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Evaluation and Characterization of Activated Carbons Prepared from Rice Hulls and Rice Straw.

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Evaluation and Characterization of Activated Carbons Prepared from Rice hulls and Rice Straw

تقييم وتوصيف الكربون النشط المحضر من قش وسرسة الأرز

By

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ملخص البحث:

فى هذا البحث أستخدمت تجارب معملية على إدمصاص الميثيلين الأزرق من محاليله المائية عند ٣٠°م بواسطة عينات من الكربون المحضرة من قش وسرسة الأرز والمحتوية علي أقل كمية ممكنة من الشوائب الغير عضوية لتقييم وتوصيف عينات الكربون المذكورة.

ومن نتائج هذه التجارب وجد أن زمن التماس اللازم للوصول لحالة الإتزان بين الصبغة بالمحلول والمدمصة على المادة المختبرة يتراوح بين ٢٠، ٥٠ دقيقة إعتمادا على الكيفية التى تم بها تحضير الكربون ومثل هذه القيم تدل على أن عملية الإدمصاص ليست إدمصاص فيزيائى بحت بل مصحوبة بعمليات تبادل أيونى وإرتباط كيميائى. كما لوحظ أن هناك تطابقا ملموسا بين منحنيات الإتزان للإدمصاص المستنتجة من تلك التجارب والمنحنيات القياسية المناظرة لكل من لا نجمير وفريندليش أما كمية الميثيلين الأزرق القصوى المدمصة بعينات الكربون المختبرة فقد إختلفت إعتمادا علي حدوث عملية المعالجة القاعدية على الرماد المتبقى من الحرق أو الكربنة للقش والسرسة أو عدم حدوثها وعلى نوع العامل المنشط المستخدم وكميته.

وقد إحتوى البحث على دراسة تكلفة مقارنة لإزالة كيلو جرام من الصبغة بين الكربون المحضر من الحرق العادى للسرسة والقش والكربون التجارى النشط إستنادا على المقدرة على الادمصاص فقط هذا ونتائج هذا البحث تبدو شيقه ومشجعه للغاية.

ABSTRACT :

The adsorption of methylene blue from equeous solutions onto some activated carbons prepared from rice hulls and rice straw with the minimum possible amounts of inorganic ash at 30°C was used to evaluate and characterize these carbons. From the sorption data, values of contact time needed to reach adsorption equilibrium were found to lie between 20 minutes up to 50 minutes depending upon how the tested carbon was prepared from rice hulls or rice straw. This suggests that a combination of physical adsorption, ion exchange and /or chemical bonding occurs in the sorption process. The determined equilibrium adsorption isotherms were found to conform well with langmuir and Freundlich isotherms. The maximum methylene blue adsorption capacities of these carbons were dependent upon whether the carbonized raw waterials were alkali treated or not and the type and amount of activating agent used. Relative costs of dye removal for carbons prepared through free firing of rice hulls and rice straw and commerical activated carbons based only upon the adsorption capacities are reported. Results obtained are very interesting and promising.

INTRODUCTION :

In the preceding paper [1], study was devoted to prepare carbons from rice hulls and rice straw with the minimum possible amount of inorganic ash. These carbons were prepared from rice hulls and rice straw through carbonization at 400°C for one hour or free firing in open air, alkali treatment of the product and activation of the alkali treated solids by either glycerol or zinc chloride and heating at 500°C for one hour. Table 1gives a summary for the sequence of processes conducted in the preparation of these carbon samples. The aim of the present work is to evaluate and characterize these carbons. The adsorption of methylene blue (MB) from aqueous solutions onto these carbons at 30°C will be used to collect kinetics and equilibrium data needed to determine the equilibrium time for the adsorption of MB onto the prepared carbons, the equilibrium adsorption capacities of these carbons towards MB and the adsorption isotherms for the adsorption processes of MB onto the tested carbons.

Experimental :

Adsorption experiments were divided into, (a) experiments to study the effect of contact time upon the adsorption of MB onto the prepared carbons, and (b) experiments to determine the adsorption isotherms for the prepared carbons. Tests consisted of laboratory-scale, constant temperature, batch adsorption experiments. A MB solution having a concentration of 200 mgl^{-1} and a P^H value of 6.5-7.0 was used. the agitation rate was kept at 400 rpm. The system temperature was kept constant at 30°C. Initial and final MB solutions concentrations were determined spectrophotometrically using Shimadzo UV-Vis. Recording Spectrophotomerter Model UV -160.

a) Contact time experiments :

These experiments were conducted for : (1) Analyzing the reaction rate of the adsorption of MB onto the prepared carbons, (2) Getting a clear idea about the reaction mechanism and the rate-limiting step in the adsorption process, and (3) Determining the maximum contact time needed to reach an equilibrium adsorbate concentration. This time would be the minimum reaction time required to reach equilibrium in the subsequent experiments for determining adsorption isotherms.

In this respect a series of experiments were conducted to determine the change in concentration of the MB solution in contact with the tested adsorbent as a function of time. Batch adsorption experiments were conducted, in each experiment 100 ml from the MB solution and 0.2 gm of the tested adsorbent were mixed in a reaction bottle. The mixture was shaken for the test period which was ranging from 5 minutes up to 1 hour. After agitation the mixture was filtered, and the residual MB concentration was measured.

b) Adsorption isotherms experiments :

These experiments were conducted to make a complete characterization and evaluation of the prepared carbons compared with

commercial activated carbon (CAC) purchased from the local market. The procedure for conducting these tests had been presented elsewhere [2-4].

Results and discussion :

Effect of contact time on the adsorption of MB onto the prepared carbons :[5-8]

The effect of contact time upon the adsorption of MB onto the tested carbon samples is shown in Figure-1. Results indicated that: (1) The amount of MB adsorbed progressively increases as the contact time increases till reaching the equilibrium distribution of MB between the solid adsorbent and liquid phase. (2) The value of the contact time needed to reach adsorptive equilibrium with the aqueous dye solution is dependent upon the type of carbon tested. Carbons activated by zinc chloride need from 20-30 minutes to reach adsorptive equilibrium depending upon the initial raw material used, while carbons activated with glycerol need from 40-50 minutes to reach adsorptive equilibrium depending also upon the initial raw material used.

(3) Activated carbons prepared from rice straw need less time to reach adsorptive equilibrium than the corresponding activated carbons prepared from rice hulls.

The overall adsorption process is assumed to occur via the following three steps :(1) Mass transfer of MB from the bulk solution to the adsorbent particle surface, (2) Intraparticle diffusion, and (3) adsorption at an interior site. Since all experiments were conducted at high agitation rate (400 rpm) using adsorbents of particle size below 150 μm, completely mixed systems can be achieved. Hence, there is a considerable shear force on the boundary layer which makes the initial resistance to mass transfer fairly low. The third step is usually assumed to happen very rapid. These encourage the assumption that the intraparticle diffusion is the rate limiting step.

The intraparticle diffusion resistance is determined by the force field surrounding the adsorbent particles. This force field depends upon the type of atoms present and their orientation relative to each other. The initial raw material used, type and amount of activating agent used and the activation conditions greatly affects such force fields. This leads to the noticed differences between the tested carbons in the values of contact time needed to reach adsorption equilibrium. Activation with zinc chloride and heating at $500^{o}C$ for one hour had produced an activated carbon with the lowest intraparticle diffusion resistance over the other prepared carbons.

Characterization and evaluation of the prepared carbons :

Figure 2 give the experimental equilibrium curves produced by plotting the amount of MB adsorbed (x/m mg dye g^{-1} adsorbent) versus the equilibrium concentration (C mg dye l^{-1} solution) on arithmetic paper for some representative carbon samples. this figure indicates that :

1- Over the quilibrium concentration range (3-15 mg l-1):

1-1 Both carbonized rice hulls and carbonized rice straw had some adsorptive power towards MB. Removal of silica adds slightly to this adsorptive power while considerable increases in this power are achieved by activation by either glycerol or zinc chloride and heating at 500°C for one hour. These increases almost go parallel with the amount of activating agent used in activation.

1-2 Using the same activation conditions, activated carbons prepared from rice straw are more active than those prepared from rice hulls.

1-3 At equilibrium concentrations higher than 5mg l^{-1}carbon $\overline{SG4}$ has the highest adsorption capacity over the other carbons prepared in this study. The activation process makes the adsorption capacity of this carbon 2.5 folds that of the nonactivated carbon. the adsorption capacity of this carbon is still less by about 5% than that for CAC.

2- Carbon $\overline{SZ4}$ has the same adsorptive capacity of carbon $\overline{SG4}$ at an equilibrium concentration of 5 mg l^{-1}. The adsorptive capacity of $\overline{SZ4}$ exceeds that for $\overline{SG4}$ at equilibrium concentration below 5mg l^{-1}. The inverse is true at equilibrium concentrations higher than 5mg l^{-1}.

3- Adsorbents prepared from the solid residue remained after free firing of rice straw and rice hulls using the same activation procedure have almost the same adsorptive power.

These effects may be attributed to the following :

1- Inorganic ash represents from 17 to 18% of rice straw while it constitutes about 20% of rice hulls, hence more carbon per unit mass is present in carbonized rice straw and in the subsequent adsorbents prepared from it compared with the corresponding adsorbents prepared from rice hulls. This illustrates why adsorbents prepared from rice straw are more reactive than those prepared from rice hulls.

2- Alkali treatment removes some of the silica present, hence the mass of carbon present per gram of the alkali treated solids is correspondingly increased. This leads to the increases in the adsorptive power of the carbonized solids after they were alkali treated.

3- Activation by zinc chloride and heating at 500°C for one hour removes the hydrogen present as HCl instead of its removal as lower hydrocarbons which produced on heating without adding zinc chloride at lower temperatures (< 500°C). Lower hydrocarbons if present readsorb on the carbonized char causing partial blocking of the pores. Also, new pores would be produced due to the dissolution of a fraction of the inorganic matter present by the HCl produced during the activation process.

4- During the activation by glycerol, while the temperature of the furnace thermostat was adjusted at 500°C during the heating step, the temperature of the treated solids inside the furnance can be raised above 500°C due to the burning of some of the glycerol present.

This can lead to opening of new pores and widening the existing pores.

5- On free firing of rice straw and rice hulls, the ease of burning of rice straw than rice hulls leads to more consumption of carbon present in rice straw. Hence the solid residues after free firing of both rice straw and rice hulls appear to contain the same amount of carbon and hence has nearly the same adsorptive capacity.

As shown in Figure 2, the adsorption of MB from aqueous solutions onto the tested carbons at 30°C exhibit curves which are similar to Langmuir isotherms accoridng to Giles classification. Such isotherms are usually indicative of molecules adsorbed flat on the surface. However, other orientations such as edge -on or end-on are not ruled out [9].

Representative plots of m/x versus 1/C for some of the prepared carbons give satisfactory straight lines as shown in Figure 3 indicating that the adsorption process conforms with the following linear from of Langmuir equation:

$$\frac{m}{x} = \frac{1}{ab} \cdot \frac{1}{C} + \frac{1}{b}$$

The best slope, 1/ab, and the intercept, 1/b, of these straight lines were obtained and the Langmuir parameters a and b for each carbon sample tested are computed and listed in Table 2. this table shows that b vaules, the monolayer capacity, are different for the tested carbon samples. The maximum recorded values are for CAC and $\overline{SG4}$. Table 2 also contains the equilibrium parameter, r*, where ($r^* = 1/1+a\,C_o$) values of r* for the tested carbons are less than unity and the minimum values are for carbons activated by zinc chloride indicating that the adsorption process is favourable for all the prepared carbon samples but it is more favourable for carbon samples activated by zinc chloride.

The same data in Figure 2 is represented in logarithmic coordinates to obtain the isotherms in Figure 4. This yield a group of straight lines, thus the adsorption data follow the Freundlich theory which is a special case of Langmuir theory at lower concentratios. Freundlich adsorption isotherm represents the following equation; $x/m = k\,C^{1/n}$. where k, and n are constants, k represents the adsorption capacity for the adsorbent, and the magnitude of the exponent, n, gives an indication of the favourability and capacity of the adsorbent / adsorbate system. Freundlich parameters, n and k were computed from these plots and are given in Table -2.

Table 2 shows that the adsorption capacity (k values) of the tested carbons as well as the ultimate capacity ($k\,C_o^{1/n}$) are noticeably increased by activation. Carbon $\overline{SG4}$ has the greatest ultimate capacity over the other carbons prepared in this study. It is well known that values of n>1 represent favourable adsorption conditions [10]. Data in Table 2 for the adsorption of MB onto the representative carbon samples clearly reflect

that the values of "n" are greater than unity for all the tested adsorbents indicating favourable adsorption of MB onto the prepared carbons. This table also indicates that while values of "n" are dependent upon the activating agent, they are independent upon the amount of the activating agent used.

The previous analysis reveals that the experimental data correlates well with the Langmuir and Freundlich isotherms. Although the adsorption is more favourable with carbon samples activated by zinc chloride, activation by glycerol produces carbons of higher adsorptive capacities (see Table -2). Keeping in mind that the price of glycerol (per kilogram) is about half that for zinc chloride and activation by glycerol adds more to the mass of the produced carbon, activation by glycerol is recommened for use in such situations.

Comparison of commerical activated carbon with activated carbons prepared by activating the solid residue after free firing of rice straw and rice hulls by glycerol:

Based upon the previous results the ultimate capacity and the cost of removing 1 kg of MB of initial concentration 200 mg l^{-1} at 30° C for the activated carbons prepared by activating the alkali treated solid residue remained after free firing of rice hulls and rice straw by 30% glycerol and heating at 500°C for one hour is compared with the corresponding value for commerical activated carbon purchased from the local market at 16.8 L.E. per kilogram. this comparison is given in Table 3 which indicates that the cost of removing 1 kg MB for the prepared carbons from rice straw and rice hulls is less by about 60% than that for CAC. This figure may be greatly improved when taking into consideration the feasibility of using rice straw and rice hulls as fuels then using the soild residue after firing for preparing activated carbons and commercially using the sodium silicate produced from the alkali treatment process.

Although the cost of removing 1kg MB for RS and RH is the lowest one, huge volumes of these materials are required compared with the other adsorbents due to their low densities (from 100-130 kg m^{-3}). This will cause many problems during the storage, handling and use of these materials.

CONCLUSION :

The adsorption of methylene blue from aqueous solution onto some activated carbon samples prepared from rice hulls and rice straw and having the minimum possible amounts of inorganic ash was investigated at 30°C to evaluate and characterize these carbons. The experimental results indicate the following :

1- The equilibrium contact time lies between 20 and 50 minutes depending upon the raw material and the type of activating agent used.
2- Carbonized rice hulls and carbonized rice straw show some adsorptive power towards the adsorption of methylene blue.

Removal of silica adds slightly to this adsorptive power while noticeable gains are recorded when activating the alkali treated solids by either glycerol or zinc chloride and heating at 500°C for one hour. The adsorptive power rises with the increase in the amount of activating agent added.

3- Rice straw gives carbons of higher adsorptive capacities.
4- Adsorption of methylene blue onto the tested carbons is not a pure physical adsorption process but ion exchange and /or chemical bonding also take place. The interaparticle diffusion seems to be the rate limiting step in this adsorption process.
5- The determined equilibrium adsorption isotherms correlates well with Langmuir and Freundlich isotherms and all isotherms were shown to be favourable.
6- Although the adsorption of methylene blue appears to be more favourable with carbon samples activated by zinc chloride, activation by glycerol produces carbons of higher adsorptive capacities.
7- The described procedure for preparing activated carbon seems to be promising when using the solid residue after using rice hulls and /or rice straw as fuels, utilizing sodium silicate produced from the alkali treatment process and activating the alkali treated solid by glycerol.

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Table 1: A summary for the sequence of processes conducted in the preparation of the tested carbon samples .

Sample symbol	Raw material		Preparation Procedure				
			Carbonization		Alkali treatment *	Activation	
	Rice hulls	Rice straw	A	B		1	2
RH	✔	-	✔	-	-	-	-
$\overline{RH}$	✔	-	✔	-	✔	-	-
SRH	✔	-	-	✔	-	-	-
$\overline{SRH}$	✔	-	-	✔	✔	-	✔
HR	✔	-	-	✔	-	-	✔
SZ	✔	-	-	✔	✔	✔	-
SG	✔	-	✔	-	✔	-	✔
RS	-	✔	✔	-	-	-	-
$\overline{RS}$	-	✔	✔	-	✔	-	-
SRS	-	✔	-	✔	-	-	-
$\overline{SRS}$	-	✔	-	✔	✔	-	✔
SR	-	✔	-	✔	-	-	✔
$\overline{SZ}$	-	✔	✔	-	✔	✔	-
$\overline{SG}$	-	✔	✔	-	✔	-	✔

A- Carbonization at 400 °C for one hour,

B- Free firing in open air.

1- Activation with glycerol and heating at 500 °C for one hour,

2- Activation with zinc chloride and heating at 500 °C for one hour.

* Alkali treatment at 100 °C for two hours with 0.4 of the mass of the tested material pure caustic soda.

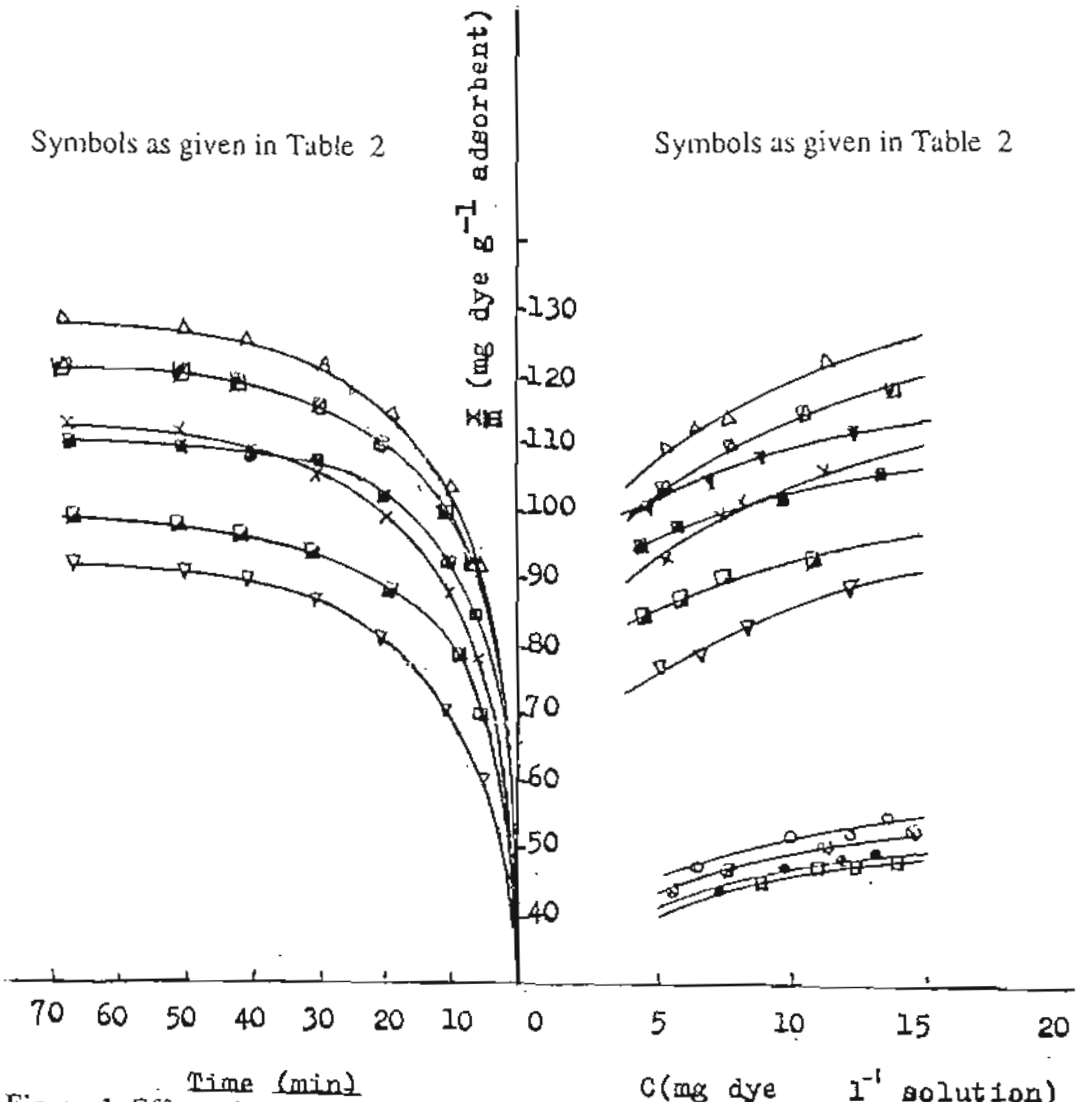

Figure 1: Effect of contact time upon the adsorption of methylene blue onto the tested carbons.

Figure 2: Equilibrium isotherms for the adsorption of methylene blue onto the tested carbons

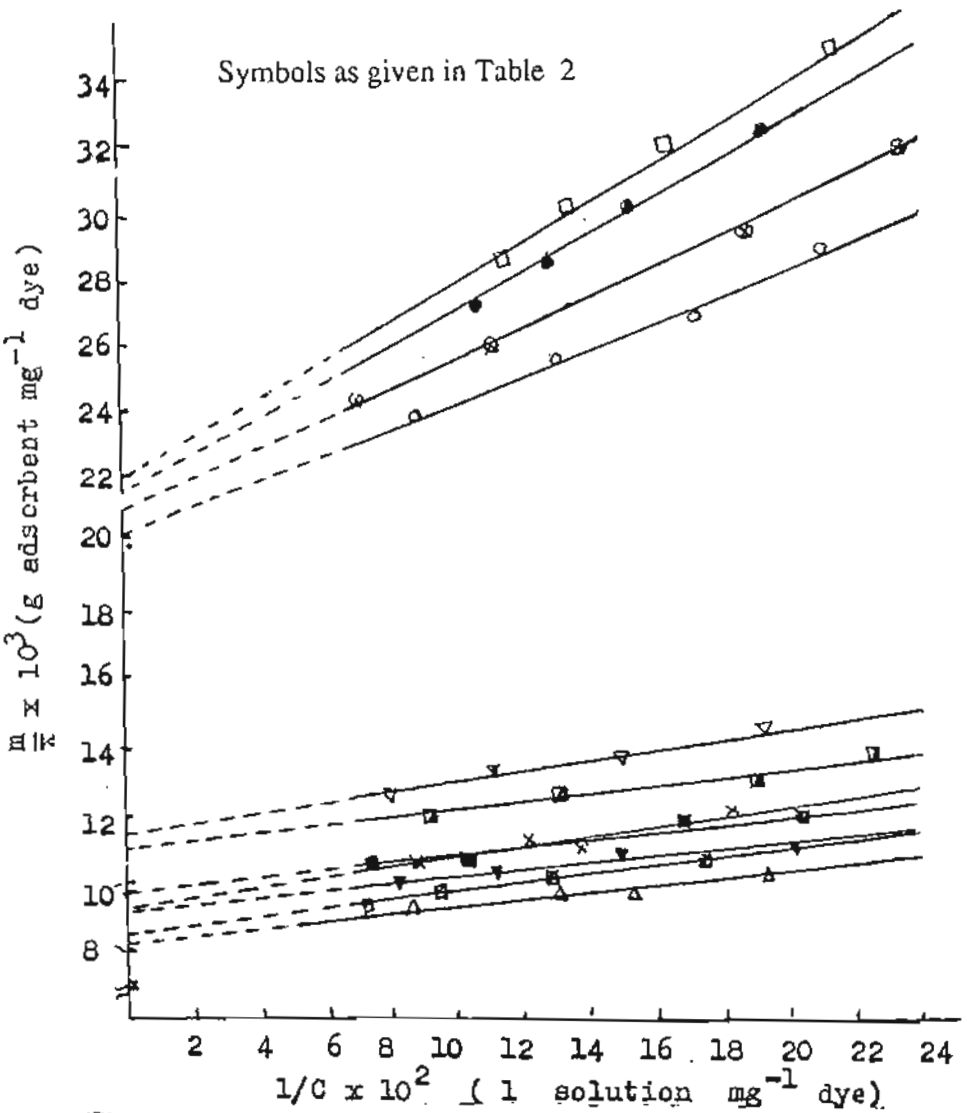

Figure 3: Application of langmuir equation to methylene blue adsorption at 30 ^{o}C onto the tested carbons.

Table 2: Analysis of Langmuir and Freundlich isotherms for the adosrption of methylene blue onto the tested carbon samples

Type of adsorbent	Symbol used in drawings	Langmuir parameters			Freundlich parameters			
		a ($l\,mg^{-1}$)	b ($mg\,g^{-1}$)	r*	k ($mg\,g^{-1}$)	n ($g\,l^{-1}$)	$\frac{1}{n}$	$KC_0^{\frac{1}{n}}$
CAC	△	0.71	125	0.007	74.5	6	0.167	180.2
$\overline{SG4}$	▨	0.65	119.05	0.0076	67.9	5.5	0.182	177.9
SG4	×	0.577	111.7	0.0086	62	5.5	0.182	162.5
$\overline{SG1}$, $\overline{SRH}$, $\overline{SRS}$	▽	0.605	89.29	0.0082	50	5.5	0.182	131
$\overline{SZ4}$	▼	0.865	111.1	0.00575	72	7.1	0.14	151.2
SZ4	■	0.832	104.5	0.00597	67.2	7.1	0.14	141.1
$\overline{SZ1}$	◪	0.855	92.5	0.0058	60	7.1	0.14	126
$\overline{RS}$	○	0.493	49.2	0.01	25.8	4.56	0.2	78.5
$\overline{RH}$	⊗	0.46	47.1	0.0106	23.6	4.567	0.219	71.8
RS	●	0.41	46	0.012	22.3	6.83	0.146	48.36
RH, SRH, SRS	□	0.38	44.9	0.013	21.9	6.61	0.15	48.48

Initial dye concentration = 200 mg l^{-1}

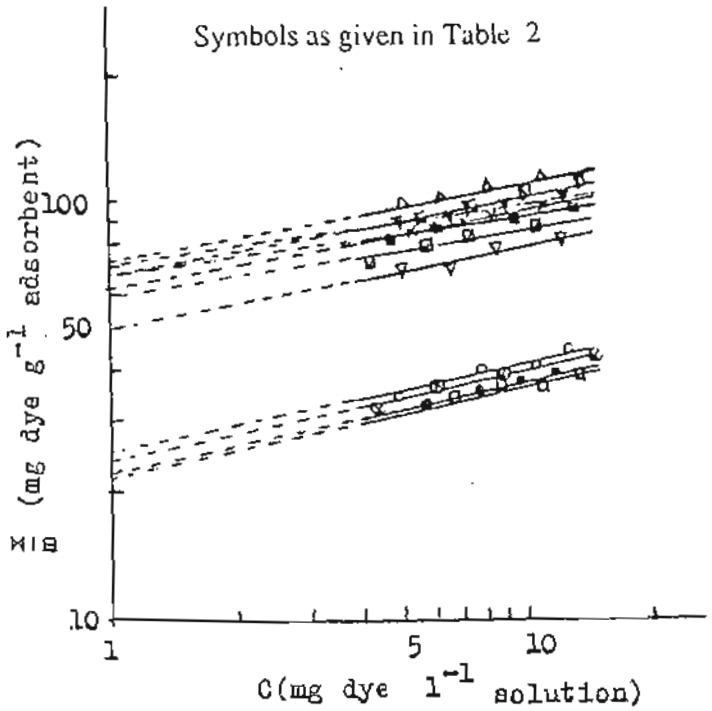

Figure 4: Application of Freundlich equation to methylene blue adsorption at 30 °C onto the tested carbons.

Table 3: Comparison between commerical activated carbon and carbon prepared by activating the alkali treated solid residue after free firing of rice straw or rice hulls by 30% glycerol and heating at 500 °C for one hour (SRS or SRH).

Adsorbent	x/m mg dye g^{-1} adsorbent	Cost per kg adsorbent*	Mass (kg) of adsorbent to remove 1 kg of dye	Cost of removing 1 kg of dye (L.E)
CAC	180.19	16.80	5.55	93.24
SRS or SRH	131.0	4.72	7.63	36.03
RS, RH**	48	1	21	21

*Every Kilogram of solid residue after free firing of rice hulls or rice straw needs about 0.4 kg solid caustic soda at L.E. 1.55 per Kg, 0.27 Kg glycerol (industrial grade) at L.E. 4.2 per kg and 6 KWh at L.E. 0.2 per KWh. Extra expenses are assumed to be 60%.

** Every 1kg RS or RH costs L.E.1 (cost of material and its handling, washing and drying expenses)