Evaluation of cassava (*Manihot Esculentum*) seed waste Activated carbon for kinetic study on methylene blue dye adsorption from aqueous solution

Gumus R.H.

Department of Chemical and Petroleum Engineering, Niger Delta University P.M.B 071 Wilberforce Island. Bayelsa State. Nigeria

ABSTRACT

The effect of activation temperature on activated carbon was studied at 400° C, 500°C and 600°C respectively. The characterization properties showed that increased in temperature reduces yield, moisture content, ash content and volatile content but increased fixed carbon, pore volume and porosity. Batch experiment was conducted by varying the dosage of activated carbon (0.2g - 0.6g) and contact time (40 -120 min) on adsorption of methylene blue dye from aqueous solution. The experimental data was fitted to pseudo first and second order kinetics in order to verify the rate controlling mechanism. The pseudo second order model showed a better fit with the highest correlation coefficient of 0.998. The adsorption capacity q computed was found to be 6.561 mg/g and 16.129 mg/g showed deviation from the experimental value of 11.00 mg/g for the both kinetics. The equilibrated isotherm data was also fitted to Langmuir, Freundlich and Dabinin-Radushkevich. Freundlich model has the best fit with R2 = 0.914. The energy of adsorption was calculated using the Dabinin-Radushkevich model and found to be 5.89 kJ/mol.

Keywords: Activated carbon, Adsorption, Cassava seed waste, Kinetics, Methylene blue dye,

*Correspondence to Author:
Gumus R.H.
Department of Chemical and Petroleum Engineering, Niger Delta University P.M.B 071 Wilberforce Island. Bayelsa State. Nigeria

1 Introduction

The treatment of waste water effluent from textile industries has attracted much attention in recent times. These industries use variety of manmade dyes which constitutes the major source of environmental pollution in developing countries like Nigeria. Although there are conventional methods of treating these effluents; such as chemical precipitation, coagulation, ion–exchange and membrane filtration, an efficient way to remove dye is the adsorption process; using low cost adsorbent which is simple and cost effective.

The reports in literature have shown that over 735 tonnes of synthetic dyes are produced worldwide, annually with 10-15 % of the dyes being lost in the effluent during the dyeing processes [1]. To overcome this predicament, several researchers have sourced for low cost , non conventional materials for adsorbent; coconut shell [2] scolymus hispanicus L: [3] bean husk [4] globe artichoke leaves [5] rice husk [6] bone [7] snail shell [8] corncob [9] chicken waste and coal [10].Molasse [11] palm flower [12] palm kernel shell [13] rice husk and sugar cane baggasse [14] olive stone [15] paper mill sludge[16] and waste tire[17].

The major problems encountered in textile discharge without treatment are: the chemical oxygen demand by the water body and the increase in toxicity. It also lowers the light penetration, photosynthesis and the damage to aesthetic nature of the water surface. Apart from the toxic, mutagenic and carcinogenic nature, the effluent components are very stable to light, temperature and microbial attack [1]. Research groups have studied the potentials of different waste materials for activated carbon on methylene blue adsorption: palm flower [12] corn cob [18] sea snail shell [19]. The use of cassava seed waste is limited in literature.

Cassava (Manihot esculentum) is a plant cultivated in abundance in the southern part of Nigeria. It has different varieties of which the tubers are edible when cooked. It is also made in to powdered form for consumption. The fruit seed is not useful after harvesting the root (tubers) of the plant. Researchers have used several precursors from waste materials; for the activated carbon but there is no report in literature relating to the use of this waste (cassava seed) activated carbon for the adsorption of methylene blue dye. This creates my interest to evaluate the potential and the adsorption behaviour using cassava seed activated carbon. In this paper cassava seed waste has been evaluated for the use of activated carbon. The kinetics of adsorption of methylene blue dye from aqueous system was also studied.

2 Experimental

2.1   Material and Methods

The Cassava seeds were obtained from farmers in Efeke -ama compound in Amassoma town situated near the Niger Delta University, Wilberforce Island all in Bayelsa state. Nigeria. The cassava seeds were washed, dried under sunlight for (6) days to reduce the moisture content. It was further dried in an oven at $105^{o}C$ for 2 hours. The Oven dried cassava seeds were carbonized at 500 in a furnace. The samples were grinded and sieved to particles sizes of 300 µm. The carbonized materials were impregnated with 0.2 mol/dm^3 of phosphoric acid H_4PO_3 and activated at $400^{o}C$, $500^{o}C$ and $600^{o}C$ for 2 hours respectively.

2.3   Characterization

The sample characterization was carried out on the following; pH, pore volume, porosity, ash content, moisture content and bulk density. Also included were yield and the fixed carbon described by [8].

Batch Adsorption studies

100 ml of dye solution of 75 mg/l concentration was prepared and 0.2 g of the activated carbon was added to the prepared dye solution and kept for 40 min in a shaker at 150 revolutions per minute. The equilibrium dye concentration was estimated at the wavelength of 530 nm, using a spectrophotometer (JASCO UV/Vis-550). The samples were withdrawn from the shaker at 40 min interval ranging from 80, 120, 160 and 200 min and the dye solution was separated from the adsorbent with a micropipette. The equilibrium concentrations were determined using the calibrated curve. The effect of adsorbent dosage was also conducted by using the same concentration and adsorbent dose and equilibrium dye concentration was recorded after repeating the

process. The process was repeated with 0.3 g, 0.4 g, 0.5 g and 0.6 g respectively. The percentage and the amount of dye adsorbed were calculated using methods used earlier in literature [8].

3. Result and Discussion

3.1 Effect of Activation temperature on properties

The result of yield, moisture content, volatile matter and ash content is presented in Table 1. The values reduced as temperature increases whilst, the fixed carbon content, pore volume and porosity of the activated carbon increased with an increase in activation temperature.

3.2 Effect of Contact Time

Fig. 2 shows the effect of contact time on the adsorption of methylene blue dye onto activated carbon prepared from cassava (Manihot Esculentum) seed. It can be seen in Fig. 1 that the adsorption increases with the increasing time up to 160 min. The rate of adsorption is initially quite rapid with most of the dye being adsorbed within the first 160 min. It was found that more than 50 % adsorption of dye occurred within this period. The rate of adsorption was found to be slow after 160 min. This indicates that equilibrium can be assumed to be achieved after 160 min, which is mainly due to saturation of active sites; indicating that, no further adsorption can take place [20].

3.3 Effect of Adsorbent Dosage

Adsorption is influenced by the dosage of adsorbent. There was marked increase in adsorption when the amount of adsorbent was increased from 0.2 g to 0.6 g at constant stirring rate of 2 hours (See Fig.3). The adsorption increases gradually and the optimal removal efficiency of 56 % was reached at adsorbent quantity of 0.5 g. Further increase in adsorbent dosage did not increase the adsorbate adsorption, which remained at level off position. This may be due to complete coverage of pore sites of the activated carbon

3.4 Kinetics of Adsorption

Kinetic models are useful for the design and optimization of effluent treatment processes. Adsorption kinetics determines the rate – controlling mechanism of the system. The experimental data obtained were fitted into pseudo first order, pseudo second order.

3.4.1 Pseudo first order kinetics

The rate of adsorption for pseudo first order of equation (1)

$$\frac{dq_t}{dt} = k_1 \left(q_e - q_t \right) \tag{1}$$

Re-arranging – equation (1) becomes

$$\frac{dq_t}{q_e - q_t} = k_1 dt \tag{2}$$

After integration and applying boundary conditions t = 0 to t = t and q_t = 0 to q_t = q_t, the integrated form of equation (3) becomes:

$$\log \left(q_e - q_t \right) = \log q_e - \frac{k_1}{2.303} t \tag{3}$$

Where q_e and q_t are the adsorption capacities (mg/g) at equilibrium and time, t respectively and k_1 is the pseudo first order rate constant (min^{-1}) and t is time (min). The rate controlling step is physical adsorption if the data fits pseudo first order whilst chemically controlled is predominant if adsorption is described by the pseudo second order [21]. The linear plot of log (q_e-q_t) versus t gives a straight line. The rate constant k_1 and q_e are determined from the slope and intercept of the plot. Figure 4 shows the fitted results using this model and k_1 and q_e were calculated to be 0.02303 min^{-1} and 6.561 mg/g with a correlation coefficient R^2 = 0.886 and the results are shown in Table 2

3.4.2 Pseudo second order kinetics

The pseudo second order kinetic is expressed in equation (4):

$$\frac{dq_t}{dt} = k_2 \left(q_e - q_t \right)^2 \tag{4}$$

For the boundary conditions, t = 0 to t = t and q_t = 0 to $q_{t\,=\,q_t}$, the integrated form of equation

becomes;

$$\frac{1}{q_e - q_t} = \frac{1}{q_t} + k_2 t \tag{5}$$

Re-arranging equation 5 to obtain

$$q_t = \frac{1}{\dfrac{1}{k_2 q_e^2}} + \frac{t}{q_e} \tag{6}$$

The linear form of the above equation is:

Table 1 Characteristics properties of Cassava seed waste Activated carbon (CSWAC)

Temperature	Yield	Moisture	Volatile	Ash	Fixed	Pore	Porosity
°C	%	content	Matter	content	carbon	volume	
400	50.19	31	50.02	87.04	98.36	0.27	0.135
500	44.91	19	36.98	76.8	98.67	0.3	0.15
600	39.73	12	22.83	59.95	99.17	0.34	0.17

Table 2 Results of Pseudo first and second order kinetic plot constants.

Pseudo first order				Pseudo second order			
k_1	q_{cal}	R		k_1	q_{cal}	q_{exp}	R^2
0.02303	6.561	0.886		0.00217	16.129	11	0.998

Table 3 Result of various model constants for the adsorption of methylene blue from CSWAC at 30°C.

Langmuir				Freundlich			Dubinin-Radushkevich			
R_L	K_L	q_{max}	R^2	K_f	n	R^2	β	q_D	E	R^2
0.448	0.0246	4.492	0.7301	3.715	1.1299	0.9714	1.44E-07	30.91	5.89	0.9253

Figure 1 Cassava (*Manihot esculentum*) seed. (a)Fresh sample seed; (b) Oven dried sample; (c) Carbonized sample.
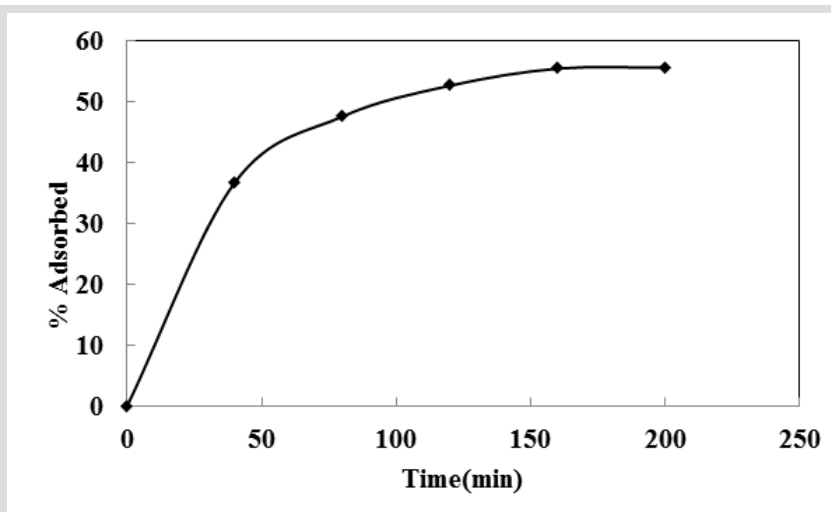
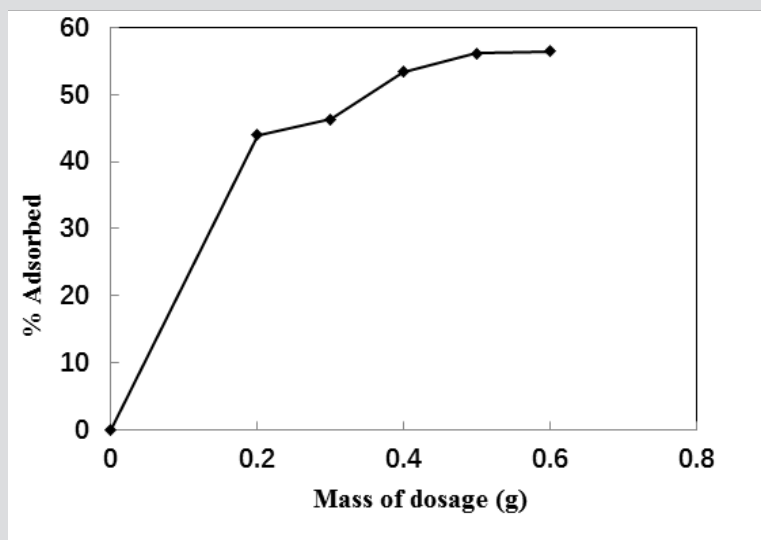**Figure 2 Effect of contact time on % adsorption of methylene blue dye**

Figure 3 Effect of dosage on adsorption of methylene blue dye

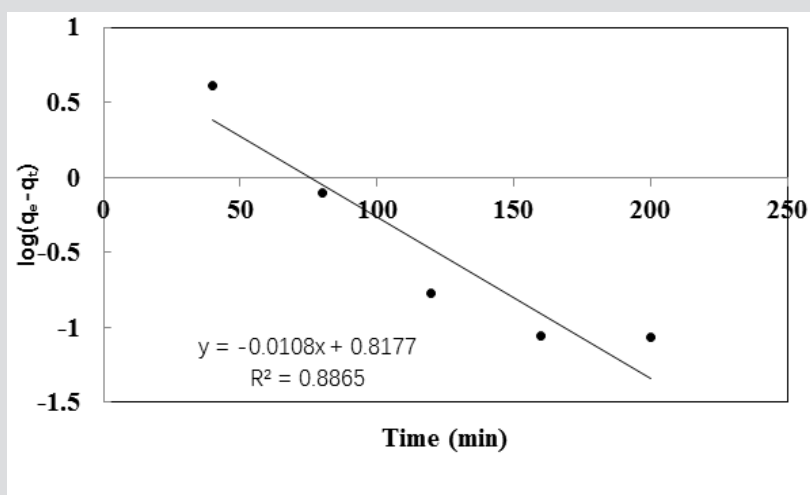y = -0.0108x + 0.8177
R² = 0.8865

Figure 4 A plot of pseudo first order kinetics

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (7)$$

The pseudo second order plot (t/q_t) versus t will give a linear relationship. Where, k_2 is the second order rate constant (g/mg min), The initial adsorption rate, h (mg/g min), as t approaches 0 can be defined as; $h = k_2 q_e^2$.

The second rate constant and correlation coefficients were computed from the plot in Fig. 5 and the results are presented in Table 2. From the plots, the pseudo second order has rate constant, k_2 of 0.0217 mg/g.min with the highest correlation coefficient value of 0.998, which indicates that chemical adsorption is the rate limiting mechanism of the Methylene blue and CSWAC system. The initial adsorption rate was found to be 461 mg/g.min. The kinetics result indicates that the adsorption process of methylene blue dye on activated carbon from cassava seed waste follows the pseudo second order kinetic model

3.5   Isotherm studies

The isotherm studies was also conducted by varying the adsorbent dosage; that furthers the understanding of the mechanism of how the methylene blue dye molecule attaches itself to the surface of activated carbon from cassava seed waste. The Langmuir, Freundlich, and Dubinin-Radushkevich isotherm models were used to fit the experimental results.

3.5.1 Langmuir model

The Langmuir model assumes that localized monolayer adsorption occurs during the process. It states that the surface of the adsorbent is homogenous with constant energy throughout the binding sites. It also assumes that each of these sites can only hold one adsorbate molecule [21].

The Langmuir model is described in the linear form in equation (8);

$$\frac{c_e}{q_e} = \frac{1}{q_{max}} k_L + \frac{1}{q_{max}} c_e \qquad (8)$$

Where C_e is the equilibrium concentration of the methylene blue dye solution. q_e and q_{max} are the equilibrium and maximum adsorption capacities of CSWAC respectively, and k_L is the

Langmuir constant. The plot of c_e/q_e versus c_e gives a straight line, with an intercept of $1/q_{max}$-k_L and slope $1/q_{max}$ respectively. Fig. 6 shows the fitted adsorption data of methylene blue dye on CSWAC. The constants q_{max}, the adsorption capacity (mg/g) and k_L, the energy of adsorption (L/mg) are obtained from slope and intercept and the results are shown in Table 2. The maximum adsorption capacity was found to be 4.492 mg/g higher than values obtained with sea snail shell activated carbon, 0.752- 0.805 [8]. However, the correlation coefficient R^2 from the plot in Fig. 6 is 0.730. The value of separation factor R_L which indicates the nature of adsorption process for Langmuir model; $0 < R_L < 1$, indicates favourable adsorption. This value was also evaluated with an equation described in earlier work (Gumus and Apre 2015) and found to be 0.448 which shows favourable adsorption.

3.5.2 Freundlich model

Freundlich model assumes that the surface of the adsorbent is heterogeneous [22], indicating that the adsorption energy is distributed and the binding sites with the same energy are grouped together in one area, thus, the formation of patches of sites, are independent of each other [23]. Equation (9) describes the model.

$$\log q_e = \log k_f + \frac{1}{n} \log c_e \qquad (9)$$

Where, k_f and n are Freundlich constant and intensity of the adsorbate molecules on the adsorbent. The parameters are determined from both the intercept and slope of the linear plot of $\log q_e$ versus $\log c_e$ which gives a straight line. Fig. 7 shows the fitted plot with a correlation coefficient $R^2 = 0.971$. Also, 1/n for the Freundlich model shows surface heterogeneity; when its value is closer to zero. But, if this value is greater than 1, then it indicates that the change in adsorbed dye concentration is greater than the change in the dye concentration in solution. The value 1/n from the fitted plot is 0.088 which is less than 1, indicating more heterogeneity. The n value was found to be 1.1299, which indicates beneficial adsorption; range of 1 and 10 [24]. The k_f value was found to be 3.715, in good agreement in earlier study [19], the adsorption of methylene blue dye on to sea snail shell activated carbon which was found to be $k_f = 3.48$.
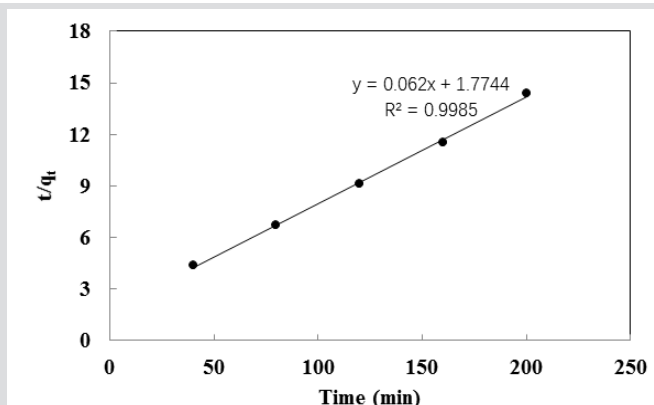
3.5.3   Dubinin-Radushkevich model

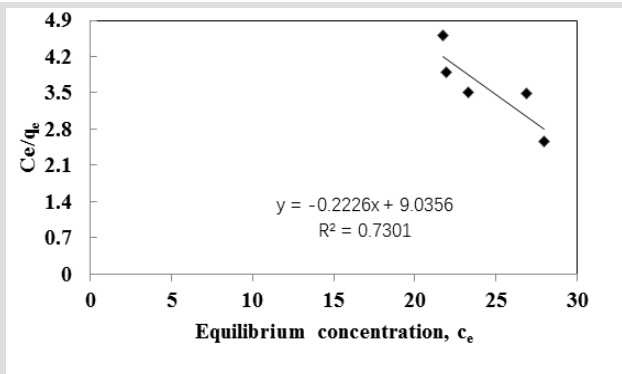**Figure. 5 Pseudo-second order kinetic plot**

Figure 6 Langmuir isotherm plot for the prepared activated carbon for methylene blue aqueous solution
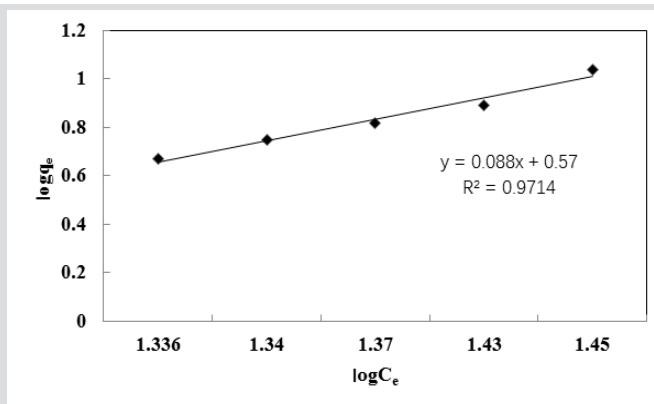

Figure 7 Freundlich isotherm plot for the prepared activated carbon for methylene blue aqueous solution.
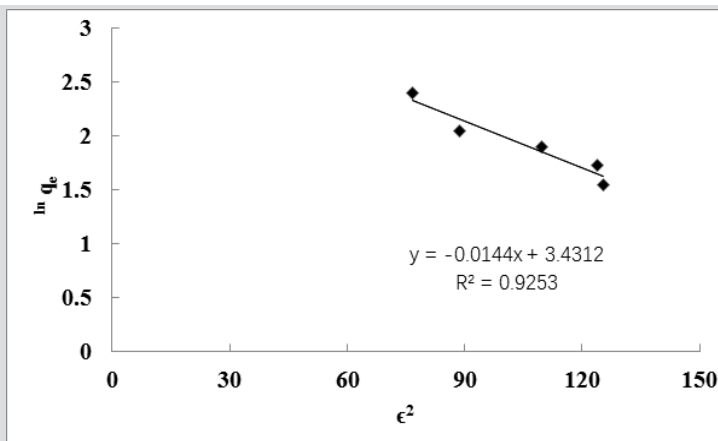

Figure8 Dubinin-Radushkevich model plot for the prepared Activated Carbon

The Dubinin-Radushkevich model was also considered, which is used to determine the dominant adsorption mechanism if it is physical or chemical adsorption by computing the value of the energy of adsorption. equation 10 describes the model.

$$q_e = q_D e - \beta\varepsilon^2 \qquad (10)$$

The linear form of the model is given in equation 11

$$\ln q_e = \ln q_D - \beta\varepsilon^2 \qquad (11)$$

Where, q_D is the theoretical saturation capacity (mg/g), B is a constant related to the mean free energy of adsorption per mole of the adsorbate (mol^2/J^2). The plot of $\ln q_e$ versus ε^2.gives a straight line, where B and q_D can be calculated from the slope and intercept of the plot. ε is Polanyi potential which is related to the equilibrium given in equation 12.

$$\varepsilon = RT\ln\left(1 + \frac{1}{c_e}\right) \qquad (12)$$

Where R is the gas constant (J/K.mol) and is the temperature $^{\circ}$C. The E, energy of adsorption can be evaluated using equation 13.

$$E = \frac{1}{\sqrt{2\beta}} \qquad (13)$$

Figure 7 shows the fitted plot and the values of β and q_D were found to be 1.44×10^{-7} mol^2/J and 30.91 mg/g respectively. The energy of adsorption was calculated to be 5.89 kJ/mol, which falls within the range of physical adsorption (< 8 kJ/mol).

4. Conclusion

The adsorption of methylene blue dye from aqueous solution using cassava seed waste adsorbent .The adsorption was found to increase by increasing the dosage and contact time. Kinetics studies showed that the results fit the second order model with an R^2 of 0.998 which indicates that chemical adsorption is the rate limiting mechanism of methylene blue dye and cassava seed waste adsorbent system. For the isotherm studies Freundlich model has the best fit with R^2 of 0.9714; indicating that the methylene blue dye was absorbed by 2 or more functional groups.

The energy of adsorption was found to be 5.89 kJ/mol; less than 8kJ/mol within the range of physical adsorption. The methylene blue dye/cassava seed waste adsorbent can be described by the two systems; chemical and physical adsorption and can be used for adsorption systems.

5. Acknowledgement

References

[1] R.S. Raveendra, P.A. Prashanth, B.R. Malini, B.M. Nagabhushana, Adsorption of Eriochrome black-T azo Dye from Aqueous solution on Low cost Activated Carbon prepared from tridax procumbens. Research Journal of Chemical Science. 5(3), 2015. 9-13.

[2] J. Laine, A. Calafat, A. and M. Labady Preparation and characterization of activated carbons from coconut shell impregnated with phosphoric acid. Carbon, 27, 1989. 191-195

[3] B. Noureddine, A. Mohammed, EL. M., Mohammed Removal of methylene blue and Eriochrome Black Tfrom aqueous solution by biosorption on scolymus hispanicus L: Kinetics, equilibrium and thermodynamics. J. Taiwan Inst. Chem. E.42, 2011. 320-326.

[4] V.G.L., Cha, N.R., Rangel-Me, O.E., Mun, D.A., Cullen, D.J., Smith, H. Terrones, and M.,Terrones, Production and detailed characterization of bean husk-based carbon: efficient cadmium (II) removal from aqueous solutions. Water Res. 42(13), 2008. 3473–3479.

[5] M. Benadjemia L., Miliere, L.N., Reinett, L.N., Bendendouche, L., Duclaux. Preparation, characterization and methylene blue adsorptionof phosphoric acid activated carbon from globe artichoke leaves. Fuel Process Technol. 92(6) 2011. 1203-1212.

[6] Y., Chen , S.R., Zhai, N., Liu, Y., Song, QD., An, and X.W., Song Dye removal of activated carbon prepared from NaOH-pretreated rice husk by low temperature solution –processed carbonization and H_3PO_4 activation Bioresource Technol. 144, 2013. 401-409.

[7] R.H., Gumus, I., Wauton, A.M., Aliu Investigation of the effect of Chemical Activation and Characterization of bone char: Cow bone. Journal of Engineering and Science, 4, 2012. 34-45.

[8] R.H. Gumus, and I., Okpeku. Production of acti-

vated carbon and characterization from snail shell waste (helix pomatia). Advances in Chemical Engineering and Science 5, 2015. 56-64.

[9] F.S. Garcia, A.M. Alonso, and J.M.D. Tascon, (2003).Porous texture of activated carbons prepared by phosphoric acid activation of apple pulp. Carbon, 39, 2003. 1103-1116.

[10] Y. Zhang, H. Cui, R. Ozao, Y. Cao, HI-I. Chen, C-W.W-P. Pan characterization of activated carbon prepared from chicken waste and coal. Energy and Fuels 21, 2007. 3735-3739.

[11] K. Legrouri, M. Ezzine, S. Ichocho, H. Hannache, R. Denoyel, R. Pailler, and R. Naslain, Production of activated carbon from a new precursor: Molasses. J. Phys. IV France, 123, 2005. 101-104.

[12] A. Shajahan, A. Bashu Sahoor, K. Basha Ariver, Biosorption and Kinetics Study on Methylene blue Dye Removal from Aqueous solution using Activated carbon Derived from palm Flower. Res.J. Chem Sci 4(12), 2014. 61-69.

[13] W.M.S.W., David Adinata, and M.K. Aroua., Prepararion and characterization of activated carbon from palm kernel shell by chemical activation with K_2CO_3, Biores Technol. 98, 2007. 145 – 149.

[14] D. Kalderis, D. Koutoulakis, P. Paraskeva, E. Diamadopoulos, E. Otal, J.O.D. Valle, and N.C. Ferna, Adsorption of polluting substances on activated carbons prepared from rice husk and sugarcane bagasse. Chem. Eng. J. 144(1), 2008. 42–50.

[15] A. Elsheikh, A. Newman, H. Al-Daffaee, S. Phull, and N. Crosswell, Characterization of activated carbon prepared from a single cultivar of Jordanian olive stones by chemical and physiochemical techniques. J. Anal. Appl. Pyrolysis, 30, 2003. 1-16.

[16] N.R. Khalili, M. Campbell, G.Sandi, and J. Gola, Production of micro and mesoporous activated carbon from paper mill sludge, I: Effect of zinc chloride activation. Carbon, 38, 2000. 1905-1915.

[17] H. Teng, Y.U. Lin, and L.Y. Hsu, (2000) Production of Activated Carbons from Pyrolysis of waste tyres impregnated with potassium hydroxide. Journal of the Air and waste management Association, 50 (B139), 2000. 1940-1946l.

[18] B.H. Diya'ddeen, I.A. Mohammed and B.Y. Jibril. Kinetics of methylene blue adsorption KOH –activated carbon using corn cobs, Malaysian Journal of Science. 30(3) 2011. 196-207.

[19] R.H. Gumus, and L.Apre Kinetic Studies of Methylene Addsorption on to Activated Carbon from Sea Snail Shell Waste (Bithynia Tentaculata), International Journal of Advances in Meaterials Scince and Engineering, 5(1) 2016. 37-49

[20] M.H. Back, C.O. Ijaghemi, O. SJ, D.S. Kim Removal of Malachite Green from aqueous solution using degreased coffee bean J. Hazard Mater, 170 2010. 820-828.

[21] D.M.M. Aquila and M.V. Ligaray Adsorption of Eriochrome Black T on MnO_2- Coated Zeolite International Journal of Environmental Science and development 6(11), 2015. 824-827.

[22] C.M. Futalan, C.C Kan, M.I. Dalida, K.J. Hsen , C. Pascun, and M.W. Van Comparative and competitive adsorption of copper , lead and nickel using chitosan immobilized on bentonite, Carbohydrates Polymers 83, 2011. 528-536.

[23] D.D. Do, Adsorption Analysis: Equilibrium and Kinetics; London . Imperial College Press 1998.

[24] P. Sivakumar and P.N. Palanizamy Adsorption studies of basic Red 29 by a non –conventional activated carbon preparedfrom euphorbia antiquor, International Journal of Chem Tech Research 1(3) 2009. 502-510.