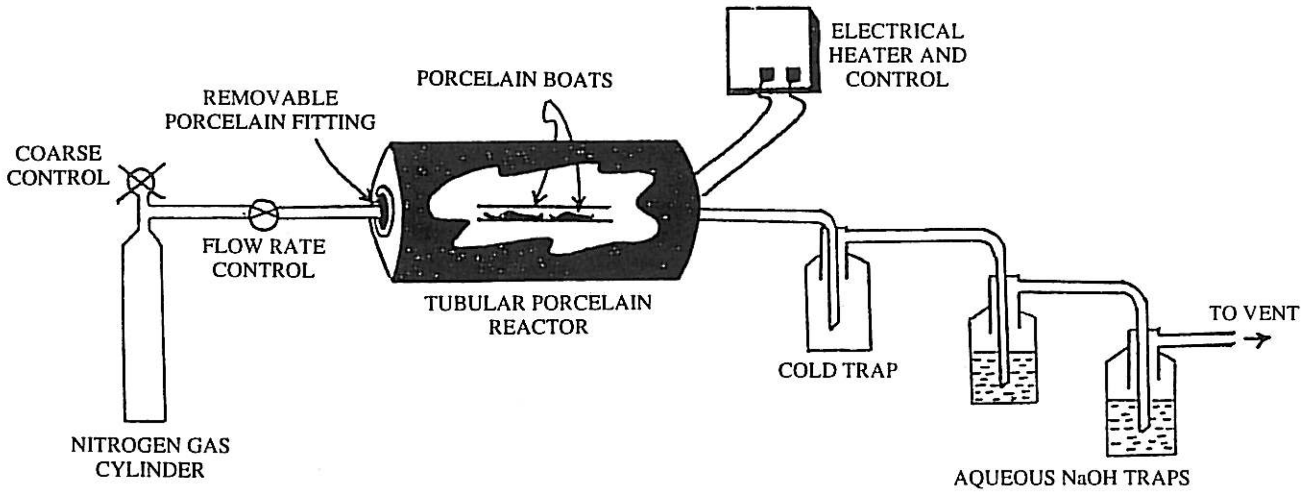


Fig. 3. Second stage carbonization and activation system.

7. Assessment of Carbon Activity by Iodine Adsorption from Aqueous Solution

0.1 g of dry AC was weighed into a stoppered 250 ml flask. 5 ml of 5% HC1 was added and the mixture was gently heated up to boiling point and was kept at this temperature for 30 min. Carbon was cooled to room temperature and 50 ml of 0.01 M I_2 aq. sol. was added. The mixture was well shaken, filtered and the first 5 ml. discarded. 20 ml of the filtrate was transferred to 100 ml conical flask and was titrated against 0.01 N sodium thio-sulfate ($Na_2S_2O_3$) aq. solution until the disappearance of the yellow color. At this point 1 ml starch solution was added and the titration was continued until blue colour disappeared.

8. Assessment of Carbon Activity by Removing Methylene Blue (MB) Dye from Aqueous Solution

Typically 0.1 g of powdered AC was added to 100 ml of MB (aq. sol.) containing 5 ppm of the dye. The solution was stirred, let settled and 5 ml quickly pipetted out, centrifuged 3 min at 2000 rpm and absorbance at 660 nm was measured. Stirring and repeating the measurements was continued at suitable intervals until colour is nearly completely removed.

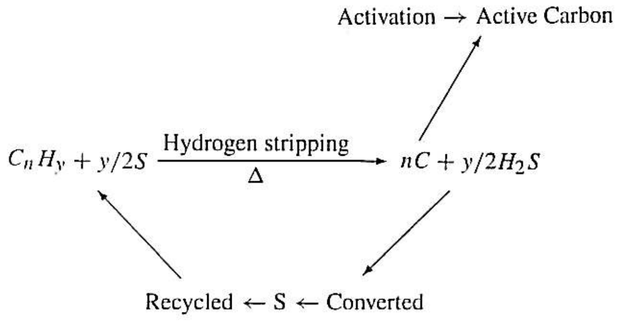
The concentration of un-adsorbed MB was determined from a calibration curve of a series of aq. sol. of MB of known concentrations and measured absorbancies as given in the following table.

Solution No	*MB conc. (ppm)*	*Absorbance* ($\lambda = 660$ *mm*)
1	1	0.189
2	2	0.386
3	4	0.724
4	5	0.898
5	7	1.376
6	10	1.865
7	12	2.254
8	15	2.473

RESULTS

1. Materials

The reaction is based on carbonizing a suitable organic material with elemental sulfur from an accessible source. The produced carbon can be activated by a variety of methods. The reaction also yields hydrogen sulfide (H_2S) as a by-product, which is converted to elemental sulfur and reused. The whole operation is generally presented as shown below.



It is proper to give short accounts on the carbon providing materials (Carbonaceous materials–CM) used in our work. We employed the following CM's:

(i) Vacuum residue (VR) 500⁺°C supplied by the crude oil assessment department at P.R.C. It contained 8.5% hydrogen.

(ii) Asphaltenes separated from bituminous matter isolated from crude oil sludges (SA). Toluene is used to extract hydrocarbons and azeotrope water in one operation. A diagram of the operation is given in Fig. 1.

Asphaltenes were separated from sludge hydrocarbons (SHC) by precipitation with n-heptane (n-C_7: SHC 33:1). Asphaltenes constituted about 30% of SHC.

(iii) Waste rubber from used tyres (WR). Rubber from used tyres was crushed either by freezing in liquid - N_2, then crushing, or by an electrical blender. The crushed rubber was sieved and suitable particle size was isolated.

Activated carbon was also prepared from a blend of WR with SA in order to improve properties.

2. Measurement of Carbon Activity

2.1. *Adsorption of Acetic Acid (AA) from Aqueous Solution*

The results on the adsorption of 0.3 g AA dissolved in 50 ml water by different weights of granulated and powdered prepared activated carbons, are given in Table 1.

2.2. *Adsorption of Iodine from Aqueous Solution*

The term Iodine Number is defined as the number of milligrams of iodine adsorbed by 1g of activated

Table 1. Assessment of activity by adsorption of acetic acid from aqueous solution.

	Granulated Carbon				*Powdered Carbon*			
Carbon Sample Abbreviation	*carbon Experimental weight (g)*	*Actual Weight of acid* $\times 10^3$	*Weight of acid removed by* 1 g[1]	*%Acid removed*	*Carbon expt. w.t. (g)*	*Wt. of acid removed by 1g*	*%Acid removed*	*Remarks on process of preparation*
VR-AC$_1$	0.1005	6.0	0.060	20.0				VR:S[2]; 1:1
	0.1996	12.0						(250 C° → 900 C°)[3]
	0.3052	14.0						
VR-AC$_2$	0.1010	12.0						VR:S; 1:1
	0.1989	14.0	0.071	23.7				(250 → 500 → 900 C°)
	0.3016	18.0						
VR-AC$_3$	0.3000	7.7	0.039	13.0	0.1076	0.028	9.3	VR:S; 1:1.5 (250 → 350 → 500 → 900 C°)
VR-AC$_{3a}$	0.1015	2.4						VR:S; 1:1.5
	0.2037	6.0						Washed with CS$_2$
	0.3099	24.0	0.077	25.8				(250 → 500 C°)
WR-AC	0.1037	6.0	0.058	19.4	0.1012	0.049	16.3	WR:S; 1:1
	0.2023	12.0						250 → 500 → 900 C°
	0.3045	27.0						
SA-AC	0.1016	12.0	0.118	39.4	0.1044	0.115	38.3	SA:S; 1:1
	0.2074	24.0						(250 → 500 → 900 C°)
	0.3060	30.0						
AWR-AC					0.1018	0.088	29.3	AWR:S; 1:1 Refer to Exp. II.5
Commercial-AC					0.1054	0.086	28.7	obtained from MERK

[1] Calculated from corresponding experimental weights.

[2] Elemental sulfur.

[3] Values in brackets represent stages of treatment temperature.

Table 2. Volumetric determination of adsorbed iodine from aqueous solution

Carbon type	ml^1 $Na_2S_2O_3$ (0.01 *N*)	I_2 *Equivalence* (*g*)	$g\ I_2$ *Adsorbed by* 0.1 *g carbon*	$mg\ I_2$ *Adsorbed by* 1 *g carbon*
WR–AC	32	0.0406	0.0112	112
SA–AC	24	0.0305	0.0213	213
AWR–AC	28.6	0.0363	0.0155	155
VR–AC3	36.7	0.0466	0.0052	52
Commercial–AC	16.6	0.0217	0.0301	301

[1] 1 ml 1N $Na_2S_2O_3 = 0.12691$ g I.

[2] May also be termed: Iodine Number.

carbon. The measurement is usually done by contacting a specified weight of AC with a standard solution of I_2, under specified conditions of time, temperature and shaking. The amount of adsorbed iodine is calculated by back titration of unadsorbed I_2 with sodium thiosulfate ($Na_2S_2O_3$) using starch as indicator. The results are given in Table 2.

2.3. *Removal of Methylene-Blue (MB) Dye from Aqueous Solution*

The results of removing MB from aqueous solution as a function of time, using different types of prepared activated carbon are given in Table 3. The same table gives also the natural logarithms of the concentrations of unadsorbed MB remained in solution after each treatment time.

Figure 4 gives a plot of lnC Vs adsorption time (in seconds) of some of the activated carbons. The slopes of lines at certain adsorption time reflect the relative activity of carbon samples.

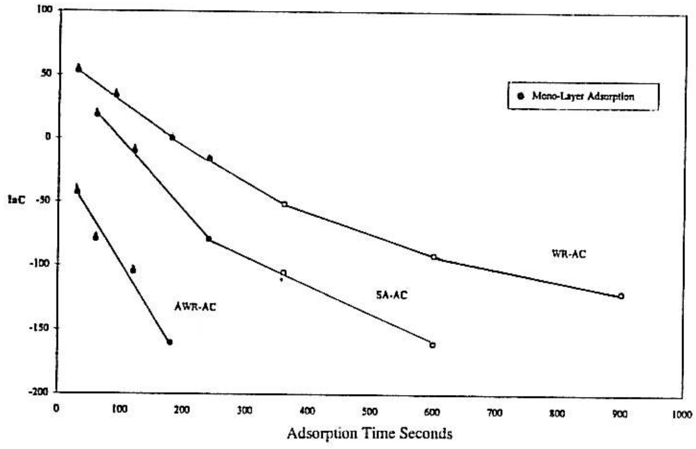


Fig. 4. Comparison of relative activity of prepared carbon.

DISCUSSION

Carbonaceous materials can be converted to carbon by a variety of methods capable of stripping hydrogen. These methods are usually thermal processes, therefore many unwanted constituents are also removed by the action of heat which effects a chain degradation of the carbonaceous material to carbon. Some of the carbon is lost during degradation and one usually looks for methods and conditions that minimize carbon loss.

For carbonaceous materials of petroleum origin, and the like, the use of elemental sulfur as a carbonizing agent has proved very effective [1, 2, 8, 9]. It is well established that elemental sulfur attacks hydrocarbons at a temperature as low as 100°C producing hydrogen sulfide [10].

$$\underset{\text{(Paraffin)}}{C_nH_{2n+2}} + S \xrightarrow{\Delta} \underset{\text{(Olefin)}}{C_nH_{2n}} + H_2S. \tag{1}$$

However production of H_2S on a large scale as a by-product in any industrial operation is a big problem from the environmental point of view. This problem has been overcomed by the development of methods of conversion of H_2S to other useful materials such as elemental sulfur or to H_2SO_4. It is of interest here to mention that nearly 50% of total world-wide needs for sulfur is supplied by recovery from tail gases [11]. One of the most developed methods is the Claus Process or some of its modifications. Reactions involved in this process are:

$$H_2S_{(g)} + \tfrac{3}{2}O_2 \longrightarrow SO_{2(g)} + H_2O_{(g)}$$

$$\Delta H = -518.8\ KJ \tag{2}$$

$$SO_{2(g)} + 2H_2S(g) \xrightarrow{(Fe_2O_3)} 3S_{(l)} + H_2O_{(g)}$$

$$\Delta H = 142.8\ KJ \tag{3}$$

Table 3. Removal of methylene–blue dye from aqueous solution containing 5 ppm with activated carbon.

Carbon sample	*Wt.(g)*	*Time (sec)*	*A (660 nm)*	*M.B. remained (ppm)*	*M.B. removed (ppm)*	*% removed*	*ln C*	*normalized slope value*
VR-AC$_1$	0.1022	1800	0.639	3.40	1.60	32*	–	–
		5100	0.584	3.15	1.85	37	–	–
VR-AC$_{3a}$	0.1053	800	0.664	3.55	1.45	29*	–	–
		5100	0.629	3.35	1.65	33	–	–
WR-AC	0.1020	30	0.318	1.70	3.30	66	53.1	
		90	0.254	1.40	3.60	72	33.7	
		180	0.193	1.00	4.00	80	0.00	
		240	0.171	0.85	4.15	83	−16.3	0.40
		360	0.120	0.65	4.40	88	−51.1	
		600	0.078	0.40	4.60	92	−91.6	
		900	0.057	0.30	4.70	94	−120.4	
SA-AC	0.1018	60	0.227	1.20	3.80	76	18.2	
		120	0.174	0.90	4.10	82	−10.5	
		240	0.088	0.45	4.55	91	−79.9	0.68
		360	0.064	0.35	4.65	93	−105.0	
		600	0.035	0.20	4.80	96	−160.9	
AWR-AC	0.1012	30	0.126	0.65	4.35	87	−43.1	
		60	0.090	0.45	4.55	91	−79.9	1.00
		120	0.075	0.35	4.65	93	−105.0	
		180	0.043	0.20	4.80	96	−160.9	

(*) Carbon sample did not mix, with the solution and stayed floating even with vigorous stirring.

Versions of Claus units of variable capacities are available in the market of Chemical Process Industries.

The general equation for the carbonization reaction is:

$$C_nH_y + y/2S \xrightarrow[\Delta]{H_2\text{–Stripping}} nC + y/2H_2S \qquad (4)$$

C_nH_y = Carbonaceous material.

The value of y and thus the amount of elemental sulfur needed for the carbonization reaction is determined by the percentage of hydrogen in the feed.

Most of the petroleum heavy ends (and the like), when used as feeds for active carbon preparation, contain around 7–9% H.

If simple calculation is made taking into consideration the approximate average molecular weight of the feed material and that 2 g of H is needed to produce 34 g of H_2S, this will give a reasonable weight ratio of 1:1 of elemental sulfur to feed to effect a proper carbonization reaction.

Activation of C from reaction (4) by a suitable method to give AC (activated carbon) follows. The recovery of the carbonization agent (elemental sulfur) should be performed which is motivated by economical and environmental considerations when applying the process on an industrial scale.

Using vacuum residue (VR) from the distillation of crude oil, namely Sarir 500^{+}°C which contained about 8.5% H did produce a type of AC (VR–AC$_{1,2,3}$ and $_{3a}$) which showed moderate activity toward acetic acid adsorption from aqueous solution (Table 1). The conditions of carbonization are mentioned in the same table which indicated that increasing the ratio of sulfur to feed to 1.5:1 deteriorated the quality (VR–AC3). Some improvement did occur when washing the prepared carbon with CS$_2$ prior to activation at 900°C. Deterioration of quality in VR–AC$_3$ was also obvious when powdered carbon was assessed in terms of acetic acid adsorption (Table 1). It is worth mentioning here that activated carbon prepared from vac.resid (VR–AC$_1$ and VR–AC$_{3a}$) repelled an organic matter dissolved in water like methylene blue (MB) and these AC stayed floating on the surface, thus effecting very little removal of MB (Table 3). On the other hand similar type of AC (VR–AC_3), mixed with solution with no problem when an inorganic matter, like I_2, was dissolved in water and some removal of I_2 from solution did occur (Table 2). This observation needs further investigation.

Asphaltenes are regarded as the heaviest constituents of crude oils, having molecular weights of 2000–5000 and unit layer sheets stacked on top of each other in a similar manner to graphite. Asphaltenes are therefore ready to form activated carbon with small needed modifications which are attained by proper carbonization conditions.

The main goal of our work is to employ refuse materials in obtaining valuable substances. Sludges from storage tanks on land or from carrier ships is a heavy burden on the oil industry and consequently on the environment. Sludges are expected to contain a high percentage of asphaltic materials. We have carried out some detailed investigations on the potentials of hydrocarbons in sludges (SHC) and at this stage we focused on separating this portion from water and inorganic fines. After we achieved that, using a laboratory scale system (Fig. 1), we proceeded further to separate the asphaltenes from SHC. The yield of n-C_7 asphaltenes from Hamada crude oil sludge was about 30%.

On the same theme of using refuse materials we proceeded to employ waste rubber (WR) in the preparation of active carbon. Even though the incorporation of WR in an industry like AC preparation will have a very minor contribution to solving the environmental problem from piling of e.g. rubber from used tires, nevertheless, from the economic point of view we have a free raw material to use.

Waste rubber from tires contains about 12% carbon black as a hardening agent, and about 1% elemental sulfur as a volcanization agent, in addition to natural and synthetic and reclaimed rubbers and other additives such as plasticisers, accelerators, antioxidants etc. Thus WR is a good feed for AC production, especially in terms of its contents of carbon black and sulfur.

Activated carbon prepared from carbonizing WR produced carbon of a medium activity compared to SA–AC. This is clear from Tables 1 and 2 in terms of acetic acid and iodine adsorption.

It was mentioned by Japanese workers in the field of carbonization that waste rubber; in a mixture with wood coal and a carboneceous binder [12], or in a mixture with high boiling (220–380°C) aromatic oils [8]; that the activated carbon produced possessed weak mechanical characteristics and adsorption properties tend to be weak. This in a way fits our findings. In an attempt to improve the physical properties and adsorption capability of WR-AC, it was coated with a petroleum binder prior to activation. Thus the carbonized matter at the 500°C stage obtained from WR was mixed with a 1:1 weight ratio of asphaltenes separated from Hamada Crude Oil sludge (SA) dissolved in benezene. After the evaporation of solvent, the SA–WR–AC mixture was further mixed with elemental sulfur in a 1:1 wt. ratio with respect to added asphaltene. The whole blend was carbonized in the usual two stages (250°C atmospheric followed by 500°C under N_2 atmosphere then activation at 900°C) was carried out to give the composite AWR-AC. The latter activated carbon showed a much improved mechanical properties as a first impression measurement when crushed by hands. Adsorption characteristics were very good with respect to acetic acid and iodine and excellent in terms of rate of removal of methylene blue from aqueous solution (Tables 1, 2 and 3 and Fig. 4).

The activity of carbon is not measured only by the amount of material adsorbed, but also by rate of adsorption (e.g. removal from solution) of the material. This rate is usually measured by the time in seconds needed to remove a certain concentration of methylene blue dye from aqueous solution. This determination required the construction of a calibration curve of MB in water, where measurements were carried out at λ660 nm.

The relative rates of removal of MB from aqueous solution by some types of AC prepared by us, are given in Table 3. Activated carbon prepared from vacuum residue. (VR-AC and VR-AC_{3a}) were excluded, since they resisted mixing with the MB solution.

A comparison is made between the slopes of the straight lines obtained for readings below 240 second (4 min.) of adsorption time and InC where C is the concentration of the remaining (unadsorbed) MB in solution. The results of this comparison study are given in Table 3 and plotted in Fig. 4. Calculated slopes normalized with respect to the slope of AWR-AC are given in the same table. It is obvious that regarding AWR-AC as a standard, the relative activities of SA-AC and WR-AC are 0.68 and 0.40 that of AWR-AC respectively.

Tentative explanation of the inflection point of the two straight lines in the plot of InC against adsorption times in WR-AC and SA-AC, is that: at this point monolayer adsorption is completed, and a slower multi-layer adsorption commenced. Higher activity AWR-AC – i.e. greater surface area – does not show inflection point with the range of MB – concentration employed (5 ppm) thus a clear straight line is obtained.

CONCLUSIONS

The following conclusions may be drawn at the present stage of this study:

1. the study successfully yielded several types of activated carbons prepared from low value, or refuse materials.
2. Even though the activating medium was quite mild, represented by N_2-gas, the quality of some of the prepared activated carbon, especially AWR-AC and SA-AC was quite acceptable and these carbons possessed considerable adsorptive characteristics as measured by conventionally accepted standard methods.
3. A new method was proposed for expressing relative carbon activity. This is accomplished by normalizing the relative values of the slopes from InC against time plot of adsorption – where C is the concentration of unadsorbed coloured material in aqueous solution expressed in part per million and time in seconds.
4. The just mentioned plot in 3 above (i.e InC Vs time) may provide a way for estimating the point at which a mono-layer adsorption is completed. This is obtained at the inflection point of the two straight lines representing the rate of adsorption (Fig. 4). The amount of material adsorbed when a mono-layer is completed may help deriving a method for surface area determination of activated carbon.

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