A STUDY ON THE PREPARATION AND ADSORPTION PROPERTIES OF ACTIVE CARBON FROM PEACH KERNEL

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ABSTRACT

Peach Kernel (PK) is considered one from many agricultural wastes that represents negative impact on the environment. This work describes a method for the preparation of activated carbon from PK, converting its negative impact on the environment, to positive to be used for removal of contamination. The activated carbon (AC) was prepared in two separate steps of carbonization and activation at 550 & 600 ^oC. The physical activation was performed by water vapor. The mechanism of adsorption varies from physical and chemical adsorptions. The Fruendlich and Langmuir equations were determined. The yields of produced AC for PK samples were 36.82 % and 15.30 % at 550 ^oC and 650 ^oC respectively. Tests were made on prepared AC activated at 650 ^oC. The percentage moisture content varied from 2.94 – 3.72 %. The percentage volatile matter content varied from 42.51- 61.93 % for PK powder and granules respectively. The percentage ash content varied from 0.49 to 2.41%. The apparent density varied from 0.508 to 0.565 g/cm^3. The pores volumes varied from 0.525 – 0.573 cm^3/cm^3. The iodine numbers for non-activated PK carbon samples were 254.80 - 344.90 for granules and powder respectively. The iodine numbers for activated PK carbon samples were 370.16 and 507.60 for granules and powder respectively. The surface areas by multi-point BET were 26.009 and 40.277 m^2/g for non-activated and activated PK respectively. The SEM (Scanning Electron Microscope) images of PK AC show irregular spherical shapes with average diameter of (5-16) nm and macro pores with diameters of greater than 50 nm. The adsorption of

iodine on PK AC followed both more Langmuir isotherm with R^2 = 0.9498 (a= 0.3877 & b= 0.3225) than Fruendlich with R^2 = 0.8419 with (n=1.4428 & k= 1.1951).
Key Words: Adsorption Mechanism, Fruendlich , Langmuir , Peach Kernel, Iodine number, SEM, BET.

INTRODUCTION

The quantities of the agricultural wastes are high in Egypt. Their disposal by the ordinary ways has a negative impact on the environment. From the information that have been collected from the Egyptian Environmental Affairs Agency (EEAA) since 2005 till 2011, the amount of agricultural solid waste (ASW) produced for other years can be estimated. It is expected that in 2020, the amount of ASW may reach 22 million tons per year. The amount of solids wastes will grow more and more. Without recycling, the environmental situation will be worse in the future.

AC is used to adsorb the organic molecules and chlorinated by-products from water that cause unwanted taste, color, odor, and toxicity. Therefore, many researchers made many successful attempts to prepare low cost high quality AC from the different agriculture wastes for application in different fields in the industry. Adsorption parameters of AC depend on pore size, surface area, moisture content, ash content, volatile matter content, apparent density, pore size, and iodine number (Krishna, 2014).

The adsorption capacity of the AC for a specific adsorbate depends strongly on the type of raw material and the processing techniques used for AC preparation (Aajish *et al.*, 2014).

Physical activation can be performed in one step of carbonization and activation simultaneously, or in two-step separate processes: carbonization followed by activation at elevated temperature in the presence of non-oxidizing gases. Physical activation process is widely adopted for production owing to the simplicity of the process and the ability to produce AC with well-developed micro porosity *(*Esfandiari *et al.*, 2011*)*.

Bio-adsorbents for the removal of copper showed that the mechanism of the adsorption followed Langmuir isotherm *(*Habib *et al.,* 2007*)*. The removal of cadmium, chromium, cobalt, and copper from solution showed that adsorption took place according to Langmuir isotherm *(*Pirajan *et al.*, 2012*)*. Adsorption isotherms by Langmuir model for mono-layer adsorption was proved for strontium *(*Abdelkreem *et al.,* 2014*)*.

In Fruendlich, the adsorption follows the following equation:

$$\ln q_e = \ln K + 1/n \ln C_e$$

The parameter K is related to the capacity of the adsorbent for the adsorbate, and 1/n is a function of the strength of adsorption.

In Langmuir, the adsorption follows the following equation:

$$1/(q_{max}b) + (1/ q_{max})\, C_e = C_e / q_e$$

The constant q_{max} corresponds to the surface concentration at monolayer coverage and represents the maximum value of q_e that can be achieved as C_e is increased. The constant b is related to the energy of adsorption and increases as the strength of the adsorption bond increases. It was suggested that the carbonization and activation temperatures were between 200°C and 800°C. As the activation temperature increased, the BET surface area and volatilization of organic materials increased *(*Jabit, 2007*)*.

EXPERIMENTAL

Preparation of AC: Samples of 653.4 g from peach kernel were taken for initial carbonization in absence of air in the furnace at 550 and 620 ^{o}C. After carbonization for 3 hours, the PK carbons were weighed. They were 240.59 and 98.01 g at 550 and 620 ^{o}C respectively. Physical activation process was adopted owing to the simplicity with well-developed micro porosity at 620 ^{o}C for 2 hours by water vapor *(*Esfandiari *et al.,* 2011 *and* Tadjarodi *et al.,* 2014*).*

The Tests made on ACs: The most important tests carried out on the prepared ACs are: moisture content, ash content, volatile matter content, apparent density, pore size, iodine number, surface area by BET and SEM imaging *(*Jabit, 2007 and Aajish *et al.*, 2014) as follows:

Determination of moisture content was made by heating at the temperature 150 ^{o}C for 3 hours and measuring percentage weight loss. Heating and cooling of sample were repeated till constant weight was reached.

Determination of volatile matter content was made by heating at 900 ^{o}C for 7 minutes, and then cooled in desiccator. The percentage loss in mass of the sample is calculated as the percentage of volatile matter corrected for moisture content.

The percentage of ash content (A_s C %) was determined by igniting dried sample at 650 ^{o}C for 16 hours, then cooled in desiccators. The weight loss in the sample is considered as the ash content.

The apparent density of powdered AC (ρ_{app}) is determined by dividing the weight of taken sample in grams by its volume after gentle trapping.

The pore size of AC is determined by putting the sample in the pycnometer filled with water, the excess water corresponds to the volume of the compressed solid. The volume of pores can be determined by subtracting the volume of the compressed solid from the total volume of AC sample.

The iodine number is determined for AC by taking 0.5 g of the sample in excess 0.1N iodine solution and by titration with 0.1N sodium thiosulphate to determine the excess iodine after mixing 15 minutes (Cefic, 1986).

The surface area was determined by BET method to investigate specific surface areas of the prepared ACs. SEM gives the morphological feature, the dimensions, shapes and degree of porosity for each sample *(*Jabit, 2007*).*

The adsorption isotherm was done by contacting 50 ml iodine solution with five different concentrations of iodine (0.1, 0.05, 0.0025, 0.00125, 0.000625 N) with 0.5 g of the studied samples with stirring constant sufficient time (15 minute) at agitation (70 rpm) till equilibrium. The iodine equilibrium concentrations were determined by titration. From initial and final concentrations of iodine, the amount adsorbed on the sample can be calculated.

Freundlich equation has the form of straight line if plotted $\ln\frac{x}{M}$ against ln C_e with slope equals 1/n and intersect ln k.

$$\ln\frac{x}{m} = \ln k + \frac{1}{n}\ln Ce$$

In Langmuir adsorption the empirical equation describes the relation between (x/m) and (C_e) the following form:

$$\mathbf{1/(a\,b) + (1/\,a)\,C_e = C_e/\,(x/M)}$$

Where “a” and “b” are constants. The constant “a” corresponds to the surface concentration at monolayer coverage. Plotting C_e /(x/m) as against C_e gives straight line if it follows Languir isotherm. The slope equals (1/ a) and intersect equals 1/ (ab) (Snoeyink *et al.,* 1990).

RESULTS AND DISCUSSION

The percentage yield of produced carbon samples was 36.82 and 15.30 at 550 and 650 ^oC respectively.

The properties of prepared activated carbon at 650 ^oC were determined. Moisture content was 2.94 and 3.72 % for granules and powder prepared activated PK. The results showed that activated PK granules have lower percentage moisture content than those of powders. That may be due to higher surface area and adsorption of water vapor on the powders than granules.

Percentage of volatile matter content was 61.93 and 42.51% for granules and powder AC. Results showed that volatile matter content of activated PK granules is more than activated PK powder. Increase of volatile matter content may increase the activity of AC due to larger specific surface area *(*Krishna, 2014*)*.

Percentage ash contents were 0.490 and 2.410 % for granules and powder PK AC. Ash content may reduce the activity of AC and increase leach out of metal.

Apparent densities were 0.510 and 0.565 for granules and powder PK AC. Higher apparent density may provide greater activity and indicates better quality of activated carbon *(*Krishna, 2014*)*.

The pore volumes were 0.525 and 0.573 cm^3/cm^3 for granules and powder PK AC. Higher pore volumes provide greater volume of activated carbon available for adsorption.

The iodine numbers were 254.80 and 344.90 for powder and granules of non-activated PK carbon samples. The iodine numbers were 370.16 and 507.60 for granules and powder PK AC. This shows clearly that physical activation increased adsorption of iodine. The Iodine number measures the activity level of micro pores (0-20 A˚). The determined iodine number is low if compared with the typical iodine number of high quality activated carbon which is around 900. The adsorption capacity of the AC varies strongly with the type of raw material and the processing techniques used for AC preparation *(*Aajish *et al.,* 2014).

The surface areas were determined by Quantachrome NovaWin version 11.03 instrument. The results showed that surface areas of PK AC equal 40.277, 34.8174 m^2/g while that of non-activated PK equal 26.009, 0.000 m^2/g by multi-point and single point BET determination respectively. The results show that the surface area increased after activation. This is due to the development of new pores during activation process *(*Jabit, 2007*)*.

SEM technique was used in this study to investigate the morphological feature and surface characteristics of the “PK AC“ (granule and powder). The structure examination of surface of these samples show that the surface is irregular of spherical shape with average diameter of (5-16) µm for powdered PK AC and some degree of porosity. It can be seen from the micrographs that the external surface of the physically AC is full of cavities of powder than granules. There are macro pores since there exist diameters of greater than 50 nm.

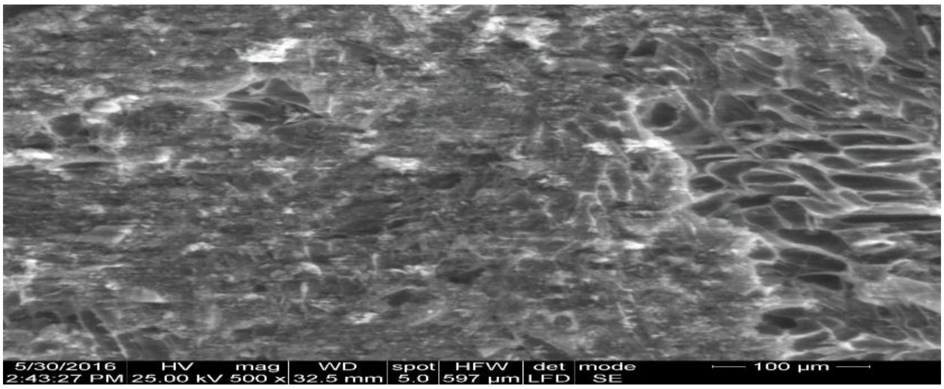

Figure (1): SEM image of granule PK AC

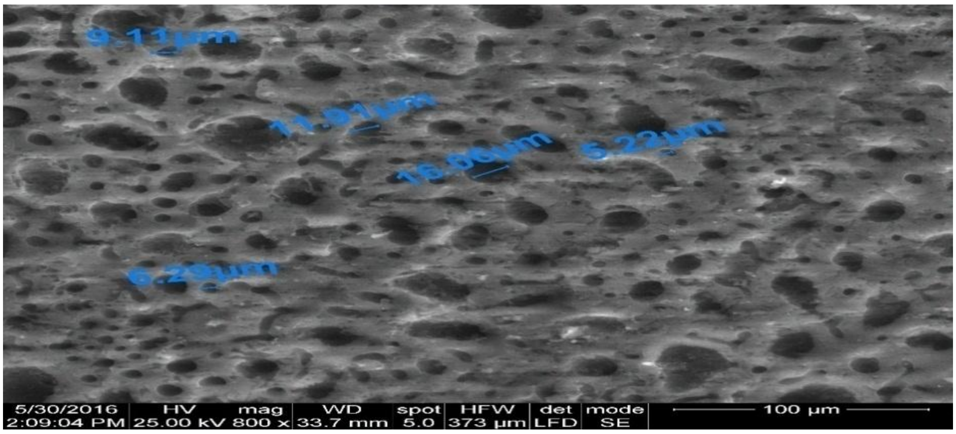

Figure (2): SEM image of powdered PK AC

Results of Adsorption Isotherms for Iodine Solutions:

The effectiveness of AC can be specified by the amount adsorbed iodine. The amount of adsorption is proportional to the value of surface area within pores. The adsorption study for PK AC powder results are shown in table (1).

Table (1): Adsorption mechanism study of PK AC powder

No	N_i	C_0 (g/l)	C_e (g/l)	X (mg)	x/m (g/g)	C_e / (x/m)	ln C_e	ln(x/m)
1	0.1	12.60	9.73	148.003	0.30	32.87	2.28	-1.21
2	0.05	6.35	4.91	121.60	0.24	20.21	1.36	-1.41
3	0.025	4.17	1.96	60.90	0.12	16.04	0.67	-2.10
4	0.0125	1.59	0.61	48.90	0.10	6.20	-0.50	-2.32
5	625×10^{-5}	0.79	0.40	19.83	0.04	10.01	-0.93	-4.23

The adsorption isotherm for PK AC powder is drawn to determine the type of the adsorption isotherm.

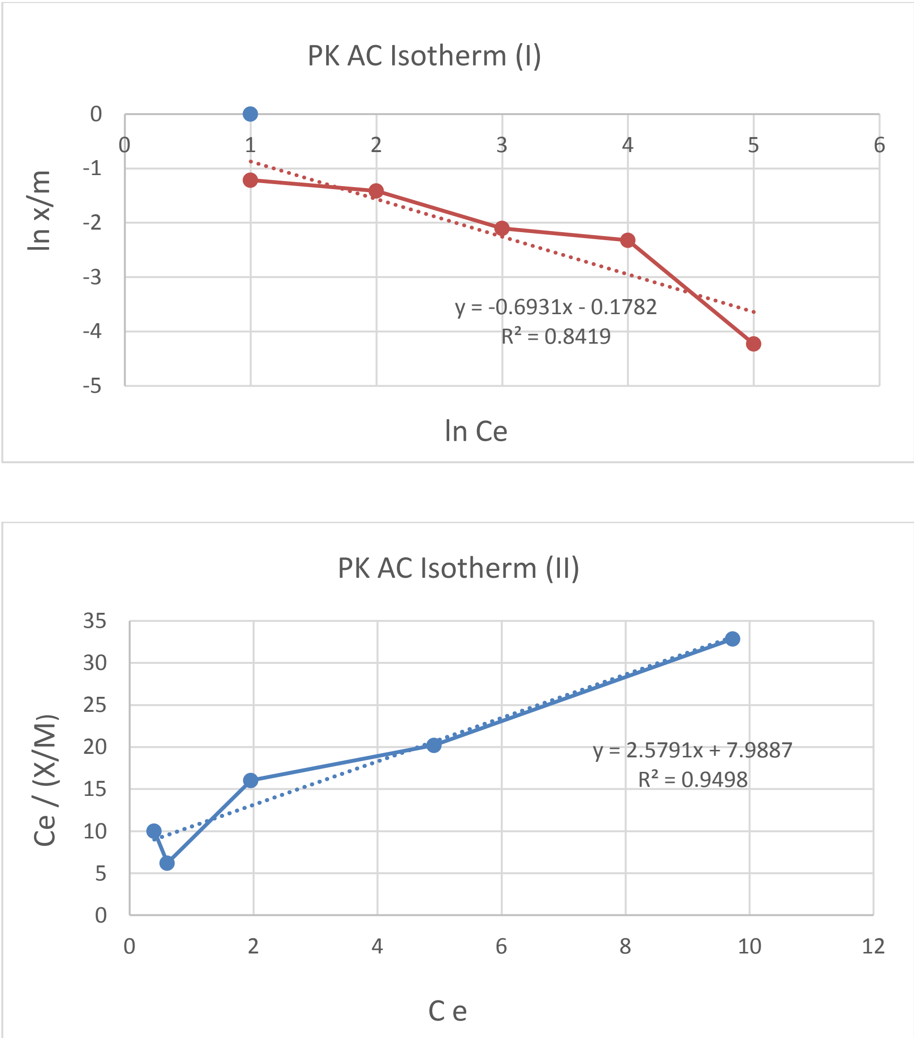

Figure (3): Adsorption mechanism study of PK AC powder

As shown from the previous figures, the adsorption process of PK AC follow both Langmuir and Fruindlich types, but more Langmuir with R^2 = 0.9498 (a= 0.3877 & b= 0.3225) than Fruindlich with R^2 = 0.8419 with (n=1.4428 & k = 1.1951) isotherm.

CONCLUSIONS

It is very important to adopt physical activation to improve the surface characteristics of the ACs. It is recommended to prepare the carbonization and activation in one step to save energy.

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دراسة تحضير وادمصاص الفحم المنشط المحضر من نوى الخوخ

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المستخلص العربى

يصف هذا البحث تحضير الكربون المنشط من نوى الخوخ (PK) كمثال من النفايات البيئية، تم تحضير الكربون المنشط عند ٥٥٠ و ٦٠٠ درجة مئوية إما في خطوة أو خطوتين (عملية الكربنة والتنشيط)، تم إجراء التنشيط الفيزيائى بواسطة بخار الماء، وبعد عملية تحضير الفحم المنشط تم تعيين الصفات المهمة له، ثم تم دراسة ميكانيكية الإدمصاص هل هى تتبع Langmuir أو Fruindlich، وتم تعيين معادلات وثوابت الإدمصاص لكل منهما.

كان ناتج العائد من الكربون المنشط لعينات نوى الخوخ 36.82٪ عند ٥٥٠ درجة مئوية و١٥,٣٠٪ عند ٦٥٠ درجة مئوية، تم إجراء اختبارات على عينات الفحم المنشط المحضر عند درجة ٦٥٠ درجة مئوية، فكانت نسبة الرطوبة تتراوح بين ٢،٩٤ حتي ٣,٧٢٪، ونسبة محتوى المواد المتطايرة تختلف من ٤٢،٥١ حتى ٦١,٩٣٪، ونسبة الرماد تختلف من ٠,٤٩٠ وحتى ٢,٤١٠٪ ، والكثافة الكلية تتراوح من ٠،٥٠٨ وحتي ٠،٥٦٥ جم/ سم^{٣}، وتفاوتت أحجام المسام من ٠،٥٢٥ وحتى ٠،٥٧٣ سم^{٣}/ سم^{٣}، وكان الرقم اليودى لعينات الكربون غير المنشطة لعينات نوى الخوخ تتراوح من ٢٥٤،٨٠ وحتى ٣٤٤،٩٠، وكان الرقم اليودى لعينات الكربون المنشطة لنوى الخوخ تتراوح من٣٧٠،١٦ للحبيبات ٥٠٧،٦٠.

كانت المساحة السطحية النوعية التي عينت بواسطة BET متعددة النقاط لعينات فحم نوى الخوخ المنشط ٤٠،٢٧٧ ولغير المنشط ٢٦،٠٠٩ م^{٢}/ جم، وتشير الصور التى تم إلتقاطها بواسطة الميكروسكوب الإلكترونى لفحم نوى الخوخ المنشط إلى أن الأسطح غير منتظمة في الشكل الكروي مع متوسط قطرها من (٥–١٦) نانومتر، والمسام الكبيرة موجودة أيضا بأقطار أكبر من ٥٠ نانومتر، كما أظهرت الصور تم التقاطها بواسطة الميكروسكوب الإلكترونى أن السطح غير منتظم فى الشكل الكروي مع متوسط قطرها من (٥–١٦) نانومتر للحبيبات.

تم دراسة إدمصاص اليود على الفحم المنشط المحضر لنوى الخوخ، وبينت النتائج أن ميكانيكية الإدمصاص تتبع كلا من نوع Langmuir [$R^2 = 0.9498$ (a= ٠,٣٨٧٧ و b = ٠,٣٢٢٥)] أكثر مع نوع Fruindlich [$R^2 = 0.8419$ مع (n = ١,٤٤٢٨ و k = ١,١٩٥١)].