ADSORPTION OF CATIONIC BASIC DYE FROM AQUEOUS SOLUTION ONTO ACTIVATED CARBON DERIVED FROM BANANA PEEL

HAZZAA R. [1] **and HUSSIEN M.**[2]

[1]Petrochemical Engineering Department, Faculty of Engineering, Pharos University in Alexandria, Egypt, [2]Chemical Engineering Department, Faculty of Engineering, Alexandria University, Egypt
E-mail: Riham17@yahoo.com

ABSTRACT

Dyes are toxic and cause severe problems to aquatic environment. Adsorption is one of the most effective applied techniques for the removal of dyes from the industrial effluents. The use of cheap and eco-friendly adsorbents has been studied as an alternative source of activated carbon for the adsorption of dye.

Banana peel, an abundant agricultural by-product in Delta region, Egypt, was used to prepare activated carbon by thermal activation in an inert atmosphere. Adsorptive removal of cationic basic dye, methylene blue (MB) from waste water onto dried banana peel (BP) and activated carbon prepared from banana peel (BPAC) were studied in a batch system. The effects of adsorbent dosage, pH, contact time, initial dye concentration, and temperature on the adsorption performance were investigated. The banana peel and its activated carbon were characterized by FT-IR and scanning electron microscopy (SEM).

The experimental equilibrium data were examined using Langmuir, Freundlich, Temkin, Dubinin–Radushkevich, and Harkins–Jura isotherms. The adsorption kinetic dye was analyzed using pseudo-first order, pseudo-second order, and Elovich models. The intraparticle diffusion model was used to study the kinetic mechanism of basic dye adsorption.

The experimental results showed that the adsorptive removal of dye increased with increasing the pH of solution, temperature, adsorbent dose, contact time and decreased with increasing the initial dye concentration. The adsorptive removal of methylene blue onto BP and BPAC were 90% and 98 % respectively at pH 6, 35 °C and adsorbent dose 5 g/L. The equilibrium contact time for the adsorption process onto BP and BPAC were 45 min and 30 min respectively. The adsorption process fitted well to pseudo-second-order kinetics (R^2 =0.998). The adsorption isotherm models fitted the data in the order: Temkin > Freundlich > Langmuir isotherms.

The results indicated that BP and BPAC are efficient and low-cost adsorbents for dye removal.

Keywords: Activated carbon, Basic Dye, Adsorption, Banana Peel, Isotherms, Kinetic models

1. Introduction

Dyes are found in effluent wastewaters from a variety of industries such as dye manufacturing, textile, printing, plastic, leather and pharmaceuticals. Contamination of water with dyes even in small amounts is undesirable because dyes can impede light penetration and cause toxicity to aquatic life if discharged directly into surface water (Chandra *et al* 2007). They are considered as hazard pollutant and threat human health. They may be mutagenic and carcinogenic and can cause dysfunction of kidney, liver, brain and central nervous system, and thus should be treated before discharging into the receiving body of water (Chen *et al* 2010) Methylene blue cationic basic dye is the most commonly used substance for dying cotton, wood and silk. Exposure to methylene blue may cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia and tissue necrosis in humans (Kumar *et al* 2011).

The removal of synthetic dyes is of great concern to the environment and the public health. Among various traditional treatment techniques, adsorption onto activated carbon has proven to be one of the most effective physicochemical treatment methods. Although activated carbon is a preferred adsorbent, its application is often restricted due to its high cost (Gurses *et al* 2014). Agriculture by-products and solid waste materials used for the production of activated carbons as inexpensive adsorbents including palm ash (Hameed *et al* 2007), wheat shells (Bulut *et al* 2007),rice husk (Chowdhury *et al* 2011), orange peel (Khaled *et al* 2009), rambutan peel (Ahmad *et al* 2011), cherry stones (Olivares *et al* 2012) , olive-waste cakes (Baccar *et al* 2010) and walnut shells (Yang 2010)

In the present study, dried banana peels (BP) and its activated carbon (BPAC) prepared by thermal activation were used as adsorbents to remove methylene blue dye (MB) from synthetic waste water. The aim of this work is to investigate the performance of the adsorbents in removing basic dyes from aqueous solutions. The effects of different parameters including contact time, initial dye concentration, pH, adsorbent dose and temperature were investigated. Adsorption isotherms and kinetic models were used to find out most suitable models.

2. Material and methods

2.1. Chemicals

Methylene blue, a cationic dye was chosen as an adsorbate. A stock solution of 1g/L was prepared in double distilled water. Solutions of different initial concentration of MB were prepared by serial dilution of the stock solution. A calibration standard curve was constructed using a UV spectrophotometer (Shimadzu Model: UV 1601) at maximum wavelength of 640 nm. The initial pH is adjusted with 0.1M HCl or 0.1M NaOH. pH meter (Model 744, metrohm) was used for measuring pH values. All chemicals were of analytical-grade reagent (Merck) and used without any further purification.

2.2. Preparation of adsorbents

Banana peels were collected from a local market , washed thoroughly with distilled water to remove surface dirt and adhering impurities ,cut into small pieces, crushed, and sieved in a mesh size 150 μm size by standard sieves (Model Φ200) .The banana peels dried in an air oven at 105°C for 2 h until a constant weight was reached. The dried banana peels was then divided into two portions. The first portion of dried banana peels was used as adsorbent termed BP, while the second portion was thermally activated by carbonization in a muffle furnace for an hour at 900 ºC in the absence of air by placing the sample in a well-sealed stainless steel tube, termed BPAC

2.3. Batch adsorption experiments

Batch equilibrium adsorption experiments were performed in a set of 250 mL stoppered flasks (Erlenmeyer flasks) using 100mL of MB solution with different initial concentrations 50,80,100,120,140, and 160 mg/L and 0.5 g of adsorbent dose. The flasks were placed in a thermostatic water bath shaker at temperature 35 ºC and shaken at 150 rpm for 60 min. Samples were taken at different time intervals 5–60 min till reach equilibrium, centrifuged at 2500 rpm and analyzed for remaining dye concentration. The experimental results were used for kinetic studies.The adsorption of methylene blue onto banana peels and its activated carbon was studied over a pH range of 2–10, adsorbent dose 2-10g/L, temperature 25-45ºC.The removal percentage (R%) of dye by the adsorbents , amount of the dye adsorbed at time t, q_t (mg.g^{-1}) and at equilibrium, q_e (mg.g^{-1}) were calculated by the following equations respectively :

$$R\,\% = \frac{(C_0 - C_t)}{C_0} \times 100, \qquad q_t = (C_0 - C_t) \times \frac{V}{W}\ , \qquad q_e = (C_0 - C_e) \times \frac{V}{W}$$

where C_0 , C_e and C_t (mg/L) are the concentrations of MB at initial and equilibrium and at time (t) respectively. *V* (L) is the volume of the solution, and *W* (g) is the mass of dry adsorbent used. Scanning electron microscopy (SEM) analysis was carried out to study the textural morphology of BP and BPAC. Chemical characterization of surface functional groups was detected by Fourier transform infrared spectrometer (FTIR-2000, Perkin Elmer).

3. Results and discussion

3.1. Characterisation of the adsorbents

The surface morphology of BP and BPAC were identified via scanning electron microscopy (SEM) as shown in figure 1. SEM micrographs of BP showed that the peels pores are highly heterogeneous while of BPAC identified the presence of well organized, pronounced and uniform cavities distributed around the surface, indicating good possibility for the methylene blue to be adsorbed. Similar observation was previously noticed (Foo *et al* 2013)

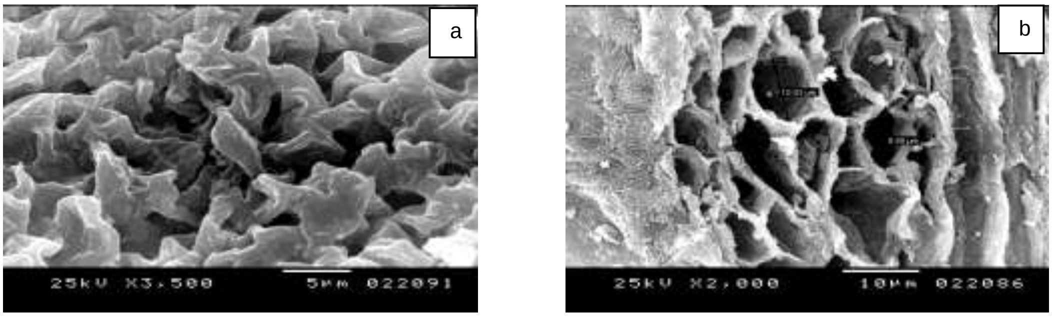

Figure1: SEM micrograph of (a) BP and (b) BPAC

FT-IR spectra of BP and BPAC were obtained to identify their functional groups. The spectrum was recorded from 4000 to 400 cm^{-1}. FT-IR spectra as shown in figure 2 (a) illustrates bands appearing at 3899-3368 cm^{-1} corresponding to OH stretching , bands at 2922.3 cm^{-1}, 1647cm^{-1} indicates C–H stretching of alkane, C–H and C=O stretching of carboxylic acid or ester respectively. Figure 2(b) shows that bands of hydroxyl group were reduced to minimum. Bands at 2360 cm^{-1} indicates cumulative double bond carbon, while at 1740-1649 cm^{-1} indicates different lactone structure. The absorption at 1063.07 cm^{-1} indicates the existence of C–O stretching vibrations of alcohols, phenols, acids, ethers or esters functional group. Similar results were previously observed (Salman *et al* 2011).

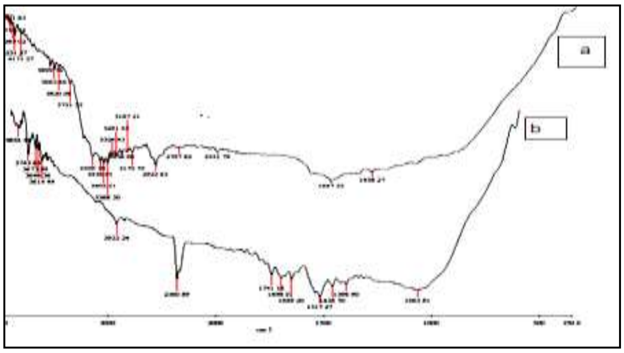

Figure 2: FT-IR spectra of (a) BP and (b) BPAC

3.2. Adsorptive removal of methylene blue

Effect of contact time on removal of MB by BP and BPAC was studied. The adsorption equilibrium time of 50 mg/L MB onto BP was obtained after 45 min with removal percent 90% of the MB and 30 min onto BPAC with removal percent 98%. The results of adsorbent dose effect revealed that the percent removal of MB onto BP increases from 75 % to 90% while removal percent of MB onto BPAC increase from 85%to 98% with the increase in adsorbent dose ranged from 2- 5 g/L after which there is no significant removal with further increase in the adsorbent dose (the figure not shown). The pH of dye solution plays an important role in the whole adsorption process and particularly on the adsorption capacity.The effect of pH on the adsorption of MB onto both adsorbents within the pH range of 2–10 was investigated at 35 ºC and 50 mg/L initial concentration of MB as shown in figure 3(a). The results indicate that the percentage removal of MB increases with the increase in pH upto pH 6 after which the removal decreases with the increase in pH. The maximum removal percent was 90 % for BP and 99 % for BPAC. Regarding the effect of initial concentrations on removal of MB the percent removal decreases with the increase in initial concentration, because high MB concentration leads to saturation of the binding capacity of adsorbent, which consequently decreases the overall removal. Figure 3(b) represents the effect of temperature on the removal percent of MB onto BP and BPAC. The results show that removal of MB onto both adsorbents increases with the increase in temperature from 25ºC to 55ºC while the removal decreases as the temperature increases to 65ºC. The increase in the amount of adsorbed dye can be explained by the endothermic nature of adsorption. The temperature has two major effects on the adsorption process. Increasing temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution. In addition, changing temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate. With increasing temperature to 65 ºC, the percentage removal is decreased due to the increased movement of MB which weakens the force of attraction between the adsorbent and adsorbate. Similar results have been previously reported (Pouretedal and Sadegh 2014).

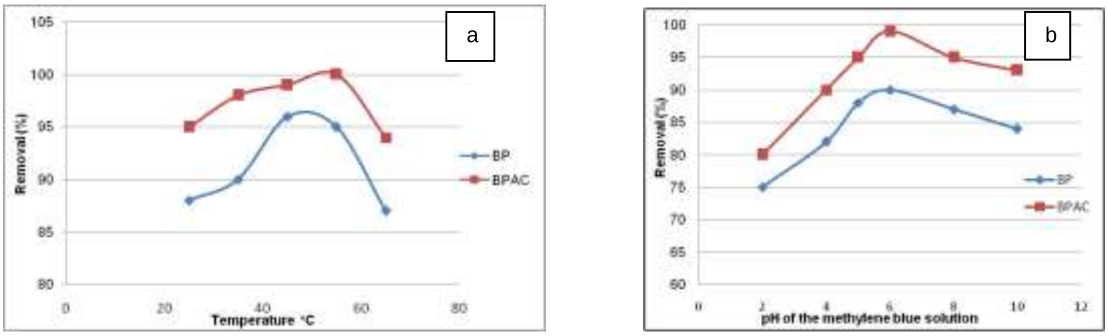

Figure 3: Removal of MB onto BP and BPAC (a) effect of pH, (b) effect of temperature

3.3. Adsorption Isotherms

The experimental data were applied to the Langmuir, Freundlich, Temkin, Dubinin–Radukevisch, and Harkins–Jura isotherm equations (Gurses *et al* 2014). The calculated isotherms parameters, correlation coefficient (R^2), the average percentage error APE% and the isotherm equations are listed in table 1(figures not shown). The average percentage errors (APE) indicate the fit between the experimental and calculated values of adsorption capacity used for plotting isotherm curves, calculated by:

$$\mathrm{APE\%} = \frac{100}{N} \times \frac{\sum_{i}^{N} |(\mathrm{qe\ exp} - \mathrm{qe\ cal}\ )|}{\mathrm{qe\ exp}}$$

where; the qe_{exp} and qe_{cal} refer to the experimental and calculated values, respectively and N is the number of data points. The correlation coefficient value R^2 obtained from Langmuir isotherm were 0.992 and 0.997 for the adsorption of MB on BPAC and BP respectively, indicate that the adsorption follows the Langmuir isotherm. R_L values were less than 1 and greater than zero indicating favorable adsorption. For Freundlich isotherm model, the 1/n values obtained were <1. This indicated that the adsorption process followed a normal Langmuir isotherm and conforms to the experimental data when fitted into the Langmuir isotherm equation (Salman and Hameed 2010). In spite of the higher coefficients of correlation obtained using Langmuir, this model does not describe perfectly the equilibrium data because of the higher values of average percentage error APE%. The Temkin isotherm model gave the highest R^2 values which was equal to 0 .999 and minimum APE% approximately equal to 1.28% showing that the adsorption of MB on BP was best described by this model. It is clear from table 1 that average percentage error values reveal a good agreement between the experimental and calculated values, suggesting that the Temkin model is valid for the experimental equilibrium data. Temkin isotherm is more suitable for the experimental results than the Langmuir, and Freundlich expression because of the lower average percentage error values.

Table1: Isotherm parameters obtained for the adsorption of MB onto BP and BPAC

Isotherms models	**Isotherms parameter**	**Adsorbents**	
		BP	BPAC
Langmuir $\frac{C_e}{q_e} = \frac{1}{Q_m K_L} + \frac{1}{Q_m} C_e$ R_L=1/ (1+$K_L \times C_0$)	**Q_m(mg/g)**	**26.315**	**34.48**
	K_L	0.096	0.318
	R_L	0.17	0.05
	APE%	**8.717**	**5.3**
	R^2	**0.998**	**0.992**
Freundlich $\log q_e = \log K_F + \frac{1}{n} \log C_e$	1/n	0.38	0.48
	K_F(L/g)	5.186	10.15
	APE%	**2.85**	**4.849**
	R^2	**0.977**	**0.977**
Temkin $q_e = B_T \ln K_T + B_T \ln C_e$	B_T(L/mg)	5.59	7.17
	K_T (J/mol)	1.02	3.53
	APE%	**1.28**	**4.37**
	R^2	**0.999**	**0.979**
Dubinin–Radukevisch $\ln q_e = \ln Q_s - B\varepsilon^2$	Q_S(mg/g)	19.25	23.59
	B	4×10^{-6}	3×10^{-7}
	E (KJ/mol)	**0.353**	**1.29**
	APE%	10.126	12.617
	R^2	0.887	0.817
Harkins–Jura $\frac{1}{q_e^2} = \frac{B_2}{A} - \frac{1}{A} \log C_e$	A	111.11	142.85
	B	1.889	1.142
	APE%	11.56	--------
	R^2	0.857	0.861

3.4. Adsorption kinetics

Pseudo-first order, pseudo-second order and Elovich model kinetic equations (Chen *et al* 2010).The parameters of kinetic models are listed in Table 2.

Table 2: Kinetic model parameters for the adsorption of various initial concentrations of MB onto BPAC and BP at 35 ºC

Type of Adsorbent	C_o mg/L	**qe exp mg/g**	PFO $\ln(q_e - q_t) = \ln q_e - k_1 t$			PSO $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$			Elovich model $q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t)$		
			qe_{cal} mg/g	K_1 1/min	R^2	**qe_{cal} mg/g**	K_2 g/mg.min	**R^2**	β g/mg	α mg/g min	R^2
BP	50	**9.1**	5.269	0.103	0.909	**9.7**	0.034	**0.997**	0.95	142.89	0.957
	100	**16**	9.669	0.079	0.860	**17.24**	0.013	**0.994**	0.48	88.77	0.939
	160	**21.76**	14.731	0.067	0.907	**23.809**	0.004	**0.993**	0.311	8.717	0.948
BPAC	50	**9.8**	4.370	0.110	0.878	**10.309**	0.047	**0.998**	1.11	1227	0.961
	100	**19.2**	10.084	0.105	0.948	**20.408**	0.018	**0.998**	0.465	470.9	0.956
	160	**28.8**	12.000	0.076	0.943	**31.25**	0.0101	**0.997**	0.317	642.5	0.950

The correlation coefficient for the pseudo-second order kinetic model for BPAC ($R^2 \geq 0.998$) and BP ($R^2 \geq 0.993$) was higher than the one for pseudo-first order kinetic model. In addition, the agreement between the calculated values obtained from the models and the experimental values were utilized in confirming the suitability of the models in fitting the kinetic data. Similar phenomena have been observed (Hameed *et al* 2007) .The correlation coefficient for the Elovich model for both BPAC and BP was greater than 0.95. This indicates that the adsorption perfectly complies with pseudo-second order reaction and the adsorption appeared to be controlled by the chemisorption process.

3.5. Adsorption mechanism

the intraparticle diffusion model was used to analyze and identify the diffusion mechanism. The intraparticle model is expressed as:

$$q_{t} = k_{diff}\, t^{1/2} + C$$

where q_t is the of MB adsorbed (mg/g) at time t, k_{diff} is intraparticle diffusion constant (mg.g^{-1} min$^{-1/2}$), and C is the intercept. Figure 5(a ,b) illustrates that the plots were linear over the whole time range $R^2 > 0.96$ but they did not pass through the origin indicating intraparticle diffusion was not the only rate controlling step, and more than one process affected the adsorption. Film boundary layer diffusion controls the adsorption rate at the beginning. (Hameed *et al* 2007).

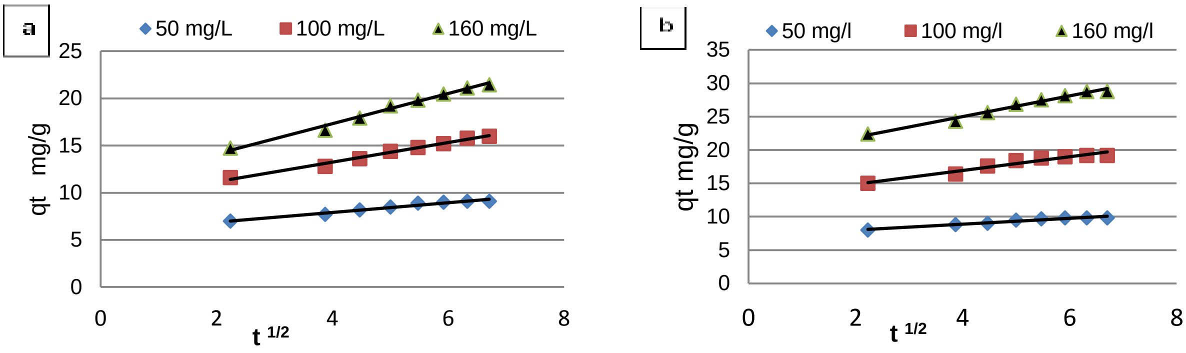

Figure 5: Intra-particle diffusion kinetics for MB removal by (a) BP and (b) BPAC (adsorbent dose =0.5 g, agitation speed =150 rpm, T =35ºC and pH= 6)

4. Conclusions

The results revealed that adsorption process was highly dependent on the pH and the favorable value was pH 6 Adsorption parameters for the Langmuir, Freundlich , Temkin, Dubinin–Radukevisch and Harkins–Jura isotherms were determined and the equilibrium data were best described by the Temkin isotherm model. The kinetics of MB adsorption onto BP and BPAC followed the pseudo-second-order model $R^2 > 0.994$. The results of the intraparticle diffusion model suggested that intraparticle diffusion was not the only rate controlling step. These results indicated that the both dried banana peels and activated carbon prepared from banana peels could be employed as a low-cost alternative to commercial activated carbon in the removal of methylene blue dye from wastewater.

REFERENCES

1. Ahmad M.A. and Alrozi R. (2011) Optimization of rambutan peel based activated carbon preparation conditions for Remazol Brilliant Blue R removal, Chem. Eng.J., **166,** 280–285.
2. Baccar R., Blanquez P., Bouzid J., Feki M.,and Sarra M. (2010) Equilibrium, thermodynamic and kinetic studies on adsorption of commercial dye by activated carbon derived from olive-waste cakes, Chem. Eng. J., **165**, 457–464.
3. Bulut Y., Gozubenli N. and Aydın H. (2007) Equilibrium and kinetics studies for adsorption of direct blue 71 from aqueous solution by wheat shells, J. Hazard. Mater., **144** ,300–306.
4. Chandra T. C., Mirna M. M, Sudaryanto Y., and Ismadji S. (2007) Adsorption of Basic Dye onto Activated Carbon Prepared from Durian Shell: Studies of Adsorption Equilibrium and Kinetics. Chem. Eng. J., **127**,121–129.
5. Chen S., Zhang J., Zhang C., Yue Q., Li Y. and Li C. (2010) Equilibrium and kinetic studies of methyl orange and methyl violet adsorption on activated carbon derived from Phragmites australis, Desalination, **252,**149–156.

6. Chowdhury S., Mishra R., Saha P. and Kushwaha P. (2011) Adsorption thermodynamics, kinetics and isosteric heat of adsorption of malachite green onto chemically modified rice husk, Desalination, **265**, 159–168.
7. Foo K.Y., Lee L.K. and Hameed B.H. (2013) Preparation of banana frond activated carbon by microwave induced activation for the removal of boron and total iron from landfill leachate, Chem. Eng. J., **22** , 604–610.
8. Gurses A., Hassani A., Kıransan M., Acıslı O¨. and Karaca S. (2014) Removal of methylene blue from aqueous solution using by untreated lignite as potential low-cost adsorbent: Kinetic, thermodynamic and equilibrium approach, Journal of Water Process Engineering, **2** 10–21
9. Hameed B.H., Ahmad A.A. and Aziz N. (2007) Isotherms, kinetics and thermodynamics of acid dye adsorption on activated palm ash, Chem. Eng. J., **133,**195–203.
10. Hameed B.H., Ahmad A.L. and Latiff K.N.A. (2007) Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust,Dyes and Pigments,**75**,143-149.
11. Khaled A., El Nemr A., El-Sikaily A. and Abdelwahab O. (2009) Removal of Direct N Blue-106 from artificial textile dye effluent using activated carbon from orange peel: Adsorption isotherm and kinetic studies, J. Hazard. Mater., **165,** 100–110
12. Kumar P.S., Ramalingam S. and Sathishkumar K. (2011) Removal of methylene blue dye from aqueous solution by activated carbon prepared from cashew nut shell as a new low-cost adsorbent, Korean J. Chem. Eng., **28**, 149–155.
13. Olivares M. M., Fernandez G. C., Macias G. A. and Gomez S. V. (2012) Preparation of activated carbon from cherry stones by physical activation in air. Influence of the chemical carbonisation with H_2SO_4 ,J. Analytical and Applied Pyrolysis,**94** ,131–137
14. Pouretedal H.R. and Sadegh N. (2014) Effective removal of Amoxicillin, Cephalexin, Tetracycline and Penicillin G from aqueous solutions using activated carbon nanoparticles prepared from vine wood, Journal of Water Process Engineering, **1** ,64–73
15. Salman J.M., Njoku V.O., and Hameed B.H. (2011) Adsorption of pesticides from aqueous solution onto banana stalk activated carbon, Chem. Eng. J.,**174**, 41– 48.
16. Salman J.M. and Hameed B.H. (2010) Removal of insecticide carbofuran from aqueous solutions by banana stalks activated carbon, J. Hazard. Mater., **176,** 814–819.
17. Yang J. and Qiu K. (2010) Preparation of activated carbons from walnut shells via vacuum chemical activation and their application for methylene blue removal, Chem. Eng. J.,**165** 209–217.