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Active Carbon Production from Modified Asphalt

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Abstract

A granular activated carbons (GACs) have been prepared from some local raw materials such as Qiayarah asphalt (QA) after some modification treatments of this asphalt by various ratios of its original constituents (asphaltenes and maltens) at 180 °C. Thermal carbonization method by sulfur and steam physical activation have been used for AC preparation. The carbons thus prepared were characterized in the term of iodine, methylene blue (MB), P-nitro phenol (PNP) and CCl_4 adsorption. The BET surface area of the prepared ACs has been estimated via a calibration curve between iodine numbers and surface area determined from N_2 adsorption isotherm from previous studies, also, the surface area of the prepared ACs were determined through another methods such as retention method by ethylene glycol mono ethyl ether (EGME), adsorption from vapor phase using acetone vapor and adsorption from solution method using PNP and MB as solutes. The results referred to the success of modification method for preparing ACs of good micro porosity as compared with the AC from the untreated asphalt as well as the commercial sample.

Keywords: *Modified asphalt; Granular activated carbons (GACs); Adsorption properties; Surface area; Retention method; Adsorption from solution.*

Introduction

Adsorption now plays a key role in modern industries, especially in the field of environmental protection engineering, with the increasing environmental awareness of people all over the world. Adsorption processes are being employed widely for large scale biochemical, chemical and environmental recovery and purification applications [1].

With the expanding demand for activated carbon due to their environmental applications, a great interest has been developed to seek steadier and cheaper feed stocks for the manufacture of AC, including the focus on by-product and waste materials [2].

Activated carbon is a highly porous material which has various applications in adsorption of both gases and solutes from aqueous solution. Granular activated carbon is widely accepted for the removal and recovery of toxic metals because of its low cost and high affinity towards the scavenging metal ions. The adsorption on GAC has many advantages [3].

1) The rate of adsorption and the capacity vary significantly for different potentially hazardous compounds and different commercial carbons. The capacity and the rate are both important determining factors in the design and operational criteria.
2) The capacity and the rate of adsorption for many organic and inorganic pollutants are affected significantly by the presence of other organic substances and by the conditions of the solutions temperature and pH.

The demand for activated carbon is growing particularly for its use for waste water and contaminated ground water treatment due to the higher awareness of the limited supply of water of this planet. Coals, lingo-cellulose materials and asphalt are good starting raw materials for preparing AC. As the production of an activated carbon must satisfy economical viability with high performance, cheap precursors materials readily available and convertible to an active carbon using minimum of resources could become very attractive raw materials [4]. The two main classical methods for preparing activated carbons are physical and chemical activation. It is known that any precursors of highly carbon content could be used for active carbon preparating [3]. Biomass waste such as fruit stones, asphalt and modified asphalt have been used to prepare activated carbon. Asphalt is a dark to black cementitious material; solid, semisolid (Bitumen) or liquid in consistency. The chemical composition of asphalt is very complicated and composed of two main parts (asphaltenes and maltenes). Asphaltenes which are dark to black friable solids, consisting of large molecular size, so they fall within the colloidal range. They are insoluble in light naphtha and their existence in asphalt imposes important effects on its physical properties (solubility, colloid, dispersion or peptization). They appear to be the final condensation products indicated from oxidation where the scheme of reaction.

Oils→resins→asphaltenes

The asphaltenes remained dispersed in the oil medium (maltenes) due to the hydrogen bonding interaction between asphaltenes and resins. The second part of asphalt is maltenes which is the soluble part of asphalt in naphtha. It can be further divided into resins and mineral oils [5].

This study is a complementary one for previous studies which have been achieved in Mosul University, and aimed to modify the rheological properties of asphalt which is found in two main types (Biji asphalt and Qiayarah asphalt) for paving purposes, whereas others such as our study make use of such modified systems for ACs preparation [5-10].

Experimental

Materials

In this work, Qiayarah asphalt (QA) which is produced from Qiayarah refinery (north of Iraq) was the cheapest staring material for AC carbon preparation. The most important properties of this asphalt are shown in table 1 [11] and the chemical analysis of this asphalt is given in table-2 [12].

Table 1. Physco-chemical properties of Qiayarah asphalt

property	ASTM	Value
Penetration at 25 C° (100 gm 5sec.01mm)	D5	55
Specific Gravity at 15 C°	D70	1.0576
Ductility at 25 C° (5cm/min.)	D113	75
Softening Point (R&B) C°	D36	55
Asphaltenes, % wt.	D4	25.67
Saturates % wt.	D4	14.22
Naphthenes, Aromatics, %wt.	D4	52.20
Polar, Aromatics,% wt.	D4	6.90

Table 2. Chemical analysis of QA

C %	82.47
H %	9.62
S %	7.73
Balance	0.18

Chemicals and Reagents

All chemicals used in this work were obtained from Fluka and Merck with 99 % purity.

Preparation of samples

Fractionation of Qiayarah asphalt

The fractionation of QA has been made according to Ali et.al method [13]. A known quantity of asphalt was shaken with petroleum spirit (60-80°) in ratio (1w/ 40v) at room temperature for 4hrs, and then the mixture is filtrated. The insoluble part (precipitate) is asphaltenes and the soluble one is maltens after solvent evaporation.

Modification and preparation methods

Qiayarah asphalt (QA) has been modified by different ratios of asphaltenes and maltens which were separated from the same asphalt in ratios (1, 5, 10, 15 and 20 % w/w) apart via physical mixing at 180°C for 2hrs followed by a chemical treatment at the same temperature for 1hr using $AlCl_3$ as catalyst.

The Carbonization method used in this study was the thermal carbonization by raw elemental sulfur (sulfur was obtained from Al-Mishraq sulfur field north of Iraq) which is characterized by containing 1% carbonaceous impurity [14]. A known quantity of modified asphalt was mixed with the same quantity of raw elemental sulfur, then, mixture was heated gradually till 240 ± 5°C was obtained, and the process went on till gases release stopped. The semi carbonized material was ground and sieved to 20-40 mesh and then activated by steam as an activating agent at 750-800°C for 1hr into stainless steel tube by means of a tubular oven to obtain the AC.

Equipments

A digital spectrophotometer (UV-Visible Spectrophotometer Shimadzu -1650PC) was used for measuring the absorbance of dyes solutions before and after adsorption.

Characterization tests

The adsorptive ability of the prepared ACs was examined through some basic tests such as:

1- Iodine number (IN): Iodine number which is defined as the mg of iodine adsorbed per gram of carbon, this test was determined by ASTM D 4607-86 method [15].
2- Service time: Quantity of CCl_4 vapor adsorbed per gram of AC at certain time [16].
3- Dyes values: Milligrams of dyes (MB and PNP) adsorbed per gram of AC .These dyes are the most common used. A known quantity (0.1g) of dried AC at 110°C for 24hrs was shaken with 100ml of MB (30ppm) or 50ml of PNP (100ppm) solutions at room temperature till equilibrium was obtained which took 24 hr. After that, the samples were filtered and the dye concentration in the supernatant solution was estimated by measuring absorbance with a Shimadzu UV-Vis 1260 PC. The wavelength was selected so as to obtain maximum absorbance for each dye stuff and the λ_{max} values are given as follows: for Methylene Blue, λ_{max} 665nmand for p-nitro phenol λ_{max} 318nm [17].

The amount of dye adsorbed on the carbons, q_e (mg/g) was calculated by mass balance relationship by Eq. (1):

$$q_e = [C_o - C_e) V / W \qquad (1)$$

Where C_o and C_e are the initial and equilibrium liquid phase concentrations, respectively (mg/L), V the volume of the solution and W the weight of the carbon used (g).

As regard surface area determination by solution adsorption, a known volume of different concentrations of used dyes (from 5-50 ppm for MB and 40-200 ppm for PNP) were contacting with 0.1 gm of AC till equilibrium was obtained. The linear form of Langmuire equation which is valid for monolayer sorption onto a surface was used for this purpose as expressed in Eq. (2):

$$C_e / Q_e = 1/ K_L Q_m + C_e / Q_m \qquad (2)$$

Where Q_m is the amount adsorbed per unit mass of adsorbent corresponding to complete monolayer coverage on the surface bound at high C_e and b is the constant related to the affinity of binding sites.

Result and Discussion

Chemical composition

It is known that any material of highly carbon content can be used for AC preparation. Qiayarah asphalt has been used as starting material for its higher carbon content as well as the nature of its chemical composition. It is one of the highly condensed aromatics types .The modification treatment of this asphalt aimed to a partial change in its chemical structure by governing reaction conditions as mentioned previously. As an evidence for this change, softening point was measured as a function of molecular weight change. Figs. 1 and 2 shows the softening point values of the modified samples.

As can be seen from Figs. 1 and 2, the chemical composition of QA has been changed due to modification treatments, but, asphaltenes modified Qiayarah asphalt (AMQAs) have been shown higher softening points than (MMQAs), this is due the ability of added asphaltenes to coalesce (compatibility) with the authentic asphaltenes of the asphaltic system, in addition, asphaltenes are highly molecular weight molecules consist mainly of polynuclear aromatic systems bearing mainly alkyl side chains up to C_{30}, therefore the molecular weight of asphalt [18] was incresead, also, asphaltenes are the heaviest part of the asphaltic system, therefore, all heavy metals and their compounds are aggregate in asphaltenes which may act as an additional catalyst for the reaction. The direct relation between softening points of (AMQAs) and asphaltenes% may reinforce our conclusions as can be seen from Fig.1.

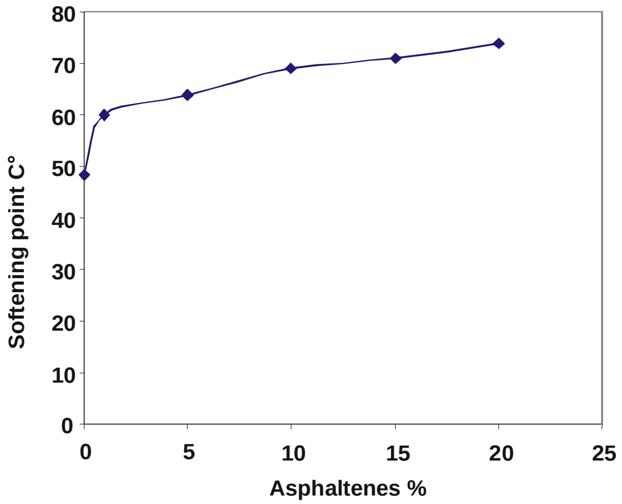

Figure 1. relation between Asphaltenes % and softening points

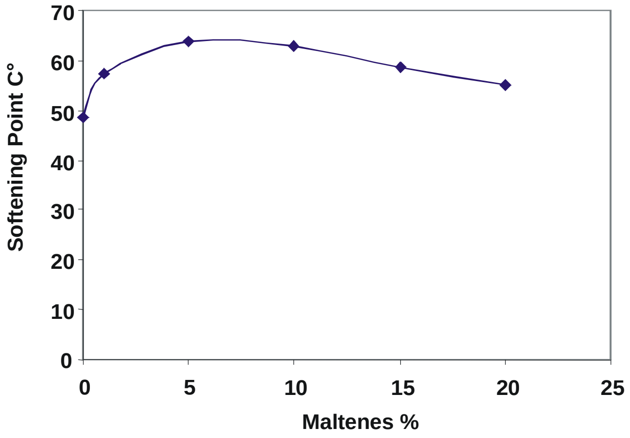

Figure 2. Relation between Maltenes % and softening points

As regard (MMQAs), slightly increase in the softening points has been observed in the beginning and then a decrease in these values, as can be seen from Fig. 2. This is due to the low molecular weight of maltenes which is less condensed aromatic rings than asphaltenes and has a large numbers of side alkyl chains leading to decrease in softening points may be because of dilution effect.

Adsorption Properties

This study is a complementary one to previous studies aimed to prepare ACs from QA after being modified by different materials such as polymer wastes and sulfur [9, 12]. Tests used to characterize the prepared ACs are given in Tables 3 and 4.

Table 3. Sorption properties of ACs from AMQAs

Sample	IN mg/g	MB mg/g	PNP mg/g	CCl_4 mg/g	Humidity%	Yield %
Q_{AC}	227.0	17.5	65	39	0.86	66
Q_{AAC1}	900	363	400	162	4.9	24.8
Q_{AAC2}	735	351	158	54	3.8	35.25
Q_{AAC3}	750	187	`73	50	4.4	36.36
Q_{AAC4}	725	207	207	81	1.4	33
Q_{AAC5}	700	133	143	41	2	41.84
AC_{BDH}	297	63.8	88	43	0.53	ND

Table 4. Adsorption properties of ACs from MMQAs

Sample	IN mg/g	MB mg/g	PNP mg/g	CCl_4 mg/g	Humidity%	Yield %
Q_{AC}	227.0	17.5	65	39	0.86	66
Q_{MAC1}	722	168	150	93	3.9	33.8
Q_{MAC2}	705	130	135	54	3.8	38.81
Q_{MAC3}	630	120	188	74	4.4	36
Q_{MAC4}	650	185	218	40	4.2	47.54
Q_{MAC5}	700	130	226	91	3.8	31.88
AC_{BDH}	297	63.8	88	43	0.53	ND

The adsorption of iodine can be used as a function of micro porosity and this test is a complementary test for N_2/77 K adsorption isotherm, and assumed to measure the micro pores sizes ≥ 10 A^2 [19] ·Phenols and their compounds are often used as reference solutes to simulate certain toxic chemicals in the liquid-phase adsorption studies and even to measure the specific surface area of adsorbents. The adsorption of PNP is another test for micro porosity since this molecule measure the microspores equals to (0.52 nm^2).The adsorption of CCl_4 is a good gauge of vapor phase adsorption capacity. This test is a rough measure of micro pore volume of the AC [16]. The dye adsorption tests help to determine the capacity of carbon to adsorb molecules of a particular size. The methylene blue molecule can be used as a function of mesoporosity and has a minimum molecular cross-section of about 0.8 nm and it has been estimated that the minimum pore diameter it can enter is 1.3 nm. Therefore, it can only enter the largest micropores, but most of it is likely to be adsorbed in mesopores, also it is good test for AC on removing colors from waste water and underground water.

From Tables 3 and 4, generally, The decreasing in yields % of the produced ACs is good evidence for the ability of modification treatments on increasing the porous structures of the produced ACs as compared with AC from the untreated asphalt, and as consequence the adsorption properties of the products were increased and gave larger values than the AC prepared from the untreated asphalt (Q_{AC}), also, our ACs were superior to the commercial AC sample (AC_{BDH}) especially the sample Q_{AAC1} which has shown highest adsorption properties than others. The prepared ACs have shown good micro porosity, where, they gave higher INs and showed good ability to remove dyes of small size molecule (PNP) from their aqueous solution, in addition to the higher adsorptive capacity toward CCl_4 adsorption as compared with AC from the untreated asphalt Q_{AC} and the commercial one. The values of MB adsorption were also higher as compared with the Q_{AC} and the commercial sample indicating that modification process was successed to increase the meso pores volume (wider micro pores) of the prepared ACs.

The adsorption properties (IN and MB values) of our ACs were superior to all ACs prepared from QA modified with different materials such as (waste poly ethylene, scrape tires, waste poly styrene and sulfur). As compared with previous studies, the ACs prepared from QA modified with aforementioned materials have been given lower adsorption values than our results. The adsorption properties of the previous studies are given in table 5 which also shows the best ratio of modifier. Therefore, depending on these results, we can say that modification of QA by its original constituents was more successful to produce ACs of highly porous structures and adsorption properties.

Surface area determination

Determination of surface area by vapor phase adsorption

The measurement of the specific surface area of finely divided solids such as AC became increasingly important in laboratory and technical process. One of the most employed methods for such measurement is vapor phase adsorption using N_2/77K or other gases such as CO_2, Ar, He and H_2O vapor.

In this work, the surface area was determined via the adsorption of acetone vapor. The measurement method is a gravimetrically one and has been explained detaily in an earlier study [20]. The $SA_{acetone}$ values are given in Table 7.

Determination of the surface area by adsorption from solution method

Liquid phase adsorption has been shown to be an effective method for color removal from aqueous solutions, and AC is the most widely adsorbent for this purpose.

Methylene blue (MB) which is a cationic dye and p-nitro phenol (PNP) are convenient solutes for many adsorbents. These solutes were used for SA measurement by many investigators [8, 9.17, 19-22]. This method gives a good correlation with N_2/77 K method for many adsorbents, therefore, they are used for the SA determination of ACs.

Surface area determination by solution adsorption was explained detaily in experimental section. The langmuire linear isotherm was used for determining mono layer capacity q_m for the prepared ACs which is given in table 6.

Figures 3 and 4 show the Langmuire linear plots used for determining the q_m of PNP and MB for the better samples (AC_{AMQA1} and AC_{MMQA5}) at 298K, whereas, figures 5 and 6 show the adsorption isotherms of PNP and MB on the same samples at 298K.

Table 5. Adsorption properties reported from previous studies

Modifier %	Adsorption properties mg/g		Reference
	IN	*MB*	
QA + 1 %S	180	21.1	12
QA + 1% PS	361	30	9
QA + 16% Scrape tyres	340.2	11.5	7
QA + 16 %PE	850	21.1	7

Table 6. Monolayer adsorption capacity of MB and PNP for the prepared ACs

Samples	Monolayer Adsorption Capacity mg/g	
	MB	PNP
Q_{AC}	44	63.5
Q_{AAC1}	379	364
Q_{AAC2}	334.2	95.5
Q_{AAC3}	271	165.25
Q_{AAC4}	294	262.55
Q_{AAC5}	167	139.5
Q_{MAC1}	214	144
Q_{MAC2}	137	129
Q_{MAC3}	152	178.5
Q_{MAC4}	294	208
Q_{MAC5}	379	216
AC_{BDH}	241	102

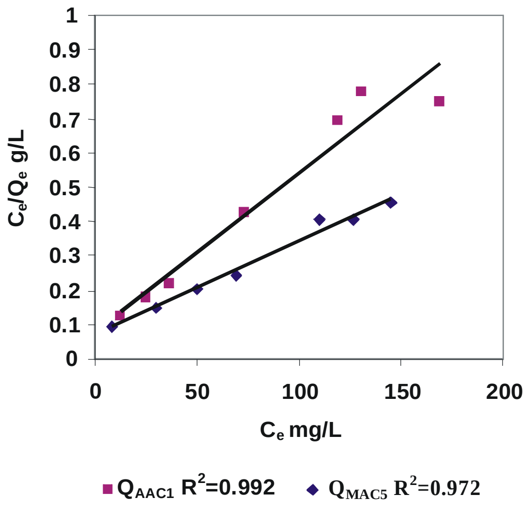

Figure 3. Langmuire linear plot of PNP on Q_{AAC1} and Q_{MAC5} at 298K

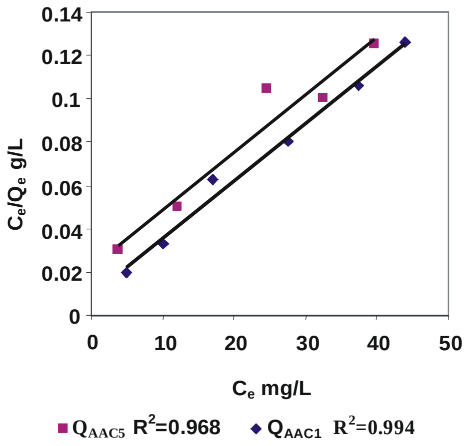

Figure 4. Langmuire linear plot of MB on Q_{AAC1} and Q_{MAC5} at 298K.

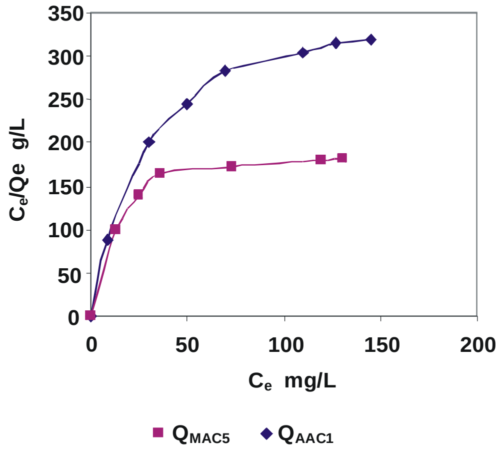

Figure 5. Adsorption isotherms of PNP on Q_{AAC1} and Q_{MAC5} at 298K.

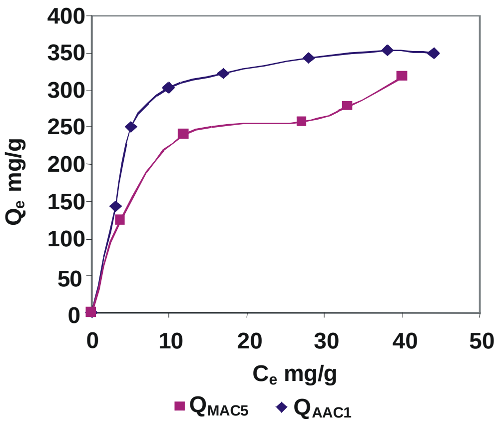

Figure 6. Adsorption isotherms of MB on Q_{AAC1} and Q_{MAC5} at 298K

Surface area related to dye adsorption was calculated using the following equation:

$$SA_{Dye} = Q_m .\ Ơ\ .10^{-20} .\ N / n \qquad (3)$$

Where SA_{Dye} is the surface area related to dye in m^2/g, Ơ is the cross sectional area of adsorbate (A^2), Q_m amount of solute adsorbed at the plateau of the isotherm in (mole/g), N the Avogadro's number and n is the coverage factor which reflects the average number of dye ions in a micelle, or the aggregation number since the dyestuff were adsorbed from aqueous solution in the form of ionic micelle, this value was 2 for MB and 1 for PNP. The SA values measured via PNP and MB adsorption are given in Table 7.

Table 7. Surface area of ACs prepared from (AMQAs and MMQAs).

Sample	$Estimated_{BET}$ m^2/g	SA_{EGME} m^2/g	$SA_{Acetone}$ m^2/g	SA_{MB} m^2/g	SA_{PNP} m^2/g
Q_{AC}	215	255	115	50	143
Q_{AAC1}	833	788	700	430	820
Q_{AAC2}	687	670	610	379	215
Q_{AAC3}	690	750	519	307	372
Q_{AAC4}	650	625	566	333	591
Q_{AAC5}	620	500	551	189	314
Q_{MAC1}	647	622	568	242	323
Q_{MAC2}	600	566	639	155	290
Q_{MAC3}	680	537	636	172	402
Q_{MAC4}	667	458.39	697	333	469
Q_{MAC5}	667	613	700	430	486
AC_{BDH}	275	ND	ND	273	230

Estimation of the BET surface area

The BET surface area of the prepared ACs was estimated via a calibration curve obtained from linear relation between iodine numbers and the BET surface area of previous studies. [23] calibration curve is shown in Fig. 5 and the estimated SA_{BET} values are also given in Table 7.

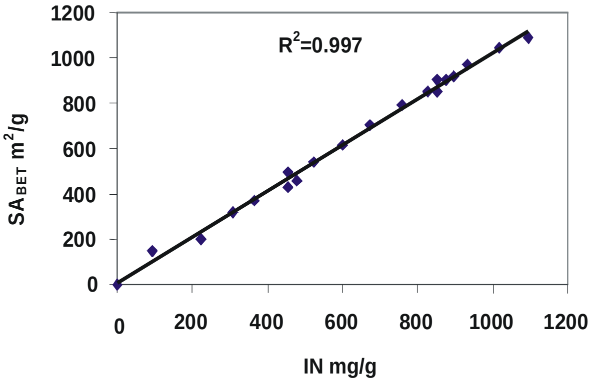

Figure 7. Calibration curve of the estimated SA_{BET}

Determination of the surface area via retention method of EGME.

The procedure includes wetting a sample with EGME, equilibrating, and then removing the excess liquid by evacuation. Samples were removed periodically and weighed until a constant mass was obtained. The specific surface area was computed from the mass of the retained liquid under the assumption that a monomolecular layer of EGME was adsorbed on the surface. The procedure applied in this work was made according to Lutengger method [24]. The SA_{EGME} values are shown in Table 7.

The adsorption of organic vapors such as acetone vapor was used for SA determination by Cal who found that it gives closer results to N_2 adsorption isotherm which refers to micro porosity [25]. PNP adsorption was used by many investigators for determining SA of finely adsorbents such as AC from their aqueous solution. Giles et.al and Uzun et.al reported a closer result of SA measured by PNP adsorption as compared to SA measured by N_2 adsorption which also indicates to the micro porosity. Velan et.al used EGME retention method for determining SA of the

AC and the results gave very closer results to those obtained using BET/ N_2 adsorption which means that this method can be used for measuring the micro porosity of the AC [26].

The estimated SA_{BET}, $SA_{Acetone}$, SA_{EGME} and SA_{PNP} of our ACs have been shown higher values than those obtained from MB (SA_{MB}) adsorption indicating that the prepared ACs have higher micro pores than meso pores (wider micro pores) since the adsorption of MB can be used as a function of mesoporosity [27], also as in adsorption properties, our ACs have been given higher SAs than Q_{AC} and AC_{BDH} which reinforces our conclusion that modification treatments have been succeeded to increase the porous structure of the resulted ACs as compared with the AC from the untreated asphalt.

Taking the estimated SA_{BET} as reference, the SA_{EGME} were given closer results of the estimated $_{BET}$ values, and this is a good indication about the higher micro porosity of our ACs and, also our results were resemble to those obtained by Velan et.al [25].

Surface area calculated from adsorption of acetone vapor $SA_{Acetone}$ and the estimated SA_{BET} have been given higher values than those calculated from adsorption solution phase, because dyes and other high molecular weight pollutants don't penetrate in the inner pores of the particles leading to a rapid saturation of adsorbent, furthermore, the penetration of the dyestuff molecules becomes more difficult because of the aggregation since the organic dyestuffs are adsorbed in the form of ionic micelles from the aqueous solution .In highly porous solids such as AC, adsorption from solution gives similar or closer results to vapor phase adsorption and some times lower. In the latter case, some pores are clearly large to admit vapors molecules such as acetone and N_2 molecules but not solute molecules (MB and PNP), but, some times, solution adsorption gives higher values than vapor, because adsorption from solution takes place under agitation conditions whereas, adsorption of vapors takes place under static conditions.

The adsorption isotherms of MB and PNP were determined for samples Q_{AAC1} and Q_{MAC5} since they gave good adsorption properties and surface area values, the isotherms were fitted to langmuire type of isotherms which indicates to the micro porosity [17].

By arranging the SA values (table 7) obtained from different adsorbates, it can be seen that the SA values increased in the order $SA_{MB} < SA_{PNP} < SA_{Acetone} < SA_{EGME} < SA_{BET} < IN$, therefore, we can conclude that our samples are meso porous in addition to developed micro porosity.

Conclusion

According to the obtained results, it can be said that modification of QA with different amounts of its constituents (asphaltenes and maltenes), therefore, we reached to the following:

1- Active carbons of very good adsorptive properties can be obtained from locally available raw materials such as QA.
2- Treatment of QA with certain amount of its constituents (asphaltenes and maltenes) via our handling has been improved the adsorptive ability of the product as compared with previous handlings and the AC from the untreated asphalt.
3- Our activated carbons have been shown high porosity for their higher adsorption properties and surface areas as compared with the AC from the untreated asphalt and the commercial AC.
4- The difference in the adsorption values belongs to many factors such as the nature and composition of modifier, surface area, pore volume, surface chemistry and the nature of adsorbate.
5- The resulted ACs shown good ability to ward adsorption from both vapor phase and liquid phase. The adsorption process follows the Langmuir isotherms as could be seen from plots showing monolayer coverage of dye molecules at the outer surface.
6- Our samples shown higher adsorption ability as compared with the commercial one that means that our preparation method was effective to prepare a high quality AC.
7- Despite that ACs prepared from AMQA were given the better sample but those prepared from MMQA were also shown good adsorption properties and SAs as

compared with ACs from AMQA and superior in SAs to some of them as well as to the AC from the untreated asphalt and the commercial one, from other hand, all our samples were shown good adsorptive properties and SAs for all ratios of asphaltenes and maltenes.

8- The samples showed the presence of both micro pores and meso pores according to the used adsorbates, therefore, we can say that they are meso porous in addition to developed micro porosity

Acknowledgement

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Abrreviatives

QA: Qiayarah asphalt.
SPs: Softening points.
GACs: Granular activated carbons.
AMQA: Qiayarah asphalt that was treated with different ratios of asphaltenes.
MMQA: Qiayarah asphalt that was treated with different ratios of Maltenes.
INs: Iodine numbers.
SA: Surface area
SAs: Surface areas

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