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Adsorption Efficiency of Acid Brown 43 and Reactive Yellow 2 onto Green House Gas Emitting Agro Waste Obtained from *Epiphyllum oxypetalum* (Cactaceae)

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ABSTRACT

Epiphyllum oxypetalum is a species of cactus and one of the most commonly grown of the Epiphyllum species. It is one of the under-utilized resources available in the tropical regions of the globe and can be used as a substitute for digitalis. The Shoshone Indian tribe calls the night blooming Cereus "Pain in the heart" and used it for heart pain. Scanty work was reported on the phytochemical properties of leaf extract. No documented research work has been reported on its leaf and flower for assessment of adsorption studies. Thus the present investigation was carried out to assess the adsorptive studies of plant wastes. The activated carbon was prepared from *Epiphyllum oxypetallum* wastes by $ZnCl_2$ activation. The adsorption kinetics of industrial dues was studied from the activated carbon. The optimum temperature was found to be 30 °C and the adsorption data fitted well onto Langmuir adsorption isotherm model. The high surface area of activated carbon was demonstrated to be promising adsorbents for pollution control and for other applications.

Keywords: Activated carbon; Adsorption; Dyeing effluents; *Epiphyllum oxypetalum* waste; Langmuir adsorption isotherm model.

1. INTRODUCTION

Epiphyllum oxypetalum is a species of cactus and one of the most cultivated species in the genus. It is a variety of night blooming Cereus. *Oxypetalum* (Lat.) = with acute petals, refers to the acute petals of this species. *Epiphyllum oxypetalum* was the most commonly grown of the *Epiphyllum species*, and it is known under several common names including Night-blooming Cereus, Dutchman's Pipe, Queen of the Night, Wijaya Kusuma (Indonesian), Nishagandhi in Hindi and Marathi, table 1.

Table 1. Taxonomy of *Epiphyllum Oxypetalum*

Kingdom	Plantae
Sub Kingdom	*Tracheobionta*
Superdivision	*Spermatophyta*
Division	*Magnoliophyta*
Class	*Magnoliopsida*
Order	*Caryophyllales*
Family	*Cactaceae*
Genus	*Epiphyllum*
Species	*Eoxypetalum*
Binomial name	***Epiphyllum oxypetalum***

The plant kingdom is a large reservoir of pharmacologically active molecules and large number of plant-derived medicines now commercially available. (Newman *et al.* 2007).

Traditionally used medicinal plants produce a variety of compounds of known therapeutic properties (Harbone *et al.* 1998). The present investigation clearly reveals the adsorption nature of this plant.

Fig. 1: *Epiphyllum oxypetalum* (Cactaceae) flowers and leaves

2. MATERIALS & METHODS

2.1 Plant Material *(Epiphyllum oxypetalum)*

The plant waste of *Epiphyllum oxypetalum* was collected from in and around the city of Coimbatore, India

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in December 2014. The plant was authenticated by Tamil Nadu Agricultural Univeristy, Coimbatore, India. (Fig. 1).

Chemical activation is one of the possible methods to produce activated carbons (ACs). It involves pyrolyzing the feed stock in the presence of a chemical activating agent such as $ZnCl_2$, H_3PO_4, H_2SO_4, Na_2SO_4, K_2CO_3, etc. The optimum temperature for zinc chloride activation of a number of precursors of vegetable is 700 K (Molina-Sabio *et al.* 1995; Laine *et al.* 1989).

2.2 Surface Area and Pore Size Distribution Analysis

The N_2 adsorption-desorption isotherms of activated carbons were measured at 77 K using a gas sorption analyzer (NOVA1000, Quanta Chrome Corporation) in order to determine the surface areas and the total pore volumes (Fig. 2). The surface areas were calculated using the BET equation. In addition, the t-plot method was applied to calculate the micropore volumes and external surface areas (mesoporous surface areas). The total pore volumes of the prepared carbons was estimated from the liquid volume of adsorbate (N_2) at a relative pressure of 0.99. All the surface areas were calculated from the nitrogen adsorption isotherms by assuming the area of a nitrogen molecule to be 0.162 nm^2 (Gregg *et al.* 1982).

Here we report on the porous texture characteristics of ACs prepared by $ZnCl_2$ activation of *Epiphyllum oxypetalum* (Cactaceae) wastes. These *Epiphyllum oxypetalum* (Cactaceae) wastes were impregnated with aqueous solution of zinc chloride following a variant of the incipient wetness method (Lartey *et al.* 1999). The pyrolysis treatments were carried out in a vertical tubular reactor made of quartz, using in all cases 10 g of impregenated and dried material. The pore size distribution of activated carbon can be classified into three groups. The groups are based on the size range of pore diameters found in activated carbon: the micropores are less than 2 nm in size, the transition pores or mesopores range in size from 2 nm to 50 nm and the macropores are greater than 50 nm (Dubinin, 1960). The porosity of activated carbon is a very important property since it greatly influences the adsorption of dyes. The macropores provide passage to the micropores and access to the interior of the carbon matrix. The micropores created during the activation process are responsible for the very large surface area used for dyes adsorption. Typically, activated carbons have BET surface areas in the range from 500 to 1400 m^2/g and the relative (%) contribution of each pore structure to the total surface area and adsorption process vary in the order: macropores (0%) < mesopores (5%) < micropores (95%) (Lartey *et al.* 1999) (Fig. 3).

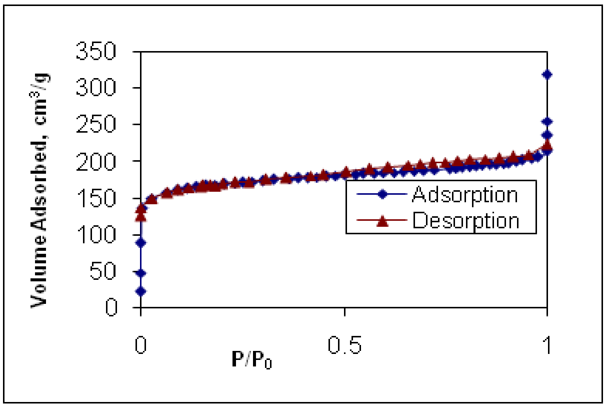

Fig. 2: Shows adsorption-desorption isotherms of N_2 at 77K ACs from *Epiphyllum oxypetalum* wastes with $ZnCl_2$

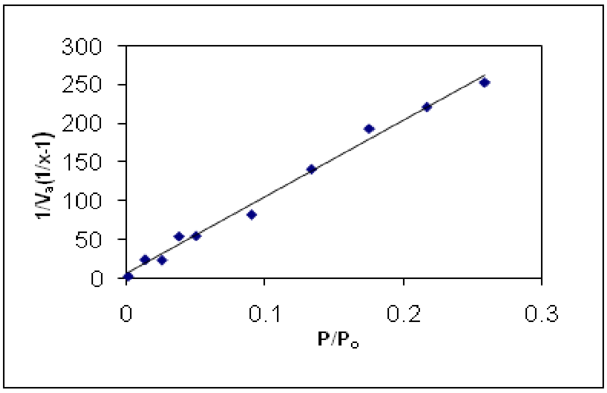

Fig. 3: BET Plot of EOAC

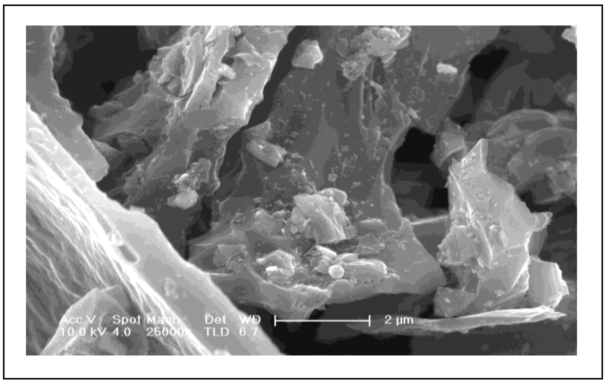

Fig. 4: SEM image of *Epiphyllum oxypetalum* wastes with $ZnCl_2$

2.3 Scanning Electron Microscope (SEM)

The surface morphologies of activated carbons were observed with SEM, Philips SIRON with EDX facility at IISc, Bangalore.

2.4 Adsorption Mechanism

According to Michelson *et al.* (1975) for the adsorption of dyes on the carbon surface, for film diffusion to be rate-determining step, the value of the film diffusion coefficient, D_f should be in the range 10^{-6} to 10^{-8} cm^2/sec. If pore diffusion were to be rate limiting, the pore diffusion coefficient, D_p should be in the range 10^{-11} to 10^{-13} cm^2/sec. In order to find out the nature of the process responsible for adsorption on to EOAC, attempts were made to calculate the diffusion co-efficient of the process.

Assuming spherical geometry of the sorbents (Bhattacharya *et al.* 1984) the overall rate constant of the process can be correlated to the pore diffusion coefficient in accordance with the expression,

$$t_{1/2} = 0.03\frac{r_o^{\,2}}{D_p}$$

or to the film diffusion coefficient in accordance with

$$t_{1/2} = 0.23\frac{r_o \partial}{D_f} \times \frac{\bar{C}}{C}$$

where r_o is radius of the sorbent (cm), D_p and D_f are pore diffusion coefficient (cm^2/sec) and film diffusion coefficient (cm^2/sec) respectively, C/C is equilibrium loading of the adsorbent , ∂ is the film thickness (cm) and $t_{1/2}$ is the time for half change (sec) .

Since the carbon particles used were of the size range (75-150 µm), the average diameter of the particle was taken as 0.0215 x 10^{-4}cm. Using these values, the film diffusion coefficients and pore diffusion coefficients were calculated.Then considering the pseudo first order rate constant k_L, for the adsorption of Acid brown 43, Reactive yellow 2 the values of D_p and D_f were calculated under the given set of operating conditions, and are presented in the table 2. The values of D_p and D_f for dyes in the present study are found to be in the order of 10^{-12} to 10^{-13} and 10^{-11} to 10^{-12} cm^2/sec which indicates that pore diffusion has some amount of influence in the rate determining step.

Table 2. D_p and D_f values for the chosen adsorbent - adsorbate system

S. No.	Dye	Particle Size (µm)	D_p , cm^2/sec x 10^{-13}	D_f , cm^2/sec x 10^{-11}
1	Acid brown 43	75 - 180	67.146	76.941
		180-250	82.980	91.013
		250-355	91.77	98.012
2	Reactive yellow 2	75 - 180	82.980	96.721
		180-250	15.247	16.081
		250-355	41.636	46.428

Gupta *et al.*(1990) have reported a D_p value in the order of 10^{-10}cm^2/sec for the removal of chrome dye by a mixture of two adsorbents and these authors suggested that the adsorption process was governed by pore diffusion even though it could not be ascertained that pore diffusion was the only rate determining step. Karthikeyan (2007) has stated that a D_p value in the order of 10^{-10} cm^2/sec would confirm that the adsorption process was under the control of intraparticle diffusion. The author has also added that both film and intraparticle diffusions have different degrees of influence on the rate determining step.

The present study indicates the D_p values in the order of 10^{-12} to 10^{-13} cm^2/sec and the D_f values in the order of 10^{-11} to 10^{-12} cm^2/sec for the respective Lagergren plots for each dye and hence, the investigator concludes that the mechanism of the removal of each dye in the present study by EOAC is complex. Since both external mass transfer and intraparticle diffusion constants varied with initial dye concentration indicating the occurrence of both surface adsorption and intra particle diffusion, the sorption data were further analyzed by the kinetic expression given by Boyd *et al.* (1947).

$$F = 1 - \frac{6}{\pi^2} \sum_{N-1}^{\alpha} \frac{1}{n^2} \exp\left[-n^2 \beta_t\right] \qquad (1)$$

where F is the fractional attainment of equilibrium at time t and is obtained by using the following equation and D_i is effective diffusion co-efficient of adsorbates in the adsorbent (assumed to be spherical) and the values of n are the integers.

$$F = \frac{q_t}{q_e} \qquad (2)$$

where q_t and q_e are the amount of dye adsorbed at time t and at equilibrium respectively.

On the basis of F values, corresponding values of B_t were obtained from eq. 1 and the linearity test was carried out by plotting B_t with respect to time for each solution at different time intervals and at 30, 45 and 60 °C. In each adsorbent-adsorbate system, the plot B_t versus time distinguishes between the film-diffusion and particle-diffusion controlled rate of adsorption. The B_t versus time plots and it was represented in the fig. 5 and fig.6 for the sorption of Reactive yellow 2 over EOAC were found to be linear but did not pass through the origin throughout the concentration ranges at 30, 45 and 60 °C. Thus the process involved can be interpreted as film diffusion. At 30 °C the B_t versus time plots for the sorption of Acid brown 43 over EOAC were found to be linear and passing through to origin. Thus the process seems to be particle diffusion controlled in the region, while during the later stages, the film diffusion mechanism also becomes operative, because of the deviation of the plot from linearity. While at 45 °C and 60 °C Acid brown 43 over EOAC exhibit linearity and it passes through the origin, thereby revealing that the rate-determining process is particle diffusion. From the slope of the straight line obtained from B_t versus time graph, the B value (time constant) was calculated.

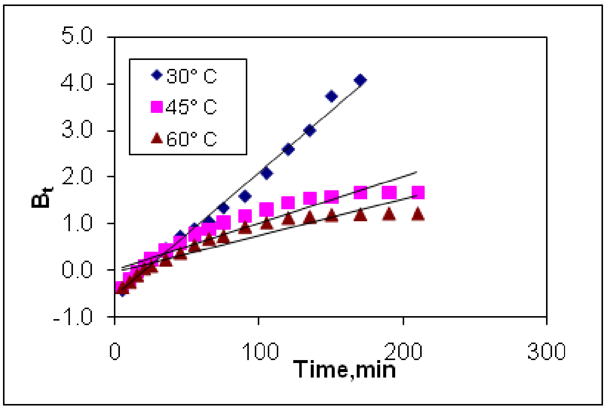

Fig. 5: Bt vs. Time for acid brown 43

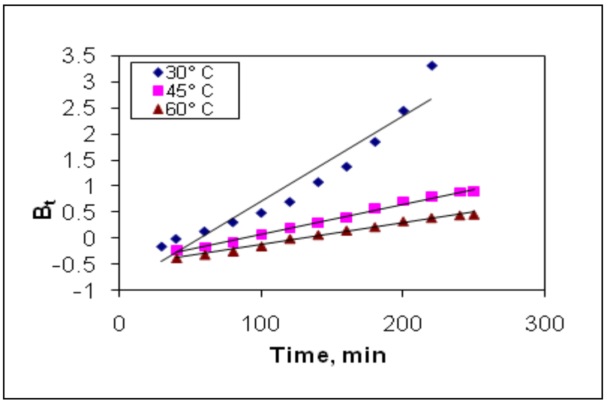

Fig. 6: Bt vs. Time for Reactive yellow 2

3. RESULTS & DISCUSSION

3.1 Carbon Properties

The characteristics of activated carbon prepared from *Epiphyllum oxypetalum* wastes in different activation methods given in the tables 3 and 4. Evaluation of the characteristics of carbon table 3 prepared from different processes indicates that the density of carbon is in comparable range. The uniform bulk density values imply that *Epiphyllum oxypetalum* wastes has high resistance towards the action of chemicals and the pore system was also uniform, irrespective of the processing methods.

From table 3 the moisture content was found to be high in the case of carbon obtained by $ZnCl_2$ process. This implies that extensive porosity has been introduced by this process in the carbon structure. Even though moisture content of the carbon has no effect on its adsorptive power, it dilutes the carbon which necessitates the use of additional weight of carbon during treatment process. Among the carbon prepared by various methods, the carbon obtained by carbonate process was found to contain less moisture. Ash content generally gives an idea about inorganic constituents associated with carbon obtained by different carbonization methods. The ash content values from table 3 indicate that the overall ash content for all the varieties of carbon was comparatively less. This may be attributed to lower inorganic content and higher fixed carbon.

Solubility studies of carbon in acid and water were performed to evaluate the amount of impurities present in the carbon prepared by different carbonization processes. From table 3 the data pertaining to the matter soluble in water indicate that the carbon prepared by all other processes exhibits moderate level of impurities except the carbon obtained by H_2SO_4 acid process. The high value of water soluble matter in the carbon prepared by carbonate process indicates that a large amount of carbonate salts would have been incorporated in the carbon structure.

The surface area of carbon prepared by various processes is found to be in the following order.

The higher surface area of carbon prepared by $ZnCl_2$ process may be to restricted pore shrinkage during activation. The iodine number of all carbon was found in the same order as that of surface area. This indicates that the carbon prepared by Zinc chloride process has the maximum adsorption capacity. Carbon samples with higher surface area are considered substance. From table 4 EOAC have higher BET Surface area, micropore, mesopore. From table 2 it is clear that acid process gives more yields followed by carbonate process. When compared to other treatment processes of the acid process, H_2SO_4 gives high yield, due to its high charring capacity. All carbon samples except $ZnCl_2$, H_2SO_4 and H_3PO_4 show significant nitrogen uptake at low relative pressure. This can be ascribed to the strong interaction between nitrogen molecules and the wall with closely spaced pores. Nitrogen adsorption for the Na_2SO_4 and K_2CO_3 samples was low, since the samples have such a low degree of activation and a low pore volume. Carbon samples from $ZnCl_2$ have higher BET surface area micropore and mesopore volume. As reported by Yu and Chou (2000), Mangun *et al.* (1998) also thought the total micropore volume is important since only a small fraction of the pores is actually occupied during adsorption. Pelekani and Snoeyink (2001) also reported that the compounds are preferentially adsorbed into pores that are similar in size to the adsorbate because of greater number of contact points between adsorbent and adsorbate.

The highest surface area was obtained for activated carbon using *Epiphyllum oxypetalum* wastes by $ZnCl_2$ process followed by activation at 800 °C under a N_2 atmosphere (621.00 m^2/g). Many studies on preparation of activated carbons using $ZnCl_2$ process have been reported.

The TGA curves of the activated carbon samples heated from 50 °C to 800 °C at 10 °C/min. These curves clearly illustrate that the carbon samples begin to lose weight at about 60 °C due to the volatilization of small molecules and it started to lose weight intensively between 700 °C and 800 °C due to the pyrolysis of aromatic molecules. The weight loss and differential plot for the starting material indicates that essentially all weight loss starts at about 60 °C and corresponds to full burn off of the activated carbon. On the activation carbon samples, the weight loss starts at a higher temperature, which suggests the conversion of carbon can be taken as the oxidation barriers.

The morphological study by SEM of the above adsorbents fig. 4 reveals the highly porous nature. From the SEM results, it was found that there are holes and cave type openings on the surface of the specimen that would definitely have increased the surface that is available for the adsorption (Khattri *et al.* 1999). The present adsorbate-adsorbent system ia found to obey Langmuir model table 5.

Table 3. EOAC waste Activated Carbon properties in various activation processes

S. No	Properties	$ZnCl_2$	H_3PO_4	H_2SO_4	Na_2SO_4	K_2CO_3
1	pH	6.1	6.1	5.7	9.1	8.7
2	Moisture Content	17.8	16.0	13.8	8.76	6.4
3	Ash Content, %	14.4	10.0	8.34	0.526	10.79
4	Bulk density,	0.426	0.419	0.853	0.649	0.8272
5	Porosity, ζp	0.725	0.632	0.546	2.8	0.248
6	Matter Soluble in water	1.16	1.56	1.81	6.7.1	2.92
7	pH_{zpc}	4.2	4.0	3.3	6	7.7

Table 4. Porosity characteristics of EOAC Waste

S_{BET} m^2/g^{-1}	S_{EXT} m^2/g^{-1}	V_{micro} m^2/g^{-1}	S_{micro} m^2/g^{-1}	V_{total} m^2/g^{-1}	APD A	% micro	% meso
621.78	143.462	0.1974	479.27	0.490	31.692	40.1611	0.90741

Table 5. Langmuir constants–Temperature, pH and particle size variation

Dye	pH = 6.5 Particle Size = 75-180 µm Agitation time = 3 hours				Temperature = 30° C, Particle Size = 75-180 µm Agitation time = 3 hours				pH = 6.5 Temperature = 30 °C Agitation time = 3 hours			
	Temp, °C	Q_o, mg/g	b, L/mg	R^2	pH	Q_o, mg/g	b, L/mg	R^2	Q_o, mg/g	b, L/mg	R^2	R^2
Acid brown 43	30	123.46	0.3188	0.9933	5.0	133.67	0.3218	0.9976	75-180	123.46	0.3188	0.9933
	45	126.00	0.6428	0.9966	6.5	123.46	0.3188	0.9933	180-250	53.19	0.3511	0.9791
	60	148.00	0.6934	0.9979	8.0	68.03	0.8215	0.9682	250-355	44.44	0.3821	0.9864
Reactive yellow 2	30	94.34	0.0639	0.9579	5.0	97.13	0.4357	0.9974	75-180	94.34	0.0639	0.9579
	45	137.67	0.0364	0.9699	6.5	94.34	0.0639	0.9579	180-250	93.46	0.0888	0.9747
	60	176.4	0.0275	0.9798	8.0	66.10	0.0428	0.9500	250-355	90.10	0.0928	0.9530

4. CONCLUSION

This research has revealed that, the physico-chemical characteristics,especially the pore size distribution of carbon samples, the activated carbon prepared using *Epiphyllum oxypetalum* (Cactaceae) waste by $ZnCl_2$ carbonization process followed by activation at 800 °C under a nitrogen atmosphere was chosen as an adsorbent for adsorption studies. The studies on the influence of pH of the experimental solution on adsorption potential have revealed that a pH value around 6.5 appears to be the most favorable for the removal of all dyes. The experimental adsorption data were fitted reasonably well to Langmuir adsorption isotherm. The study of the influence of the adsorbent size on the adsorption indicates the significant influence of the size of the adsorbent on dye removal. The values of D_p and D_f for all dyes in the present study are found to be in the order of 10^{-10} to 10^{-13} and 10^{-9} to 10^{-11} cm^2/sec which indicates that pore diffusion has some amount of influence in the rate determining step. The applicability of the Langmuir model to the present system confirms the formation of monolayer of dye species onto the surface of the adsorbent. The R_L values were determined and these are found to lie between one and zero, suggesting that the *Epiphyllum oxypetalum* (Cactaceae) waste carbon can be used successfully as the adsorbent for the removal of dyes.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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REFERENCES

Bhattacharya, A. K. and Venkobachar, C., Removal of Cd(II) by lowcost adsorbents. *J. Env. Eng. Div.*, 110(1), 110-122(1984). https://doi.org/10.1061/(ASCE)0733-9372(1984)110:1(110)

Boyd, G. E., Adamson, A. W. and Meyers, L. S., The exchange adsorption of ions from aqueous solutions of organic zeolites II kinetics, *J. Am. Chem. Soc.*, 69(11), 2836-2848(1947). https://doi.org/10.1021/ja01203a066

Dubinin, M. M., The potential theory of adsorption of gases and vapors for adsorbents with energetically non-uniform surfaces, *Chem. Rev.*, 60, 235-241(1960). https://doi.org/10.1021/cr60204a006

Gregg, S. J. and Sing, K. S. W., Adsorption, Surface area and Porosity. 2nd Edition, *Academic Press*, London; Newyork(1982).

Gupta, G. S., Prasad, G. and Singh, V. N., Removal of chrome dye from aqueous solutions by mixed adsorbents, fly ash and coal, *Water Res.*, 24(1), 45-50(1990). https://doi.org/10.1016/0043-1354(90)90063-C

Harborne, J. B., Phytochemical Methods : A guide to modern techniques plant analysis, 3rd Ed., New York: *Chapman and Hall Int. Ed.*, 234-245(1998).

Karthikeyan, S., Jambulingam, M., Shekhar, A. P. and Sivakumar, B., Kinetic, Isotherm and Transport modeling for sorption of basic red onto activated carbon prepared from *Ipomoea carnea* steam waste, *22nd International Conference on Solid Waste Technology and Management* (ICSW 2007), Widener University, Philadelphia, PA, USA.

Khattri, S. D. and Singh, M. K., Adsorption of basic dyes from aqueous solution by natural adsorbents, *Indian J. Chem. Technol.*, 6(2), 112-116(1999).

Laine, J., Catafat, A. and Labady, M., Preperation and characterization of activated carbons from coconut shell impregnated with phosphoric acid, *Carbon*, 25, 191-195(1989). https://doi.org/10.1016/0008-6223(89)90123-1

Lartey, R. B., Acquah, F. and Nketia, K. S., Developing national capability for manufacture of activated carbons from Agri Wastes, *Ghana Engineer*, 76(1999).

Michelson, L. D., Gideon, P. G., Pace, E. G. and Kutal, L. H., Removal of soluble mercury from wastewater by complexing techniques, USDI. Off., *Water Res. Technol. Bull.*, 74(1975).

Mangun, C. L., Daley, A. M., Braatz, R. D. and Economy, J., Effect of pore size on adsorption of hydrocarbons in phenolic based activated carbon fibres, *Carbon*, 36(1-2), 123-129(1998). https://doi.org/10.1016/S0008-6223(97)00169-3

Molina-Sabio, M., Rodriguez-Reinoso, F., Caturla, F., and Selles, M. J., Porosity in granular carbons activated with phosphoric acid, *Carbon*, 33, 1105-1113(1995). https://doi.org/10.1016/0008-6223(95)00059-M

Newman, D. J. and Cragg, G. M., Natural products as sources of new drugs over the last 25 years, *J. Nat. Prod.*, 70(3), 461- 477(2007). https://doi.org/10.1021/np068054v

Pelekani, C. and Snoeyink, V. L., Competitive adsorption in natural wayer: Role of activated carbon pore size. *Water Res.*, 33(5),1209-1219(1999). https://doi.org/10.1016/S0043-1354(98)00329-7

Yu, J. J. and Chou, S. Y., Contaminated site remedial investigation and feasibility removal of chlorinated volatile compounds from ground water by activated carbon fiber adsorption, *Chemosphere*., 41(3), 371-378(2000). https://doi.org/10.1016/S0045-6535(99)00437-3