

Preparation of Activated Carbons with the Minimum Possible Amount of Inorganic Ash from Rice Hulls and Rice Straw

تحضير كربون نشيط يحتوى على أقل كمية ممكنة من الرماد الغير محضووع من

سوسة وقش الأرز

By

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ملخص البحث :

عملية كبرنة قش الأرز وسوسة الأرز بعد غسلها جيدا بالماء ينتج عنها رماد يتكون أساسا من الكربون والسليكا والمعالجة القاعدية لهذا الرماد عند 100م يزدى لإذابة جزء من السليكا وقد وجد أن كمية السليكا المذابة تعتمد على درجة حرارة عملية الكبرنة وعلى كمية الصودا الكاوية المضافة وزمن المعالجة القاعدية بينما تعتمد كمية الكربون الموجودة في الرماد على زمن ودرجة حرارة عملية الكبرنة وكذلك على مدى توافر الهواء أثناء عملية الكبرنة . أما عملية التنشيط فقد تمت بإضافة كلوريد الزنك أو الجلسرول لنتائج المعالجة القاعدية الصلب وبعد خلطهما جيدا يتم التسخين عند 500م لمدة ساعة . هذا والنشاط الملحوظ لبعض عينات الكربون التي تم تحضيرها بمقاسا بالمقدرة على إزالة لون الميثيلين الأزرق ومقارنا مع الكربون النشط التجارى يبين إمكانية تحضير كميات كبيرة من الكربون النشط من قش وسوسة الأرز المتوافرين محليا بكميات هائلة وليس لهما سوى بعض الاستخدامات المحدودة جدا .

ABSTRACT :

The carbonization of dirt-free rice hulls and rice straw results in the production of ash which is mainly carbon and silica. The alkali treatment of this ash at 100°C removed some of the silica present. The amount of silica removed was dependent upon the carbonization temperature, the amount of caustic soda added and the duration of the alkali treatment process, while the amount of carbon present was greatly affected by the carbonization time and temperature and air availability during carbonization. Activation was done through addition and thorough mixing with either zinc chloride or glycerol followed by heating at 500 °C for one hour. The higher activity of some of the prepared carbons determined through the decolorizing power technique and compared with commercial activated carbon, suggests the possibility of manufacturing large quantities of activated carbon from rice straw and rice hulls which are available locally in huge amounts with very limited uses.

Introduction :

Many raw materials can produce activated carbon. The main differences between these products are their residual ash content, their physical characteristics, and their activity . Agricultural wastes represent an important source for the production of activated carbon particularly for countries like Egypt where these wastes are available in huge quantities at very low costs with minor useful uses. Many studies had been conducted for the preparation and characterization of carbons from sawdust, olive stones, almond shells, ... etc. Activation of carbons produced are carried out either by chemical activation with certain chemicals or by physical activation with oxidizing gases such as steam or carbon dioxide [1-5] .

For agricultural wastes, inorganic ash forms 5 to 20 percent of the total initial mass of the raw material and its mass represents not less than 25% of the mass of the solid residue after carbonization depending upon the carbonization conditions. Silica constitutes about 94% of such ash while the remainder are alkali and basic alkali metal oxides [6,7] . These oxides adds to the mass of carbon produced without any provable benefit. They may affect the activation and adsorption processes, so it is better to remove as much as possible of this ash before the activation process.

To the author knowledge inorganic ash was not considered in the work previously reported in the literature [1-5]. In this paper, experimental methods and results are reported on the preparation and evaluation of activated carbons with the minimum possible amount of inorganic ash. Raw materials used are rice hulls and rice straw which are locally available in large quantities at central collection points at very low cost with minor useful uses.

Experimental details :

The experiments were conducted on a laboratory scale and employed the following steps:

- 1- **Preparation of the raw materials :** Raw materials (rice hulls and rice straw) were thoroughly washed with water to remove fines and dirt, dried and packed in clean dry containers. Rice straw was torn into shreds before use while rice hulls were used without crushing.
- 2- **Carbonization :** It is well known that for a certain mass of a carbonaceous material, the mass of carbon remained after carbonization depends upon the heating rate, carbonization temperature and duration, and the atmosphere in which the carbonization process is conducted [6-10] . In the present work the heating rate was kept constant at 10°C/min. as recommended in the literature for similar situations [8] . The effect of carbonization

temperature was studied in the range 350-750 °C while keeping the carbonization duration constant at one hour. The effect of carbonization duration was studied at 400°C.

Carbonization was conducted in a closed muffle furnace . The volume of the furnace chamber was $25 \times 10^{-4} \text{ m}^3$ while the bulk volume of the raw material sample was kept around $30 \times 10^{-5} \text{ m}^3$ The carbonized materials were ground by a home grinder to a particle size less than 150 μm and stored for subsequent use.

- 3- **Burning in open air :** In these tests samples of 150 grams of rice hulls or rice straw were burnt in open air either completely by using a direct flame till obtaining a white ash or fired as usual after spraying some kerosene (about 5-ml) to start firing . After burning, the solid residue of the tested sample was ground to a particle size less than 150 μm , weighed and stored.
- 4- **Removal of silica :** This was conducted by treating the solid residue remained after carbonization or free burning with caustic soda solution at 100°C for a certain period of time where some of the silica present reacts with caustic soda to produce soluble sodium silicate . The rate of this reaction depends upon the state of the silica present (either amorphous or crystalline) and hence upon the carbonization temperature, the particle size of the solid reactant, the mass of caustic soda added per gram of the solid reactant (r) , the duration of the reaction and reaction temperature [13]. The reaction temperature was kept constant at 100°C due to the available facilities while the particle size of the solid reactant was kept below 150 μm . The effect of the other mentioned factors upon the amount of silica removed from the carbonized material were studied . Values of (r) used were 0.1, 0.2, 0.4 and 0.6 while the reaction durations studied were 1,2,4 and 6 hours .

In each experiment about five grams from the carbonized material were placed in a 500-ml flat -bottom flask fitted with a dropping funnel, a thermometer and a reflux water condenser. The alkali solution was made by dissolving a mass of ($5r$) grams solid caustic soda in 200 ml distilled water. This solution was then added to the contents of the reaction flask the flask was heated and maintained at 100°C for the period of the reaction then its contents were filtered under reduced pressure. The filter cake was mixed with an excess of distilled water with vigorous stirring for ten minutes and filtered . Washing was repeated until the pH of the wash water reaches 7-7.5 The solid residue was then dried and weighed to find the mass of the carbonized material reacted with caustic soda under the specified test conditions.

5- **Activation** : Activation was accomplished by treating the tested solid material with chemical reagents then heating at 500°C for one hour . The activating agents employed were zinc chloride or glycerol. Zinc chloride activated samples were prepared by impregnating the solid residue previously obtained with a certain mass of 60% zinc chloride solution followed by thorough mixing, drying and heating at 500°C for one hour in a limited volume of air. The resulting solid material was washed with dilute hydrochloric acid and then twice with distilled water. The product was then dried, ground to a particle size below 150µm and stored [9] Four zinc chloride activated samples designated SZ1, SZ2 , SZ3 and SZ4 were prepared from rice hulls. In these samples masses of zinc chloride added per gram of non-activated sample were 0.25, 0.5, 1, and 2 grams respectively. Similar samples designated $\overline{SZ1}$, $\overline{SZ2}$, $\overline{SZ3}$, and $\overline{SZ4}$ were prepared from rice straw by the previous described procedure.

Glycerol activated samples were prepared by impregnating the tested solid samples with certain masses of 50% glycerol solution followed by thorough mixing, drying and heating at 500°C for one hour in a limited volume of air [11, 12].

Four glycerol activated samples designated SG1, SG2, SG3 and SG4 were prepared from rice hulls. In these samples masses of glycerol added per gram of non-activated samples were 0.05, 0.1, 0.2 and 0.3 grams respectively. Similar samples designated $\overline{SG1}$, $\overline{SG2}$, $\overline{SG3}$ and $\overline{SG4}$ were prepared from rice straw by the same procedure .

Samples RS and RH designates the solid residue remained after carbonizing rice straw and rice hulls at 400°C for one hour respectively without any further treatment, while samples \overline{RS} and \overline{RH} represent the alkali treated carbonized rice straw and rice hulls without activation. During the alkali treatment process the temperature was kept constant at 100°C, (τ) was equal to 0.4 and the reaction duration was 2 hours .

Samples SRS and SRH were prepared from the solid residue remained after the free firing of rice straw and rice hulls respectively without any further treatment . Samples \overline{SRS} and \overline{SRH} were prepared from SRS and SRH by the same procedure previously outlined in the preparation of SG4 and SG4.

Samples SR and HR were prepared by activating the solid remained after free firing of rice straw and rice hulls with 0.3 of its mass glycerol followed by heating at 500°C for one hour . In the following, these samples are termed as carbons for simplicity.

Table 1: gives a key for the carbon samples prepared in this study .

6- Determination of decolorizing power of the prepared carbons:

This was done in accordance with the Indian Standards [14]. In this respect methylene blue (MB) solution was prepared by dissolving 0.15 g of MB (solid) in 100 ml of water. The procedure was weighing about 0.1 g of the tested carbon and transfer to a 50-ml glass stoppered flask. Add from a burette 10ml of MB solution and shake for 5 minutes. After the first 10 ml are decolourized continue to add MB solution (1 ml at a time) till the blue colour does not disappear for 5 minutes. Decolorizing power of the tested carbon is expressed in terms of milligrams of MB adsorbed per/gram of the tested carbon.

Decolourising power = $1.5 \frac{V}{m}$ (mg MB g⁻¹ carbon) where v= volume in ml of MB solution consumed, and m=mass in grams of the tested carbon taken for the test.

In some cases incomplete decolorization were noticed for the first 10ml MB solution. In these cases initial and final colours were measured colorimetrically as described in details else where [9]. The decolorizing power is calculated as the mass of MB removed (in mg) per gram of the tested carbon.

Results and discussion :

1- Carbonization of rice hulls and rice straw :

Figure 1 shows the effect of carbonization conditions upon the amount of solid residue remained after carbonization for rice hulls and rice straw. This figure reveals that:(1) The mass of solid remained after carbonization was dependent upon the type of raw material used in addition to carbonization duration and temperature, (2) More than 50% of the original mass of both raw materials were decomposed when carbonizing at 400°C for one hour. This percentage increases with the increase in carbonization temperature and/or carbonization duration, (3) About 20% and 17.6% of the original mass of rice hulls and rice straw respectively were remained when carbonizing for more than six hours at 400°C or when carbonizing for one hour at temperatures exceeding 750°C.

When burning rice hulls and rice straw completely in open air, the masses of ash remained represent about 19.8% and 17.1% of the original masses respectively. This result is compatible with the relevant results in the literature which indicate by chemical analysis that about 95% of this ash is pure silica while the remainder are metal oxides like Na₂O, K₂O and Mg O [5,6,7] This means that the carbonaceous matters present in rice hulls and rice straw are almost completely consumed on heating at temperatures above 350°C for a certain period of time that depend upon the carbonization temperature. In the contrary preliminary tests proved that some of the tested raw materials had remained uncarbonized either when heating for one hour at temperatures below 375°C or when heating at 400°C for less than 1 hour.

According to these results, carbonization of rice hulls and rice straw at 400°C for one hour seems to be suitable for obtaining reasonable amounts of carbon in the solid residue remained after carbonization .

2- **Removal of silica :** Figure 2-a shows the effect of the mass of caustic soda added per gram of the carbonized solid material (r) upon the mass of this material reacted with caustic soda at 100°C during two hours Figure 2-b gives the effect of the duration of the reaction between caustic soda and the carbonized materials at 100°C when (r) is kept constant at 0.4 upon the mass reacted from these solid materials.

Figure -2 reveals the following: (1) Under the same test conditions, for one gram of the carbonized material the mass reacted with caustic soda is greater for rice hulls than for rice straw A noticeable difference between the mass reacted from these materials is clear over the reaction conditions tested. such a difference grows with the increase either in the mass of caustic soda added per gram of the carbonized material (r) when the reaction duration is kept constant at 2 hours or in the reaction duration when (r) is kept constant at a value of 0.4. This difference reaches an almost constant value of 2.5% when (r) equals to/or greater than 0.4 or when the reaction duration exceeds two hours.

- 2) About 12.5% of the mass of carbonized rice hulls is removed when reacting for two hours at 100°C with an alkali solution containing 0.4 of its mass pure caustic soda.
- 3) Increasing either the mass of caustic soda added per gram of the carbonized material (r) beyond 0.4 while keeping the reaction duration at 2 hours or the reaction duration than two hours while keeping (r) equals to 0.4 adds negligible increases in the masses of the carbonized materials removed by the alkali. the above effects may attributed to the previous deduction that the amount of inorganic ash per gram of the carbonized material is greater for rice hulls than that for rice straw. As caustic soda reacts with the silica present in the inorganic ash, the mass removed from one gram of carbonized rice hulls by the reaction with caustic soda at 100°C for two hours exceeds that removed from one gram of carbonized rice straw under the same test conditions.

Figure 3 gives the effect of carbonization temperature upon the amount of the carbonized material reacted with the alkali solution and dissolved in it. This figure reveals that when either rice straw or rice hulls carbonized at 400°C for one hour is reacted with 0.4 of its mass pure caustic soda in solution at 100°C for two hours, about 10% and 12.5% of their original masses are reacted and dissolved in the alkali solution. A rapid decrease in the mass of solid reacted with caustic soda accompanies

the rise in the carbonization temperature. This means that the rise in the carbonization temperature leads to a growth in the difficulty of dissolving silica present by the caustic soda added. This can be attributed to the fact that with the rise in the carbonization temperature, changes in the state of the silica present take place. This was proved by DTA elsewhere [10], which gives that amorphous silica is produced when carbonizing below 450°C while crystalline silica is produced at higher carbonization temperatures.

3- Decolorizing powers of the prepared carbons :

Preliminary experiment proved that ashes obtained by complete firing of rice hulls and rice straw in open air and those obtained by heating these raw materials either over 750°C for one hour or at 400°C for more than 6 hours were nearly inactive adsorbents for MB. Other solids prepared from rice hulls and rice straw under other conditions than those previously mentioned are active adsorbent for MB. Figure 4 gives the decolorizing power of these carbons relative to that measured for commercial activated carbons (CAC) under similar test conditions. This figure indicates the following:

- 1- All carbons prepared in this study have some decolorizing power towards MB. Carbon SG4 has the best decolorizing power while carbon SRH has the worst one.
- 2- Alkali treatment adds slightly to the decolorizing power of the carbonized raw materials. This can be attributed to the fact that mass of carbon per gram of the carbonized material is greater after the alkali treatment process than prior to it.
- 3- Noticeable increases in the decolorizing power of the alkali treated carbonized materials were recorded after activation by either glycerol or zinc chloride and heating at 500°C for one hour. The decolorizing power rises as the amount of activating agent added increases.
- 4- Activation by glycerol produced more active carbones than those produced when activating by the same or even more masses of zinc chloride. This may be due to the differences in the characteristics of the force fields surrounding the prepared carbon particles which depend upon the type of atoms present and their orientation relative to each other. Type and mass of activating agent used determine to a great extent the characteristics of these fields.

Conclusion :

Preparation of activated carbons with the minimum possible amount of inorganic ash from rice hulls and rice straw was studied . From the experimental results the following can be concluded:

- 1- Carbonization of rice hulls and rice straw at 400°C for one hour seems to be suitable for obtaining reasonable amounts of carbon in the solid residue remained after carbonization.

- 2- About 12.5% and 10% of the mass of carbonized rice hulls and carbonized rice straw respectively are dissolved when reacting for two hours at 100°C with caustic soda solution containing 0.4 of the mass of the carbonized material pure caustic soda.
- 3- A rapid decrease in the mass of the inorganic ash reacted with the caustic soda solution accompanies the rise in the carbonization temperature over 400°C.
- 4- Carbonized rice straw and carbonized rice hulls have some decolorizing power towards MB. Removal of some of the inorganic ash present by the alkali treatment adds little to this decolorizing power. Noticeable gains in the decolorizing power can be achieved by activation using either zinc chloride or glycerol and heating at 500°C for one hour.
- 5- The decolorizing power rises as the amount of activating agent added increases.
- 6- Activation by glycerol produces more active carbons than those produced when activating by the same or even more masses of zinc chloride.
- 7- Using the same preparation procedure, carbons prepared from rice straw are more active than those prepared from rice hulls.
- 8- Carbons with reasonable decolorizing powers can be prepared from solid residues remained after free firing of rice hulls and rice straw in open air.

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Table 1: A key to the prepared carbon samples

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

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.

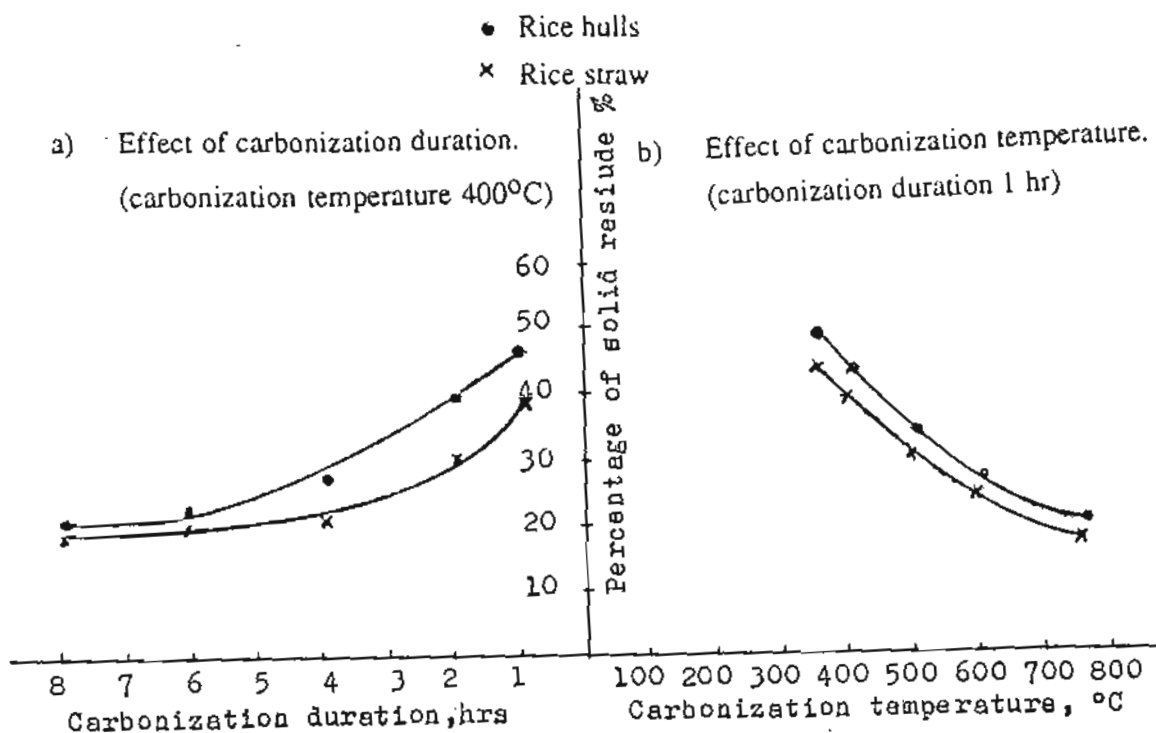


Figure 1: Effect of carbonization conditions upon the amount of solid residue remained after carbonization for rice hulls and rice straw.

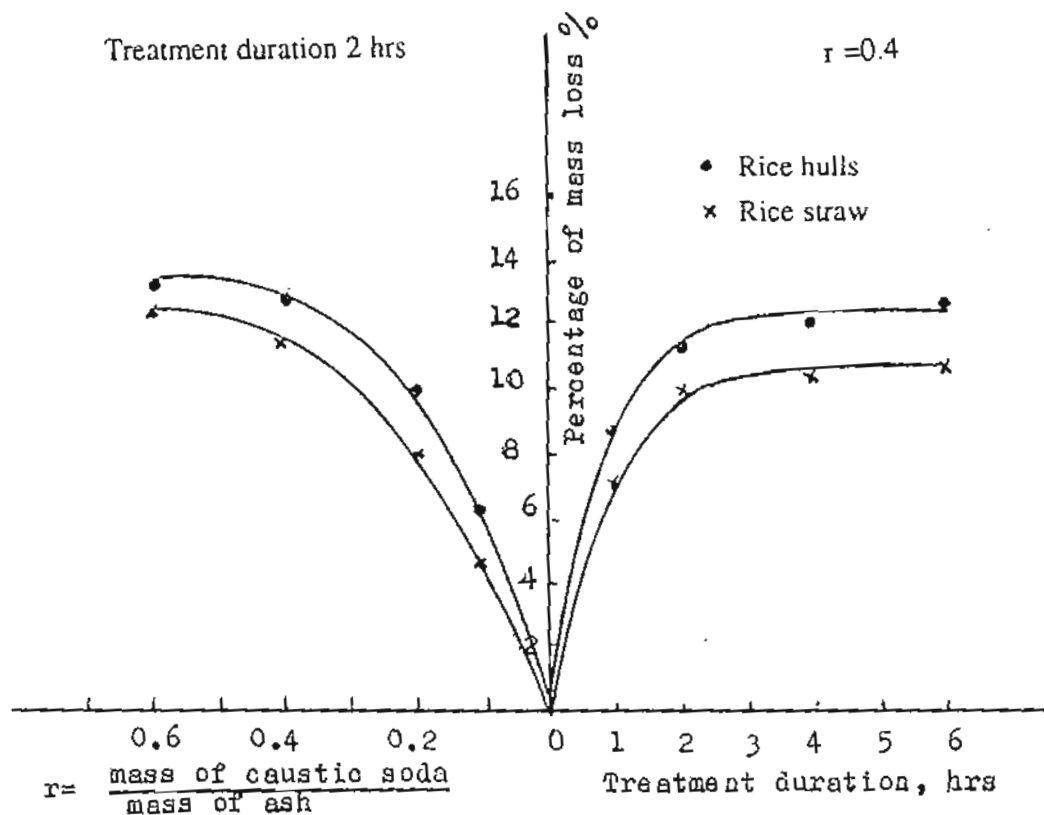


Figure 2 : Effect of mass of caustic soda added and treatment duration upon the removal of silica from the carbonized rice hulls and rice straw.

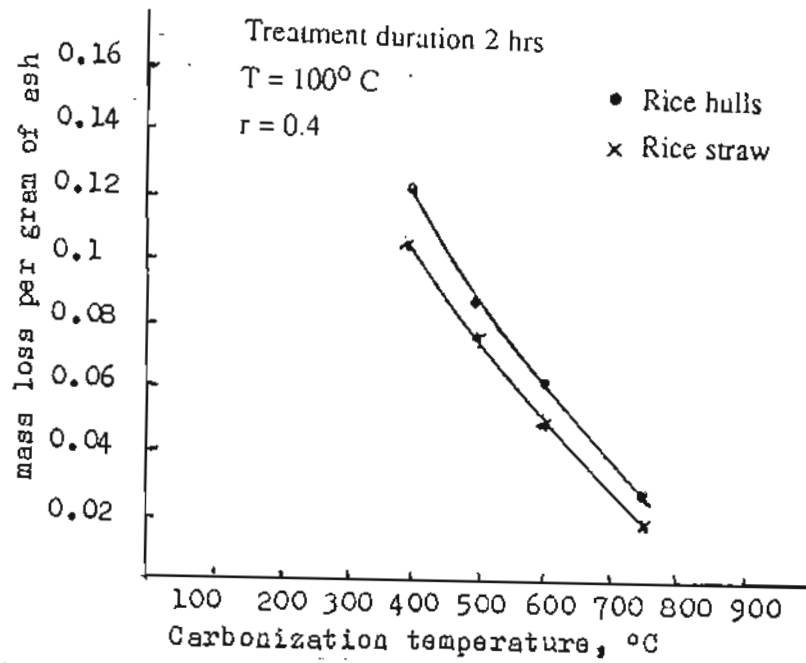


Figure 3: Effect of carbonization temperature upon the amount of the carbonized material reacted with caustic soda.

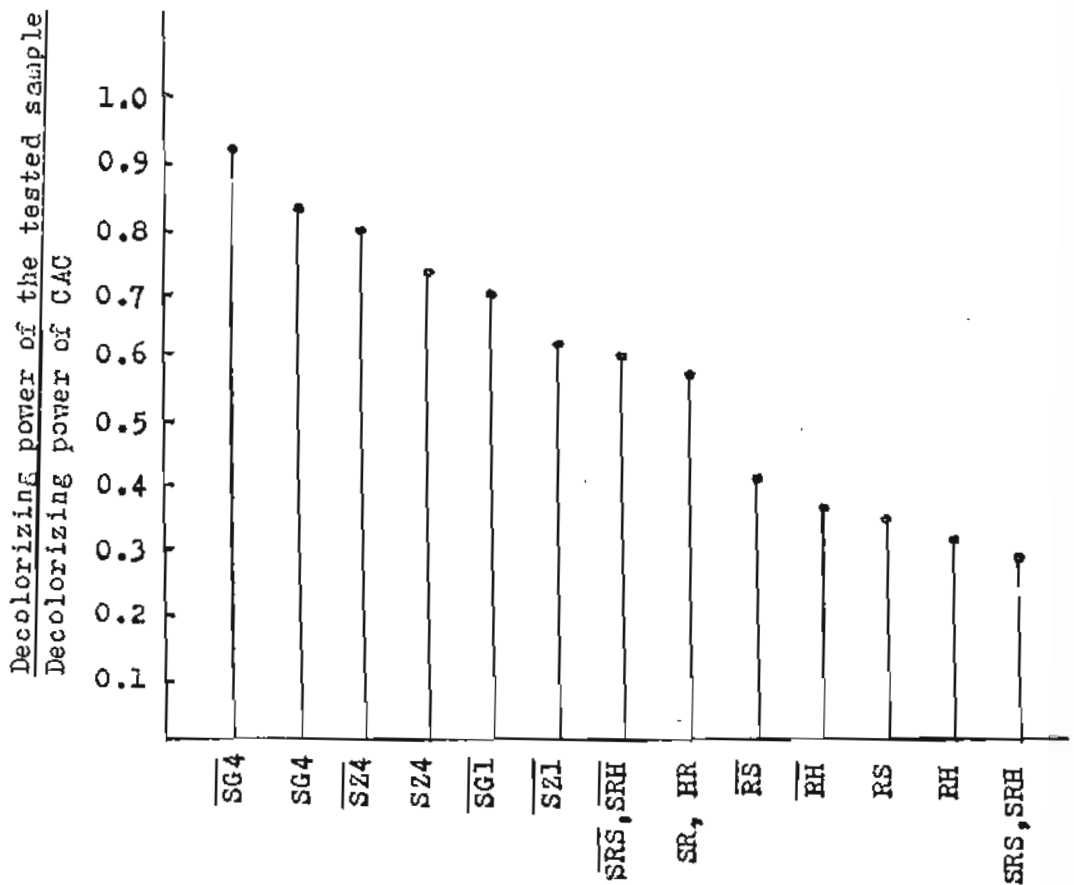


Figure 4: Measured decolorizing power of the tested carbons towards MB compared with that measured for CAC.