Malaysian Journal of Chemistry, 2003, Vol. 5, No. 1, 008 - 014

Utilization of Guava Seeds as a Source of Activated Carbon for Removal of Methylene Blue from Aqueous Solution

I. A. Rahman* and B. Saad
School of Chemical Sciences, Universiti Sains Malaysia, 11800 Penang, Malaysia

Abstract :Guava seeds have been used as a raw material to produce activated carbon. Dried, milled, guava seeds were activated by pyrolysis at temperature up to 700 ^{o} C, and by using zinc chloride as chemical activation agent. The adsorption capacity was demonstrated by the isotherms of methylene blue from aqueous solution. Pyrolysis alone yields a poor adsorbing carbon with adsorbing capability of only ~ 55 % due to the blockage of pores by decomposition products of lignocellulosic materials. Optimum absorption capacity was obtained when the samples were subjected to chemical activation, followed by pyrolysis at 700 ^{o}C.

Abstrak : Biji jambu batu telah digunakan sebagai bahan mentah untuk menghasilkan karbon teraktif. Biji jambu yang dikering dan dikisar telah diaktifkan secara pirolisis pada suhu sehingga 700 ^{o}C dengan menggunakan zink klorida sebagai agen pengaktifan. Muatan penjerapan ditentukan dengan menggunakan larutan akueus metilena biru. Pirolisis hanya menghasilkan karbon dengan muatan penjerapan ~ 55% sahaja kerana penutupan liang oleh hasil-hasil penguraian bahan lignoselulosa. Muatan penjerapan optimum diperoleh apabila pengaktifan kimia dilakukan kepada sampel, dan diikuti pirolisis pada 700 ^{o}C.

Received : 18.01.02, accepted : 11.04.03

Introduction

Activated carbon has widely been used for the removal of inorganic and organic pollutants from aqueous solution. In a continuing search for the adsorbents, various lignocellulosic materials or agriculture wastes such as coconut shell, rice husks, saw dust, and wheat straw were used[1-3]. These materials were pyrolysed or carbonized in an inert atmosphere in order to remove volatile organic constituents, leaving behind a highly porous carbonaceous residue, followed by either chemicals, steam or gas activation for removal of the pollutants. Methylene blue has long been used as a model for the adsorption of organic pollutants from aqueous solution. A number of studies on the removal of methylene blue from aqueous solution by using corncobs[4], palm-tree cobs[5], oil palm nut shells[6], olive-waste[7], oil shale rock[8], and chitin[9] were reported.

Activated carbons have been prepared from the above materials by application of both physical and chemical activations. Activation and pyrolysis of rice husks with $ZnCl_2$, H_3PO_4 or CO_2 have been used for the adsorption of methylene blue[10] and benzene[11]. Separate and sequential application of physical activation with steam and chemical activation with H_3PO_4 were also reported[4,12]. Hu and Srinivasan[13] employed simultaneous activation by using $ZnCl_2$ and CO_2 to produce activated carbon from coconut shells and palm seeds.

Guava seeds are agricultural by-product that are currently of no economic value. The seeds consist of tiny bean-like particles and are disseminated throughout the guava pulp, and are considered as waste product during guava juice processing. The seeds represent about 5 % of the fresh fruit, and have a horny shell. It was reported[14] that the seeds consist of high amount of lignocellulosic materials. Thus, it should be possible to carbonize or pyrolyse the material to form a porous carbon that is suitable to be used as adsorbent. In this work, we used guava seeds as a raw material to produce activated carbons. We used physical activation (carbonization or pyrolysis) in an inert gas, followed by sequential chemical ($ZnCl_2$) and physical activations to produce activated carbon. The use of such materials for the production of activated carbon has not been reported before.

Experimental

Raw materials

The guava seeds were obtained from a guava juice processing plant (Golden Hope Plantation, Selangor, Malaysia). The sample was washed with distilled water, and dried in an oven at 105 ^{o} C for 24 h. The dried seeds were ball-milled into powder by using an alumina milling medium.

Analysis of the constituents of the seeds

The milled sample (2.0 g) was continuously extracted with 0.200 dm^3 of boiling ethanol-benzene solvent mixture (1:1) for 8 h in a Soxhlet extractor. The solvent was then evaporated in a rotary evaporator, and the residue was dried in an oven at 105 ^{o} C for 1 h. The organic constituents of the residue were analysed according to the procedure of Test Analysis of the Pulp and Paper Industries (TAPPI)[15].

Pyrolysis and activation

Pyrolysis was carried out in a horizontal controlled atmosphere furnace (Carbolite, CTE 12/75). The sample was placed in an alumina boat, and pushed into the hot zone of the furnace. The sample was heated between 200^o – 750 ^oC under a slow flowing argon gas for 1 h. The weight loss was then obtained from the weight before and after pyrolysis. The pyrolysed sample was ball-milled into powder form.

The activation process was carried out with zinc chloride solution. A weighted sample (50 g) of seeds was crushed into smaller size and was soaked in zinc chloride solution (50 %) for 48 h. After decantation, the sample was pyrolysed at 700 ^oC for 1 h, washed with HCl and deionized water, and finally dried at 105 ^oC overnight.

The pyrolysed and activated samples were characterized by using a porosimeter (ASAP 2000, USA).

Methylene blue adsorption isotherm

Various concentrations of methylene blue solutions ranging from 10 – 100 mg dm^{-3} were prepared by dissolving methylene blue crystals in distilled water. A calibration curve of absorbance versus concentration was constructed, using a UV Spectrophotometer (Hitachi Model, U-2000) at maximum wavelength of 670 nm.

Adsorption isotherm of methylene blue were obtained by adding 0.1 g of guava seeds sample to a 0.250 dm^3 flask containing 0.100 dm^3 of 10 mg dm^{-3} aqueous solution of methylene blue. The flask was kept in a thermostat shaker at 30 ^oC for 45 min. The suspension was then filtered, and the concentration of the methylene blue was determined by difference. The procedure was extended to determine optimum shaking time, concentration and the amount of adsorbent used.

Results and discussion

Characterization of adsorbent

The composition of guava seeds is shown in Table 1. The organic constituents of cellulose, hemicellulose and lignin constitute ~ 86.0 %, while moisture and soluble materials contribute ~ 13.5 %. There is negligible amount of ash present in the seeds. Owing to the high lignocellulosic content, guava seeds can be readily pyrolysed or carbonized in an inert atmosphere to form porous material. The effect of temperature on the pyrolysis of the seeds under flowing argon is given in Figure 1. The results show that the mass loss increases with increasing temperature up to 600 ^oC and remained constant on further increase in temperature. The pyrolysed materials at 600 ^oC and above consisted of black carbonaceous material which is considered as carbon. The material was easily milled into powder to produce adsorbent for adsorption study. The pyrolysis pattern reflect on the decomposition of lignocellulosic materials into organic volatiles, CO, water and char. The decomposition profile of the guava seeds is characterized by an initial slow decomposition up to 400 ^oC, only thereafter is decomposition rapid. This is in contrast to that of other lignocellulosic materials such as rice husks[16], where rapid decomposition takes place even at temperature below 400 ^oC. This feature is probably due to the different nature of guava seed as compared to the rice husks. A rapid mass loss in the region 400 – 600 ^oC corresponds to the decomposition of cellulose, hemicellulose and lignin[16,17].

Constituents	% mass
Cellulose	31.40
Hemicellulose	14.30
Lignin	40.20
Solubles	6.96
Moisture	6.51
Ash	~ 0.10

Table 1: Composition as percentage of organic mass of guava seeds

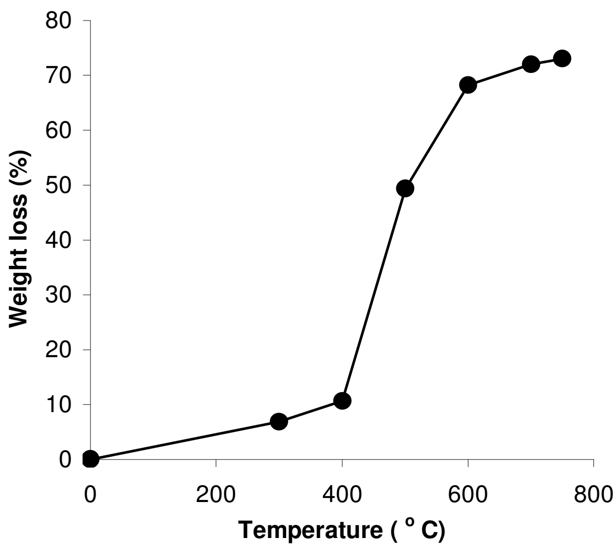


Figure 1: Effect of temperature on pyrolysis of guava seeds.

The surface area of the samples was analysed by nitrogen adsorption technique and the results are given in Table 2. The results show that the surface area increases significantly with the temperature of pyrolysis. After activation, the surface area of the sample pyrolysed at 700 °C was double, thus creating a larger internal surface area or a maximum porous structure.

Pyrolysis temperature(° C)	Surface area ($m^2 g^{-1}$)
Raw seeds (no pyrolysis)	13
400	178
600	308
700	314
700 (activated)	600

Table 2: Surface area of the pyrolysed, activated and raw guava seeds.

Adsorption studies

The adsorption behaviours of the samples were studied by evaluating the removal efficiency, R_E, of methylene blue, calculated as

$$R_E = (C_o - C)/C_o \times 100 \quad (1)$$

where C_o is the initial concentration of aqueous solution of methylene blue placed in a flask and shaken at room temperature for a certain time with a weighed samples, and C is the solution concentration after adsorption, R_E is expressed in term of percentage. Figure 2 shows the removal efficiency of the pyrolysed samples versus shaking time. For comparison, adsorption pattern of raw seeds was also included. The adsorption pattern of methylene blue by guava seeds can be described into two regions. The first corresponds to a fast removal rate, followed by the second slow removal until equilibrium is achieved. The equilibrium time reduces with corresponding increase in surface area of the samples (Table 3).

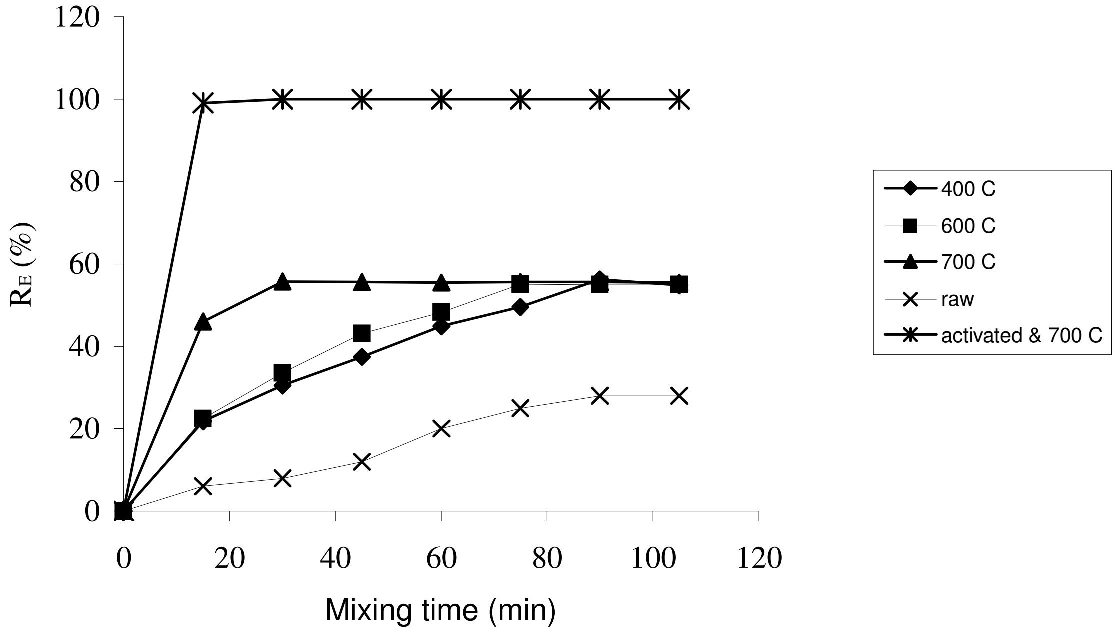
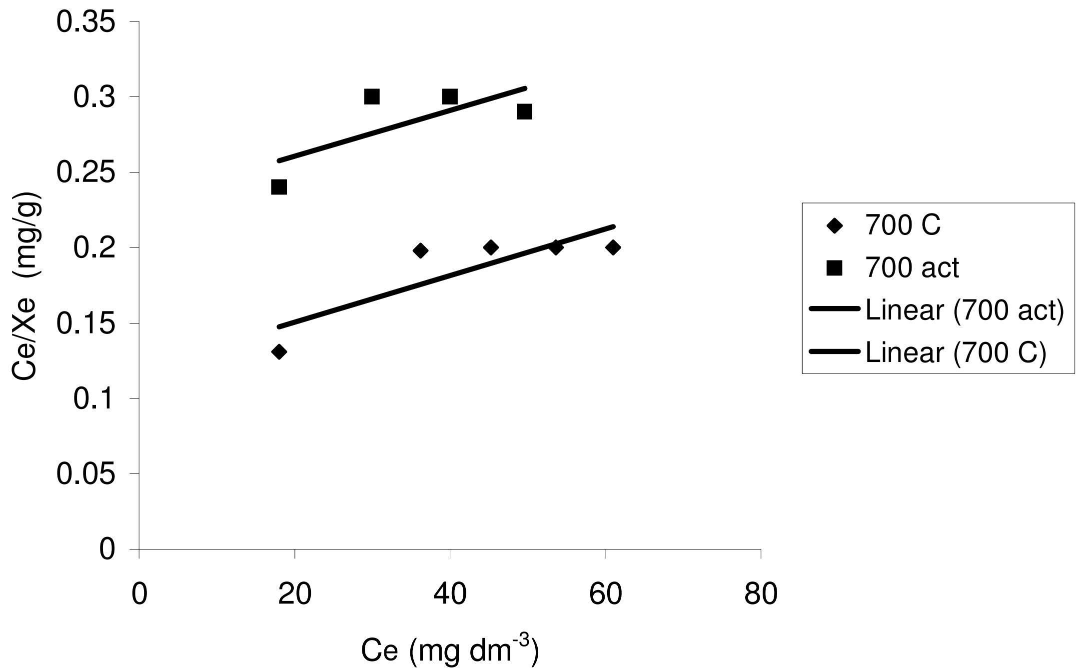


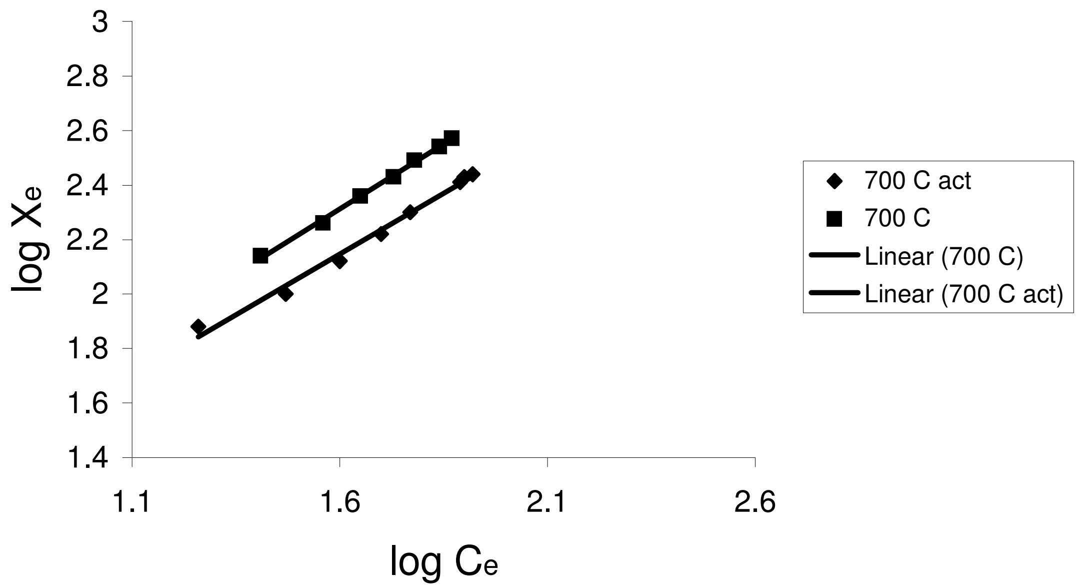
Figure 2: Removal efficiency of methylene blue versus time.

Pyrolysis temperature (^{o} C) ***(Surface area, m^2 g^{-1})***	**Equilibrium time (min)**
Without Pyrolysis *(13)*	100
400 *(178)*	90
600 *(308)*	74
700 *(314)*	30
700 (activated) *(600)*	15

Table 3: Equilibrium time for the adsorption of methylene blue on the pyrolysed samples at different temperature (sample = 0.1 g, 0.100 dm^3 of 10 mg dm^{-3} methylene blue).



(a)



(b)

Figure 3: Fitting adsorption data with (a) Langmuir model, and (b) Freundlich model.

The adsorption mechanism of the above data can be expressed in-terms of logarithmic plot of R_E versus mixing time in hour as:

$$\log R_E = m \log t + \log K \qquad (2)$$

where *m* is the slope and may represent adsorption mechanism while K is a constant may represent rate factor[14]. Regression analysis of the data reveal that increase in the surface area of the samples results in a decrease in slope values with corresponding increase in the factor K. Smaller values of *m* for larger surface areas indicate better adsorption, whereas higher values of rate factor, K, indicate a faster rate of methylene blue removal (Table 4). Additional experiment showed that a relatively small quantity of activated sample with surface area of 600 $m^2 g^{-1}$, required only 0.3 g to remove all methylene blue (10 mg dm^{-3}), as compared to 2.0 g required for the raw sample. Smaller values of K for comparatively smaller surface area may be due to the comparatively smaller pore volume or active sites on the guava seeds.

Surface area ($m^2 g^{-1}$)	**Slope *m***	**log K**	**r^2**
13	0.89	1.25	0.94
178	0.49	1.64	0.99
308	0.49	1.67	0.99
314	0.09	1.74	0.96
600	0.04	2.00	0.96

Table 4: Parameters for the log R_E versus log t (concentration = 10 mg dm^{-3}, volume 0.100 dm^3).

On pyrolysis of guava seeds up to 700 ^{o}C, organic constituents were decomposed, leaving behind porous materials containing exposed active sites. However, the surface areas at these temperatures were relatively low and the materials were able to remove methylene blue up to ~ 55 %. Since only pores larger than the size of adsorbate molecule were accessible to the adsorbate, it is believed that the some pores in the pyrolysed samples were blocked by decomposition products of the organic constituents, thus inhibiting the accessibility of the active sites for the adsorption. After activation of the sample with $ZnCl_2$, a double increase in surface area was observed, resulting in complete removal of methylene blue (Table 2 and Figure 2). The effectiveness of $ZnCl_2$ as activation agent was widely noted in the literature[2,6,13]. The salt might have penetrated into the guava seeds, and effectively remove the decomposition products during pyrolysis.

The adsorption isotherms of methylene blue onto the activated guava seeds were carried out by applying the linear Langmuir equation

$$\frac{C_e}{X_e} = \frac{1}{X_m K} + \frac{1}{X_m} C_e \qquad (3)$$

and the Freundlich equation

$$\log X_e = \log K_F + 1/n \log C_e \qquad (4)$$

where C_e is the amount of adsorbate in the solution at equilibrium, X_e is the amount of adsorbate adsorbed, X_m is the amount of adsorbated adsorbed to form monolayer coverage, and K_L, n and K_F are the equation constants.

When the adsorption data was tested using equations (3) and (4), they best fitted to the Freundlich model as indicated by its relatively higher linear correlation coefficients (Table 5). Figure 3(a) and (b) represent comparison of the experimental data of activated carbons with Langmuir and Freundlich equations. The results show that activated carbon prepared from guava seeds exhibit good capacity to remove the bulky dye molecule through chemical activation followed by pyrolysis at 700 ^{o}C.

Conclusion

Production of activated carbon derived from guava seeds had been demonstrated to be feasible. Carbonization in inert gas produced poorly activated carbons due to the incomplete decomposition of organic constituents as the pores were blocked by carbonization by-products. However, activation by $ZnCl_2$ followed by pyrolysis at 700 ^{o}C proved very effective in producing a good quality activated carbon with well-developed porosity and optimum adsorption capacity.

Acknowledgements

The authors thank the School of Chemical Sciences, Universiti Sains Malaysia for financial support. The authors also express their sincere appreciation to Mr. Poon Yew Chin of Golden Hope Plantation for providing the guava seeds sample.

References

1. Srivastava S.K., Pant N. and Pal N. (1987) *Water Res.*, **21**(11), 1389-94.
2. Usmani T. H., Wahab T. and Ahmand S. Z. (1988) *Pakistan J. Sci. Res.*, **31**(3), 221-24.
3. Rahman I. A., Ismail J and Osman H. (2000) *Malaysian Journal of Chemistry*, **2**(1), 12-15 .
4. El-Hendawy A. A, Samra S. E. and Girgis B.S. (2001*) Colloids and Surface A: Physicochemical and Engineering Aspects,* **180**(3), 209-221.
5. Avon J., Ketcha Mbadcam J., Noubactep C. and Germain P. (1997) *Carbon*, **35**(3), 365-369.
6. Chan K.C., Goh S.H., Toh T.H., Tan W.I. and Tang T.S. (1980) *Malaysian J. Sci*., **6**, 131- 137.
7. Bcaoui A., Yaacoubi A., Dahbi A., Bennouna C., Phan Tan Luu R., Maldonado-Hodar F.J., Rivera-Utrilla J. and Moreno-Castilla C. (2001) *Carbon,* **39**, 425-432.

		Samples	
Model	Parameter	700 ^{o}C	700 ^{o}C activated
Langmuir	r^2	0.508	0.713
	K_L	6.504	13.400
	X_m	0.667	0.625
Freundlich	r^2	0.988	0.999
	K_F	5.261	6.174
	n	1.052	1.122

Table 5: Parameters for the adsorption of methylene blue.

8. Abu-El-Sha'r W.Y., Gharaibeh S.H., and Mahmoud S. (2000) *Enviromental Geology*, **39**, 1090-1094.
9. Annadurai G., Sheeja R.Y., Mathalai S., Murugesan T., Srinivasamoorthy V.R. (1999) *Bioprocess Eng*., **20**, 37-43.
10. Tanin S. and Gurgey I. (1987) *Chimica Acta Turcica*, **15**, 461-75.
11. Tanin S. and Gurgey I. (1988) *Chimica Acta Turcica*, **16**, 57-63.
12. Lafi W.K. (2000) *Biomass & Bioenergy*, **20**, 57-62.
13. Hu Z., Srinivasan M.P. (2001) *Microporous and Mesoporous Materials*, **34**, 267 – 275.
14. Bourgeois P., Guylene S, Jacqueline A., Joseph H. (1988) *Agricultures*, **7**(2), 105.
15. TAPPI. T203. Revised T203, 05 (1974).
16. Rahman I.A. and Ismail J. (1993) *J. Mater. Chem.,* **3**(9), 931-934.
17. Rahman I.A., Ismail J. and Osman H. (1997) *J. Mater. Chem*., 7(8), 1505-1509.