

# Efficiency of activated carbon from maize cob as fuel and as an adsorbent

Eman A. Ashour

Chemical Engineering Dept., Faculty of Eng., Minia University, Minia 61111, Egypt

Much research is directed recently for finding low cost adsorbents for removal of heavy metals. Agricultural residues and activated carbon were found to be effective adsorbents. Activated carbon from maize cob (low-cost activated carbon) was prepared by impregnating maize cob with phosphoric acid. Thermal behaviour for maize cob and activated maize cob was investigated using Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA). The results showed that the thermal decomposition pattern can be divided into three peaks. The first peak is endothermic while the second and the third peaks are exothermic. The peak intensities and corresponding temperatures were different for the maize cob and activated maize cob. Kinetic studies were based on weight loss obtained from TG analysis. The reaction rate, activation energy, entropy change, enthalpy change and Gibb's free energy of the thermal stages were calculated. The prepared carbon exhibits a high adsorption capacity for removal of lead and cadmium. Studies of Langmuir and Freundlich parameters proved that activated maize cobs favorably adsorb lead and cadmium ions.

وجهت الكثير من الأبحاث نحو إيجاد مادة مازة قليلة التكاليف لإزالة المعادن الثقيلة . وقد وجد أن المخلفات الزراعية والفحم المنشط مواد مازة ذات تأثير عال . ويحضر الفحم المنشط من كوالح الذرة وهي مادة رخيصة وذلك بغمر الكوالح في حامض الفوسفوريك . وقد تم دراسة السلوك الحرارى لكوالح الذرة والفحم المنشط المحضر من كوالح الذرة عن طريق استخدام التحليل الحرارى التفاضلى والتحليل الحرارى الوزنى والنتائج توضح أن منحنيات التحليل الحرارى يمكن أن تنقسم إلى ثلاث قمم :- القمة الأولى متمصة للحرارة والقمة الثانية والثالثة طارديتان للحرارة وقد وجد أن شدة القمم ودرجات الحرارة تختلف فى كوالح الذرة عنها فى الفحم المنشط . تم حساب معدل التفاعل وطاقة التنشيط والتغير فى الاضطراب والتغير فى المحتوى الحرارى وكذلك الطاقة الحرة لكل من كوالح الذرة والفحم المنشط والمحضر من كوالح الذرة ووجد أن القيمة الحرارية للفحم المنشط أعلى منها فى كوالح الذرة . وقد أوضحت الدراسة أن سعة الإدمصاص للفحم المنشط لإزالة الرصاص والكاديوم أعلى من كوالح الذرة وقد تم دراسة منحنيات الثبات الحرارى لكل من الكوالح والفحم المنشط المحضر من الكوالح ووجد أنهما يتبعان علاقة لانجمير و فروندليش .

**Keywords:** Maize cob, Chemical activation, Thermodynamic parameters, Adsorption isotherms

## 1. Introduction

The concentration of toxic metals; such as mercury, cadmium, lead, arsenic and copper, increases with the growth of technology. Anthropogenic sources of heavy metals include wastes from the electroplating and metal finishing industries, metallurgical industries, tannery operations, chemical manufacturing, mine drainage, battery manufacturing and contaminated ground water from hazardous waste sites [1].

Lead is toxic. It substitutes calcium in bony tissue, and accumulates there, where it may cause impairment of motor and neurologic development and also kidney damage.

Cadmium harmfulness is associated with the readiness that it can accumulate in the body. It alters the bone structure of the victims and gives rise to a painful rheumatic disease [2,3].

The traditional treatment of heavy metals is either precipitation as metal hydroxide or ion exchange; however adsorption seems a good alternative method [4]. Carbon adsorbents have attracted special attention on account of their well-developed porous structure, large active- surface area and good mechanical properties [5-7].

Activated carbon made from conventional raw materials such as bituminous coal, peat and lignite are expensive. So there is a need to investigate non- conventional materials for the



production of low-cost activated carbon. Many reports have appeared on the preparation of activated carbon from cheaper and readily-available materials [8-10]. Activated carbon from rice husk and coconut shell has been successfully employed for the removal of heavy metals from aqueous solutions [11-12]. Recently it was reported that maize cob and carbon derived from maize cob removed heavy metals [13-15]. Although the application of maize cob in adsorption process shows promising results, several studies show that it could be utilized as a renewable source of energy. It has a lower sulphur content in comparison with other fossil fuels; therefore clean environments are obtained [16,17].

The goal of this research is to investigate the efficiency of maize cob and Activated Maize Cob (AMC) for removal of cadmium and lead and the effect of activation on the adsorption behaviour of maize cob. This will provide basic data and information for the combustion of this material.

## 2. Experimental

Maize Cobs (MC) used in this study was collected from El-Minia Governorate, Egypt. It was dried for 3 hours at 110 °C. Maize cob was not subjected to any form of pretreatment prior to use. The dried materials was crushed to obtain the desired particle size  $\leq 1000 \mu\text{m}$  using sieve analysis. The dried maize cob was subjected to chemical analysis and the results are listed in table 1.

Dried, crushed maize cob (50 g) was mixed with 100 ml  $\text{H}_3\text{PO}_4$  at ratio 1:2.5 solid to acid. It was kept in an oven at  $80 \pm 5^\circ\text{C}$  for 12 hours. The dried slurry was transferred to an electric tubular furnace. The temperature was raised gradually ( $200^\circ\text{C}/\text{h}$ ) so as to permit release of the volatiles and to prevent splashing of the heated mass. Upon reaching  $500^\circ\text{C}$ , the mass was soaked for one hour in a nitrogen atmosphere, then cooled to room

temperature. The carbonised material was washed with tap water and finally with distilled water to remove any residual acid. Then it was soaked with 1.0 % sodium bicarbonate solution over night to remove any residual acid traces. The material (AMC) was washed with distilled water and dried at  $100^\circ\text{C}$ .

Differential Thermal Analysis (DTA) and Thermal Gravimetric Analysis (TGA) were carried out for the samples by using Du Pont analyzer Model 9900 with temperature programmed at  $10^\circ\text{C}/\text{min}$ , heating from room temperature to  $900^\circ\text{C}$  in an atmosphere of air. The amount of material used was 10 mg. The reference material was aluminum oxide.

Adsorption equilibrium isotherms were obtained by contacting a constant mass of MC and AMC (1 g) with  $0.05 \text{ dm}^3$  of Pb or Cd solution of different concentrations adjusted to the desired pH. The bottles were placed on a shaker bath at constant temperature ( $25 \pm 1^\circ\text{C}$ ). The samples were centrifuged and their equilibrium concentration ( $C_e$ ) in the clear supernatant liquid was determined by spectrophotometric methods. The difference between the initial concentration ( $C_o$ ) and the equilibrium concentration ( $C_e$ ) per unit mass of adsorbent was used to compute the amount of Pb or Cd removed ( $q_e$ ) in mg/g from its solutions by using the relationship

$$q_e = 0.05 (C_o - C_e) / M. \quad (1)$$

## 3. Results and discussion

Elemental analysis of raw maize cob and activated maize cob show an increase in carbon content from 40.78 to 78.68 and a decrease in hydrogen content from 6.57 to 3.39 for MC and AMC, respectively. Thermal analysis of maize cob MC and activated Maize cob AMC are shown in figs. 1 and 2 using TGA and DTA techniques. The results are summarized in table 2.

Table 1  
Chemical analysis for maize cob

Component	Cellulose	Hemicellulose	Lignin	Protein	Ash
Percentage	52.5	28.3	13.08	2.9	3.22

Table 2  
TGA results for maize cob and activated maize cob

Stage of weight loss	MC	AMC
First		
Weight loss %	2.0	12.0
T <sub>max</sub> °C	70	100
T <sub>range</sub> °C	50-200	50-400
Second		
Weight loss %	28.0	78.0
T <sub>max</sub> °C	340	550
T <sub>range</sub> °C	200-400	400-700
Third		
Weight loss %	40.0	
T <sub>max</sub> °C	455	
T <sub>range</sub> °C	400-500	
Fourth		
Weight loss %	10.0	
T <sub>range</sub> °C	500-900	
Total	80.0	90
% residue	20	10

The TGA and DTA curves for MC (fig.1) show four degradation stages. The first stage (an endothermic peak) appears at about 70 °C in DTA with slight weight loss of about 2% in TGA curve which represents the evaporation of adsorbed moisture. The main degradation processes are two exothermic peaks in DTA curve at 340°C and 455°C with the major weight losses of 28 and 40 % respectively. The two exothermic peaks are due to dehydration and depolymerization of lignocellulosic components. The last exothermic peak appears at about 520°C is attributed to degradation of the result products [18-22].

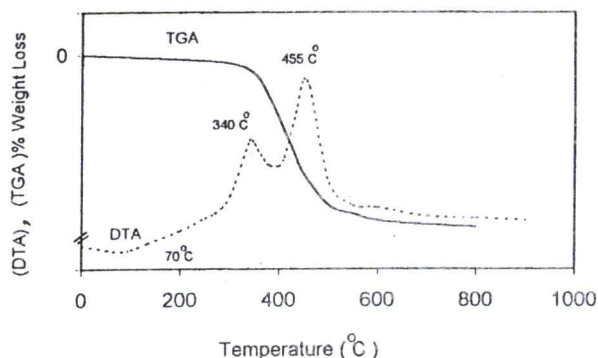


Fig. 1. DTA and TGA thermogram for maize cob.

Comparing thermal analyses of activated maize cob (fig. 2), the TGA and DTA have two degradation stages. The first peak in DTA curve at 100 °C with weight loss of about 12% is related to elimination of moisture. The

second degradation stage, one exothermic peak in DTA at 550 °C with the major weight loss of 78% is due to degradation of more stable organic compounds. It is clear that depolymerization stage disappears in case of activated carbon. This means that all cellulosic material is converted to carbon.

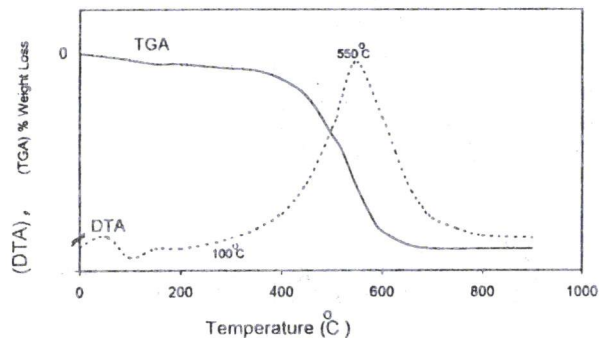


Fig. 2. DTA and TGA thermogram for activated maize cob.

In kinetic studies based on thermogravimetric analysis, a first order reaction is assumed and it is usually expressed as:

$$-\frac{dC}{dt} = kC \tag{2}$$

Where C is concentration of reactant in moles/dm<sup>3</sup>, t is time of reaction in minutes and k is rate constant in min<sup>-1</sup>. If the concentration is replaced by the observed weight w<sub>t</sub>, then,

$$\frac{d(w_0 - w_t)}{dt} = kw_t \tag{3}$$

The amount of residue at the end of heating w<sub>α</sub> and using the limit

$$\text{at } t=0 \quad w_0 - w_t = 0,$$

eq. (3) will take the form:

$$\log \frac{w_0 - w_\alpha}{w_t - w_\alpha} = kt \tag{4}$$

Plotting log (w<sub>0</sub>-w<sub>α</sub>) / w<sub>t</sub> - w<sub>α</sub> against time t for a first order reaction gives a straight line with a slope k at the considered temperature.



Applying the Arrhenius principle, and plotting  $\log k$  against  $1/T$ , the activation energies of volatilization and carbonization stages are calculated and given in table 3. The activation energy of carbon prepared from maize cob is higher than raw maize cob which adds confirmation that all cellulosic material is converted to carbon.

Thermodynamic parameters  $\Delta H$ ,  $\Delta S$  and  $\Delta G^\circ$  were determined according to procedure given in reference [22]. The rate constant values in table 3, represent the average value of the rate constant for the chosen temperature range, the positive values of  $\Delta G^\circ$  indicate the non spontaneous nature of the reactions as the free energy of the products are higher than those of reactants.

The capacity of maize cob and activated maize cob for removal of lead and cadmium can be determined by measuring equilibrium isotherms. The adsorption isotherms are constructed by plotting values of  $q_e$  versus  $C_e$  and as depicted in figs. 3 and 4 of lead and cadmium onto MC and AMC, respectively. The adsorption capacity of activated maize cob is higher than that of MC. Analysis of isotherms data is important in order to develop an equation which accurately represents the results and could be used for design purposes.

The first isotherm tested was that of Langmuir which may be represented by the equation :

$$q_e = (k_L C_e) / (1 + a_L C_e) \tag{5}$$

This may be converted into a linear form convenient for plotting and determining the constant  $k_L$  and  $a_L$ ,

$$C_e / q_e = (1/k_L) + (a_L / k_L) C_e \tag{6}$$

Where  $a_L$  is the parameter of Langmuir – isotherm  $dm^3 / mg$ ,  $k_L$  is the parameter of Langmuir-isotherm  $dm^3/g$ . Linear plots of  $C_e/q_e$  against  $C_e$  of lead and cadmium onto MC and AMC figs. 5 and 6 suggest the applicability of Langmuir isotherm for the present system.

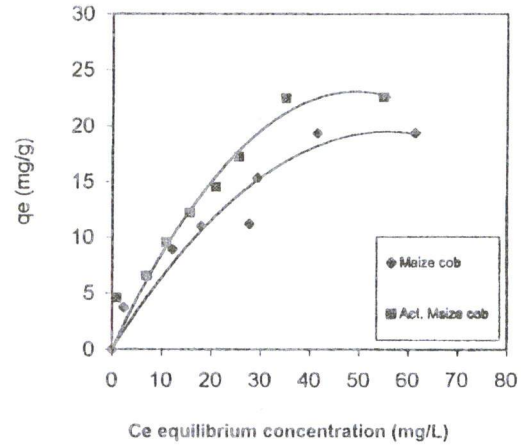


Fig. 3. Adsorption isotherms for lead onto MC and AMC.

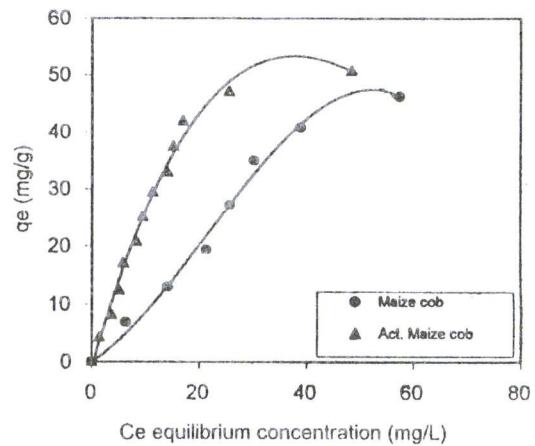


Fig. 4. Adsorption isotherms for cadmium onto MC and AMC.

Table 3  
Thermodynamical parameters of maize cob and activated maize cob

Stage	K min <sup>-1</sup>	Temp. °C	E kJ/mole	Δ H kJ/mole	Δ S kJ/mole k	Δ G° kJ/mole
Vol.* maize cob	0.0544	340	86.918	85.69	-0.1726	190.8
Dec.** maize cob	0.2421	455	30.37	28.92	-0.2584	217.06
Dec.activated MC	0.0515	550	95.89	94.25	-0.1975	256.8

\* volatilization stage  
\*\* carbonization stage

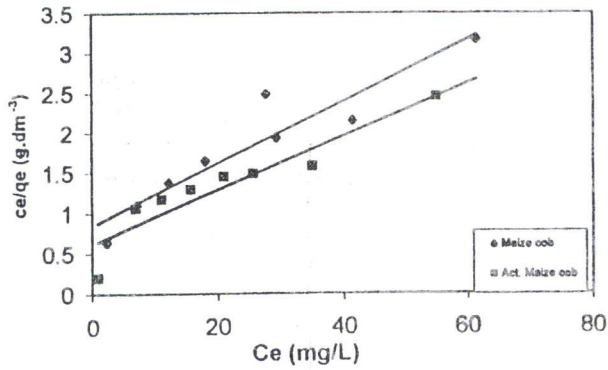


Fig. 5. Langmuir plots for the adsorption of lead onto MC and AMC.

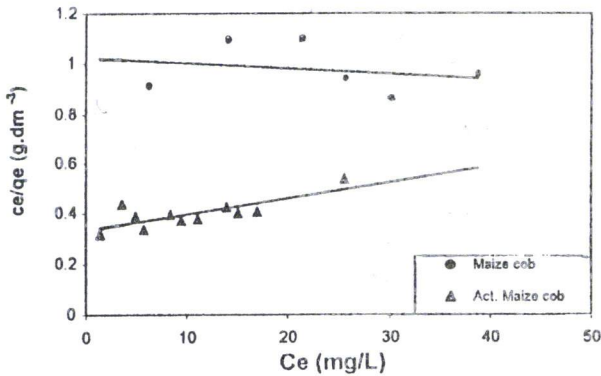


Fig. 6. Langmuir plots for the adsorption of cadmium onto MC and AMC.

The values of  $k_L$  and  $a_L$  of lead and cadmium onto MC and AMC have been calculated using least-squares methods and are tabulated in tables 4 and 5. The values of constant  $k_L/a_L$  represent the maximum adsorption capacity.

The influence of isotherm shape for adsorption is favorable or unfavorable has been considered using separation factor  $R$ -as shown in the following equation [23]:

$$R = 1 / (1 + a_L C_e) \tag{7}$$

The experimental results given in tables 4 and 5 show that MC, and AMC are favorable for adsorption of lead and cadmium, but the adsorption capacity of AMC is higher than MC.

The experimental equilibrium data for the adsorption of lead and cadmium onto MC and AMC have also been analyzed using Freundlich isotherm as given by eq. (8),

$$q_e = k_f C_e^n \tag{8}$$

Where  $k_f$  is the parameters of Freundlich-isotherm ( $\text{dm}^3/\text{g}$ ). Eq. (8) was used to fit the data obtained for two types of adsorbents. The data were plotted on a log-log scale to produce a straight line of each adsorbent, figs. 7 and 8.

Tables 6 and 7 includes Freundlich Parameters, show that Freundlich constant is higher than 1 and the capacity factor of AMC to remove lead and cadmium is higher than for MC.

Table 4  
Langmuir isotherm parameters for adsorption of lead

Parameter	MC	AMC
$m^3 / g$	1.191	1.553
$a_L \text{ dm}^3 / \text{mg}$	0.0462	0.0545
R	0.1779	0.155
Correl. coeff.	0.863	0.885

Table 5  
Langmuir isotherm parameters for adsorption of cadmium

Parameter	MC	(AMC)
$m^3 / g$	1.096	3.58
$a_L \text{ dm}^3 / \text{mg}$	0.042	0.044
R	0.041	0.132
Correl. coeff.	0.86	0.89

Table. 6  
Freundlich isotherm parameters for adsorption of lead

Parameter	MC	AMC
n	1.88	2.35
$k_f (\text{dm}^3 / \text{g})$	2.33	3.98
$q_{max} (\text{mg} / \text{g})$	19.36	22.5
Capacity factor	25.8	28.49
Correl. Coeff.	0.887	0.902

Table. 7  
Freundlich isotherm parameters for adsorption of cadmium

Parameter	MC	AMC
n	1.071	1.28
$K_f (\text{dm}^3 / \text{g})$	1.202	3.83
$q_{max} (\text{mg} / \text{g})$	44.79	50.79
Capacity factor	26.09	81.38
Correl. coeff.	0.89	0.91



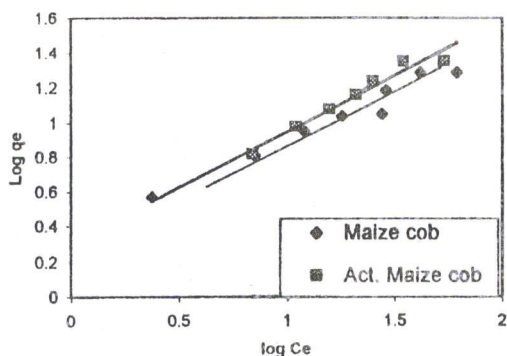


Fig. 7. Freundlich plots for adsorption of lead onto MC and AMC.

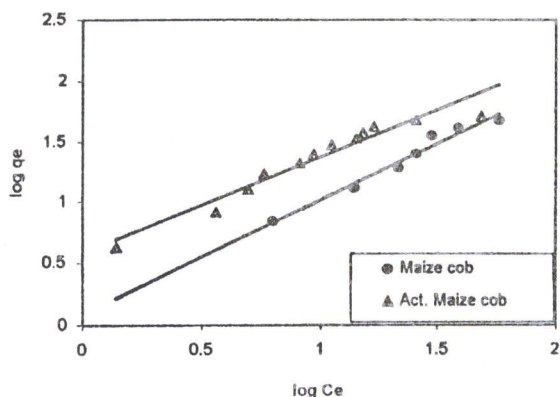


Fig. 8. Freundlich plots for adsorption of cadmium onto MC and AMC.

**4. Conclusions**

- 1- Maize cob as a low cost waste agricultural by- product, can be effectively used as a raw material for preparation of activated carbon.
- 2- Thermal analysis studies show the capability of AMC to be used as a source of energy due to its high carbon content.
- 3- Maize cob carbon is an effective adsorbent for removal of lead and cadmium from aqueous solutions. Its adsorption capacity is higher than maize cob in raw form.

**References**

[1] E.R. Brian and A. Selvam, "Removal of Lead and Cadmium from Aqueous Waste Streams using Granular Activated Carbon (GAC) Columns", *Environmental Progress*, Vol. 13 (1), pp. 60-64 (1994 ).

[2] J. Bayo, S. Moreno-Grau, J.M. Moreno, and I.J. Moreno-Clave "Contribution of Risk Factors to High Lead and Cadmium Levels in Deciduous Teeth", *International Conference of Environmental Health Risk*, Boston, England (2001).

[3] E.W. Eckenfelder *Industrial Water Pollution Control*, Mc Graw- Hill, New York, USA (1998).

[4] *Water Quality and Treatment, A Handbook of Community Water Supplies*, American Waters Works Association , 4<sup>th</sup> Edition, Mc-Graw Hill , Inc (1990).

[5] J.R. Decey "Active Carbon in the Solid – Gas Interface", Ed.E. Alison Flood, 995 Marcel , Dekker, New York, Vol. 12, pp. (1967).

[6] D.M. Mackay and P.V. Roberts, "The Dependence of Char and Carbon Yield on Lignocellulosic Precursor Composition", *Carbon*, Vol. 20(59) (1984).

[7] W.J.Jr.Weber and E.H. Smith, "Activated Carbon Adsorption", In *Chemistry for Protection of the Environment* , Elsevier Science Publishers, pp. 455 (1986).

[8] R. Torregrosa and J.M. Martin-Martinez, "Activation of Lignocellulosic: A Comparison Between Chemical in Terms of Porous Texture", *Fuel*, Vol. 70, pp. 1173-1180 (1991).

[9] F. Rodriguez-Reinaso and M. Molina-Sabio, "Activated Carbons from Lignocellulosic Materials by Chemical and/or Physical Activation an Overview", *Carbon*, Vol. 30, pp. 1111-1118 (1992).

[10] C.A. Philip and B.S. Girgis, "Adsorption Characteristics of Microporous Carbons from Apricot Stones Activated by Phosphoric Acid", *J. Chem. Tech. Biotechnol*, Vol. 67, pp.248-254 (1996).

[11] K. Srinivasan, N. Balasubramanian and T.V. Ramakrishna, "Studies on Chromium Removal by Rice Husk Carbon", *Indian J. Environ. Health*, Vol. 30, pp. 376-387 (1988).

[12] A. Arulanatham, n. Balasubramanian and T.V. Ramakrishna, "Coconut Shell Carbon for Treatment of Cadmium and Lead Containing Wastewater", *Met. Finish. Nov*, pp. 51-55 (1989).

- [13] S. Bosinco, J. Roussy, E. Guibal, and L. Ecloirec, P., "Interaction Mechanisms between Hexavalent Chromium and Corncob", *Environmental Technology*, Vol. 17, pp. 55-62 (1996).
- [14] C. Namasivayam and K. Kadirvelu, "Uptake of Mercury (II) from Wastewater by Activated Carbon from an Unwanted Agricultural Solid by-product: Coirpith", *Carbon*, Vol. 37 (1), pp. 79-84 (1999).
- [15] E.A. Ashour, "Removal of Heavy Metal by Activated Carbon Prepared from Maize cobs using Different Chemical Activation", 3<sup>rd</sup> International Conference of: Role of Engineering Towards Better Environment, 18-20, Nov. (2000).
- [16] M.M. Nassar, "Kinetic Studies on Thermal Degradation of Nonwood Plants", *Wood and Fiber Science*, Vol. 17 (2), pp. 266-263 (1985).
- [17] M.M. Nassar, M. El-Gendi, M.A. Khttab and A.Y. Hosny, "Thermal Studies of Some Adsorbent Materials", *Alexandria Engineering Journal*, Vol. 31 (3), pp. 223-228 (1992).
- [18] Wu, Y.W. and D. Dollimore, "Kinetic Studies of Thermal Degradation of Natural Cellulosic Materials", *Thermochim. Acta*, 324, pp. 49-57 (1998).
- [19] G. Varhegyi, P. Szabo and M.J. Antal, "Reaction Kinetics of Thermal Decomposition of Hemicellulose and Cellulose in Biomass Materials", *Advances in Thermochemical Biomass Conversion*, A.V. Bridgwater (ed) Blackie, London, pp. 760-770 (1994).
- [20] A.M. Kanury, "Combustion Characteristics of Biomass Fuels", *Combustion Science and Tech.* Vol. 97, pp. 469-491 (1994).
- [21] M.M. Nassar, "Thermal Analysis of Bagasse and Rice Straw", *Energy Source*, Vol. 21, pp. 131-137 (1999).
- [22] S. Glasstone, "Text Book of Physical Chemistry", Mac Millan Co., London, 828 (1962).
- [23] D. Ruthven and M. Goddard, "Fundamentals of Adsorption", Myers A.L., Belford, G., Eds., American Institute of Chemical Engineering New York (1984).

Received July 3, 2002

Accepted September 2, 2002

