Surface Area Determination of Activated Carbons Produced from Waste Tires Using Adsorption from Solution

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Abstract:

The following study demonstrates the possibility of producing different activated carbons from a mixture of waste tires and tubes. The mixture was pyrolyzed at different temperatures namely (400,450 and 500^{o}C) for two hours for the determination of best condition of heating. It was found through the study that semi carbonized marital produced via pyrolyis at 500 ^{o}C was the best; thus it was used as a precursor for producing different activated carbon samples. The aforementioned precursor was converted into activated carbons via different method of activation i.e. thermally activation and steam activation at 800 ^{o}C for two hours as well as microwave heating at 450 watt for four minutes.

Adsorption from solution technique was used to determine the surface areas of the produced chars using I_2 and methylene blue as solutes. The produced carbons showed the presence of microporosity with development in mesoporosity. This was detected from the higher surface area by I_2 adsorption and lower surface area using methylene blue.

Langmuir and Freundlich models of adsorption were used to analyze the adsorption date of the produced carbon adsorbents. The results showed that Langmuir model was more suitable than Freundlich to analyze the adsorption data. Thus, it was used to determine the monolayer coverage of solutes through this study. Also, adsorption isotherms followed Langmuir type of adsorption according to Giles classification which indicates the microporosity of the prepared activated carbon.

Keywords*:* Waste tires; Activated carbons; Thermal and steam activation; Microwave heating; Adsorption from solution; Surface area; Adsorption isotherms.

1. Introduction:

Activated carbon (AC) is an amorphous form of carbon that is specially treated to produce a highly developed internal pore structure with a large surface area, thus, producing reasonably cheap and excellent adsorbent [1-3].

Activated carbons are widely used as adsorbents in both gas-phase and liquid-phase separation processes and can be produced from various carbonaceous materials, for instance, coal, coconut shell, wood, and polymer scrap [4].

Adsorption has long been used as a wastewater purification technique on an industrial scale. In general the adsorption capacity of an adsorbent like activated carbon is the function of surface area, pore volume, pore size distribution and surface chemistry [5,6]. There are numerous reports of more organic adsorption in pores that are barely large enough to admit the adsorbate molecule [7].

Activated carbons are extremely versatile adsorbents with major industrial significance. The world consumption of activated carbons is steadily increasing and new applications are always emerging, particularly those concerning environmental pollution remediation, which should help to sustain demand for them. Important applications are related to their use in water treatment for the removal of flavor, color, odor and other undesirable organic impurities from water. Activated carbon is also used in industrial wastewater and gas treatment due to the necessity for environment protection and also for material recovery purposes. The food and pharmaceutical industries are also a major consumer of activated carbon [8].

The disposal of waste tires has become an increasingly important issue worldwide in recent years. Tires not only take up large amounts of valuable landfill space, but also create fire hazards and provide a refuge for disease-carrying creatures. Because of their high heating value, tire incineration presents an option of solving the disposal problem as well as of producing additional energy [8].

The use of rubber tire as a feedstock for activated carbon production was investigated by many authors [9–15]. Many methods including physical and chemical have been used for this purpose [15]. This needs to pyrolysed the tire at first, followed by an activation step. Beside the solid material generated during the pyrolysis of tire rubber, a volatile fraction that can be separated into condensable hydrocarbon oil and a gas can be obtained [16].

The accumulation of scrap tires results in large spaces occupation and a wastage of a valuable energy resource. The huge amount and high stability of scrap tires have made their disposal a serious environmental problem [(17].

In principle, the methods for production of activated carbon can be divided into two categories: physical and chemical activation. The physical activation method involves carbonization of a precursor at elevated temperatures (500–900 °C) in an inert atmosphere, followed by activation of the resulting char at high temperatures (800–1000 °C) in the presence of a CO_2 or steam atmosphere.

In the chemical activation method, raw material is impregnated with an activating reagent and the impregnated material is heated under an inert atmosphere. The carbonization and the activation steps are progress simultaneously in the chemical activation method. Different well-known chemical agents can be used in the chemical activation process as phosphoric acid and zinc chloride [18].

The presence of dyes and pigments in water, even at very low concentrations, is highly visible and undesirable [8]. These dyes are primarily of synthetic origin and have complex aromatic structures, which make them more stable to light, heat and oxidizing agents, and are usually biologically non-degradable[19]. Among various treatment technologies, adsorption onto activated carbon has proven to be one of the most effective and reliable physicochemical treatment methods.

The following paper demonstrates the possibility of activated carbon production from a mixture of waste tires and tubes. The mixture was pyrolyzed at different temperatures namely 400, 450 and 500 ^{o}C for two hours. The produced semi carbonized material was converted into activated carbon via different method such as thermal activation at 800 ^{o}C for 1h, steam activation at 800 ^{o}C for 1h and micro wave heating at 450w for 4 minutes. The adsorption results were analyzed in term of Langmuir model using iodine and methylene blue as solutes.

2. Experimental

An equal mixture of waste tires and tubes (50 % wt/wt) was used as a precursor for activated carbon preparation. At first, the mixture was washed with tap water to remove dirt and dust, then it was cut into small pieces with a diameter of (2mm) and left for drying. The mixture was pydrolyzed at different temperatures namely 400, 450 and 500 ^{o}C by the mean of a fixed tubular furnace for 2hrs. Then, the desired semi carbonized material (SCM) was converted into different activated carbons as following:

1- A known quantity of the SCM was thermally activated at 800^{o}C for 1hr to produce AC_{TH}.

2- A known quantity was activated in the presence of steam at 800^{o}C for 1h to give AC_{ST} , and

3- Another quantity of SCM was subjected to microwave heating at 450 watt for 4 minutes to produce AC_{WM}.

The adsorption capacities for the produced AC samples were measured via the adsorption of iodine (I_2) and methylene blue (MB) from their aqueous solutions.

A calibration curves were *used* in the concentration range of 100–2000 mg /l and 10–100 mg/l for I_2 and MB respectively in order to determine the dye concentration in the solution after adsorption.

The concentration of I_2 and MB in the clear solution was analyzed by a (Shimadzu UV–Vis 1260 PC) through measuring their absorbance at λ=447 and λ=665 nm respectively. The following equation was used for determining the adsorbed amount of dye.

$$Q_e = (C_o - C_e)\, V / W \qquad (1)$$

Where Qe is the adsorbed quantity of dye at equilibrium, C_o and C_e are the initial and the equilibrium liquid phase concentrations, respectively (mg/l), V is the volume of the solution, and W is the weight of the carbon used (*g*).

3. Results and Discussion

3.1 Products Yield

It is known that the pyrolysis of any hydrocarbon material produces liquids, solids, and volatiles. The pyrolysis of our mixture was conducted at different temperatures namely 400,450 and 500 °C for 2hr. Percentage yield of the products resulting from pyrolysis is given in Table 1.

Table1: Yield percentages of solids.

Temperature ^{o}C	Yield %
400	45.0
450	43.11
500	35.12

It's noticeable in Table1 that pyrolysis of the mixture at different temperatures was accompanied by a decrement in the percentage yield of char. In turn, the percentage yields of liquids and gases increased. Increasing pyrolysis temperature leads to further removal of the volatile components; as a result, char percentage decreases [20].

The adsorption capacity represented by iodine number (ASTM D 1510 – 06a) was measured for the SCM produced via pyrolysis of the mixture at different temperatures. The (IN) values are listed in Table2.

Table 2: Iodine adsorption capacity of the produced semi carbonized materials.

Temperature ^{o}C	IN mg/g
400	40.12
450	62.12
500	90.13

It is clear from Table2 that SCM produced via pyrolysis of the mixture at 500°C had the highest IN. This is for higher temperature pyrolysis accompanied by a further removal of volatiles leaving behind a porous structure. Thus, the SCM produced at this temperature was used as a precursor for AC production. Prior to use , it was soaked in HCl (1N) solution for 24hr to eliminate some inorganic impurities, after that it was filtrated and washed with distilled water until a neutral water was obtained. Finally, it was dried at 110°C for 5 hr and its IN was measured which was found to be 191 mg/g. This means that acid treatment was successful to enhance the adsorptive capacity of the used SCM. Then, this SCM was used as a feedstock for AC production as mentioned in the experimental section.

3.2 Surface area determination

Powdered activated carbon is the most widely used adsorbent for color removal, because it has an excellent adsorption capability for organic compounds. Liquid phase adsorption applies to many purification processes, one of the most relevant is that related to waste water treatment [21]. The adsorption process was done by contacting (0.1g) of the AC with solutions of different concentrations ranging from (100– 2000 mg/l) and (10–100 mg/l) of I_2 and MB respectively, in stoppard conical flasks. After equilibrium, the linear form of Langmuir equation, which is valid for monolayer adsorption on the surface, was applied for this purpose, as expressed in Equation 2.

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

Where Q_m is the amount adsorbed per mass unit of adsorbent corresponding to complete monolayer coverage on the surface, and K_L is the Langmuir constant. Langmuir linear plots of the adsorbates used are depicted in figures 1 and 2 respectively.

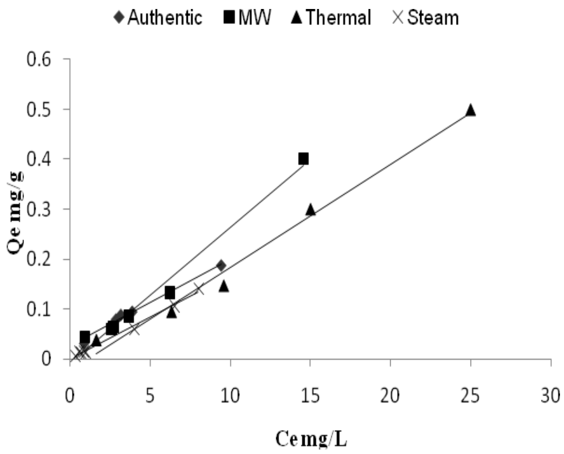

Figure1: Langmuir Linear plots of MB on the produced ACs.

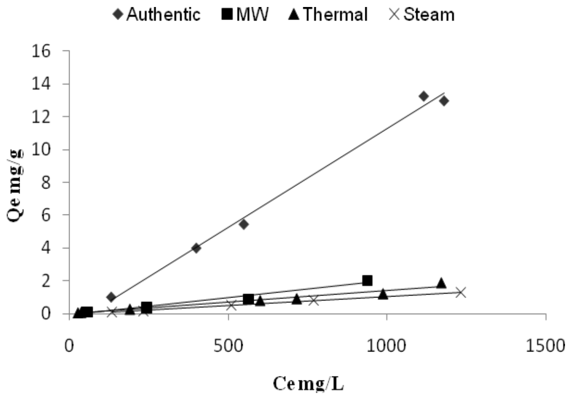

Figure2: Langmuir Linear plots of I_2 on the produced ACs.

The values of Q_m and Langmuir constants of I_2 and MB adsorption on the produced ACs are given in Tables 3 and 4 respectively.

Table 3: Langmuir and Freundlich Constants and Monolayer Coverage Values of MB.

Sample	Langmuir			Freundlich		
	Q_m mg/g	K_L mg/l	R^2	n	k mg/g	R^2
AC_{AT}	21.50	0.023	0.988	4.32	26.84	0.938
AC_{ST}	59.06	0.013	0.991	2.83	38.82	0.949
AC_{TH}	47.00	0.338	0.993	4.09	39.40	0.951
AC_{MW}	36.15	0.074	0.980	5.02	34.29	0.929

Table 4: Langmuir and Freundlich Constants and Monolayer Coverage Values of Iodine.

Sample	Langmuir			Freundlich		
	Q_m mg/g	K_L mg/g	R^2	n	k mg/g	R^2
AC_{AT}	79.06	$1.8 X10^{-4}$	0.993	2.94	35.69	0.982
AC_{ST}	672.16	$4.33X10^{-5}$	0.965	12.65	614.61	0.935
AC_{TH}	877.70	$1.68X10^{-5}$	0.994	9.00	384.13	0.964
AC_{MW}	476.82	$4.6X10^{-5}$	0.970	8.26	323.75	0.938

The adsorption data for I_2 and MB were also fitted to a Freundlich isotherm described by the equation:

$$\ln qe = \ln k + 1/n \ \ln Ce \qquad (3)$$

Where, *Ce* is equilibrium concentration of the sorbet in mg/l, *qe* is the amount adsorbed in mg per gram of AC., *k* is the so-called unit capacity factor, and *n* is an empirical parameter that represents the heterogeneity of the site energies [19] or the affinity of the adsorbate to the carbon surface. Figures 3 and 4 show Freundlich linear plots of I_2 and MB of the produced carbons, while Freundlich constants are given in Tables 3 and 4 respectively.

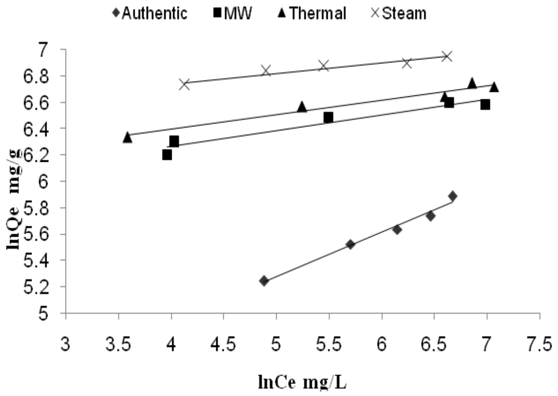

Figure3: Freundlich Linear plots of MB on the produced ACs.

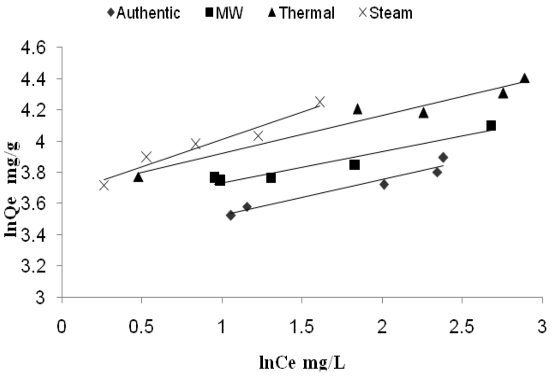

Figure4: Freundlich Linear plots of I_2 on the produced ACs.

Surface area (SA) related to dye adsorption in (m^2/g) is calculated from the following equation:

$SA_{DYE} = Q_m \times Ơ \times 10\text{-}20 \times N / n$ *(4)*

Where, Ơ is the cross sectional area of solute in m^2/g, N is Avogadro's number, and *n* is the aggregation factor [20].

The capacity of adsorbents for removing color can be evaluated through iodine adsorption from aqueous solutions using test conditions referred to as iodine number determination. This indicates their relative activation level and the surface area available for micropores. Usually adsorbents with a high iodine number have a high surface area and are suitable for adsorbing small compounds [22]. 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 [23]. Surface area of the produced ACs was measured via adsorption of solution technique using I_2 and MB as solutes. Table5 lists the (SA) values obtained from the adsorption of I_2 and MB on the produced ACs.

Table 5: Surface Areas of the produced activated carbons via solution adsorption.

Sample	SAI_2 m^2/g	SA_{MB} m^2/g
AC_{AT}	75	54
AC_{ST}	833	145
AC_{TH}	595	118
AC_{MW}	444	89

It is quite clear that SA using iodine as a solute are in the following order: $AC_{ST} > AC_{TH} > AC_{MW}$. Activated carbon sample produced via steam activation had the highest SA. This is due to the steam activation that helps to increase the porous structure via further removal of volatiles remained during the pyrolysis, thus the surface area increases.

Thermal activation leads to further pyrolysis of the SCM which may in turn lead to block micro pores, hence the SA decreases or/and oxygen functional groups formed during thermal activation may block micro pores causing a decrement in the SA [24]. Microwave heating has the advantages of reducing the energy consumption. It is noteworthy that the considerable changes in the surface properties were achieved within a short time, which should be attributed to the distinct mechanism of MW heating. In conventional heating, the energy transfers from outside to the interior part by conduction and convection, which results in a thermal gradient reduced from the surface to the inside. On the other hand, MW heating leading to a thermal gradient opposite to that in conventional heating. As a result, the interior part of activated carbon is heated more favorably under MW radiation, which facilities the modification process [25].

It can be seen that SA of AC_{MW} via iodine adsorption was the lowest. This can be attributed to the blockage of the pores by functional groups formed during MW heating or/and MW leading to break walls between two micro pores causing enlargement of the pores.

The adsorption of MB is good tests for the ability of AC on removing of dyes from their aqueous solutions. Methylene blue adsorption studies are widely used for the evaluation of adsorbents because this dye can be viewed as a model for visible pollution and is an indicator of mesoporosity [20,22,23].

From Table 5 it could be seen that adsorption of MB was similar to that observed with the adsorption of iodine, where SA_{MB} of AC_S was the highest. This is for MB is a cationic dyes, and steam activation provides carbon surface with some acidic groups, thus interaction increased between these groups and the MB molecules. As a result, the adsorption increases. In contrast, thermal activation and MW heating may decrease the acidic groups, thus adsorption of MB decreases [24].

The SA_{MB} values were lower than those of SA_{I2}. Two reasons could be responsible for this phenomenon, the first reason is the large molecular size of the MB molecule, and therefore, the penetration of solute into the pores is very difficult, leading to earlier saturation of the adsorbent surface. The second reason relates to the aggregation effect, since the MB molecule tends to be adsorbed in the form of ionic micelles from the aqueous solution and its aggregation number is 2, whereas I_2 is a neutral molecule and its aggregation number is 1 [20, 21, 26]. Bestani et.al prepared activated carbons from desert plant and found that under similar conditions of preparation, SA_{I2} was higher than that of MB [22].

3.3 Adsorption Isotherms:

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose [27].

The adsorption isotherms, which represent the relationship between the equilibrium concentration and the adsorbed quantity, of the ACs have been determined using I_2 and MB as solutes, and these are shown in Figures 5 and 6.

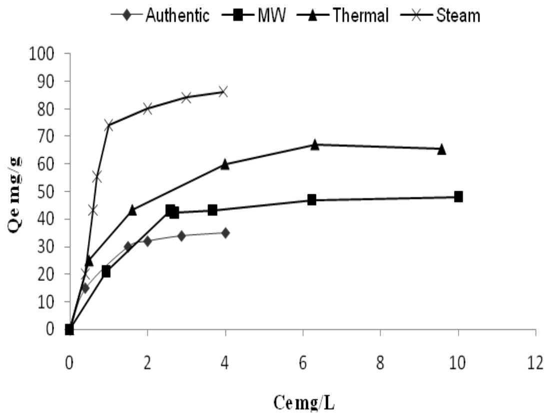

Figure5: Adsorption isotherm of MB on the produced ACs.

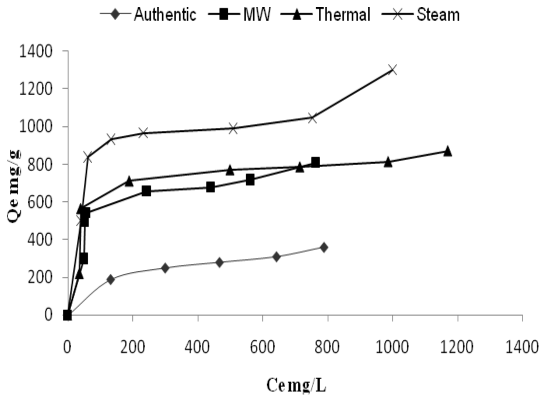

Figure6: Adsorption isotherm of I_2 on the produced ACs.

These figures were coinciding to Langmuir isotherms, according to Giles classification [21]. These types of isotherms were fitted to L_2 and L_3 types. In this type of isotherm, the initial curvature shows that, as more sites in the adsorbent are filled, it becomes increasingly difficult for a bombarding solute molecule to find a vacant site available. This implies either that the adsorbed solute molecule is not vertically oriented or that there is no strong competition from the solvent. The types of systems which give this curve do in fact fulfill these conditions. Thus they have one of the following characteristics: (1) the adsorbed molecules are most likely to be adsorbed flat; or (2) if adsorbed end-on, they suffer little solvent competition. Examples of (2) are (a) systems with highly polar solute and adsorbent, and a non-polar solvent, and (b) systems in which nonfunctional ionic substances with very strong intermolecular attraction are adsorbed from water by ion–ion attraction. It is possible that in these cases (systems b) the adsorbed ions may have become associated into very large clusters as adsorption took place [20, 21].

The adsorption isotherms of I_2 and MB of our samples showed the presence of both mesoporosity and micro porosity in the structure of the prepared ACs, this was detected from the adsorption isotherms which showed the ability of the ACs on removing I_2 from their aqueous solution with highly quantities as compared with MB, this may be due to the large molecular size of MB molecule as compared with I_2 molecule and also as we mentioned formerly that MB adsorbed in form of aggregate (n = 2), so they cannot enter only the pores that match their size. Consequently, we can say that our samples have mixed meso and micro pores in their structures [20, 26].

4. Conclusion

The main points that can be concluded from our study:

1. Waste tires and tubes are good starting materials for activated carbon production. This will help to reduce huge quantities of what it could be a media for insects breading.
2. Activated carbon of good adsorptive capacity can be obtained from such waste.
3. Activated carbon produced via steam activation was the best sample. This was concluded from its highest SA measured by iodine adsorption.
4. The produced ACs also showed the presence of mesoporosity. This may mean that our samples are micro porous in addition to devolved mesoporosity.

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تعيين المساحة السطحية للكاربون المنشط المنتج من نفايات الإطارات عن طريق امتزازه من المحلول

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الملخص:

توضح الدراسة التالية إمكانية إنتاج أنواع مختلفة من الكاربون المنشط من خليط نفايات الإطارات والأنابيب. وقد تم إجراء الانحلال الحراري للخليط عند درجات حرارية مختلفة هي: (٤٠٠–٥٠٠ ^{o}م) لمدة ساعتين للحصول على الظروف المناسبة للدراسة. وقد تبين من خلال الدراسة أن المادة شبه الكاربونية المنتجة بالانحلال الحراري عند ٥٠٠^{o}م كانت هي الأفضل، وعليه استخدمت لإنتاج عينات مختلفة من الكاربون المنشط. لذلك تم تحويل هذه المادة شبه الكاربونية المذكورة من خلال طرق مختلفة من التنشيط مثل التنشيط الحراري والبخاري عند ٨٠٠ ^{o}م لمدة ساعتين، وكذلك التسخين بواسطة المايكروويف عند ٤٥٠ واط لمدة أربع دقائق.

تم استخدام تقنية الامتزاز من المحلول لتحديد المساحات السطحية للفحوم المنتجة باستخدام اليود وصبغة المثيلين الزرقاء كمواد ممتزة. وأظهرت الفحوم المنتجة وجود المسامات الدقيقة مع وجود بعض المسامات الانتقالية. وقد تم استنتاج ذلك من خلال قيم المساحة السطحية العالية لامتزاز اليود مقارنة بامتزاز صبغة المثيلين الزرقاء. وقد استخدمت كل من أنماط لانكماير وفرندلج لتحليل نتائج الامتزاز. وأظهرت النتائج أن نمط لانكماير كان هو أكثر ملائمة في تحليل نتائج الامتزاز للفحوم المحضرة، وان نتائج ايزوثرم الامتزاز كانت متطابقة مع نمط لانكماير من الامتزاز طبقا لتصنيفات غيلز للامتزاز والتي تشير إلى وجود المسامات الدقيقة.