

Sorption Isotherm and Kinetic Studies of Methylene Blue Uptake onto Activated Carbon Prepared from Wood Apple Shell

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Abstract

In this study we used wood apple shell (waste biomass) as a raw material to produce activated carbon. Crushed wood apple shells were activated by using concentrated sulphuric acid at 160°C. Batch mode experiments were conducted to assess the potential for the removal of Methylene blue dye from aqueous solution using the above carbon. Sorption isotherm and kinetic studies have been done by varying the parameters like initial concentration of Methylene blue dye solution, pH of the dye solution, sorbent dose and varying the contact time. The equilibrium data obtained were tested using Langmuir, Freundlich, and Redlich-Peterson isotherms models and the kinetic data obtained were fitted to pseudo-first order and pseudo-second order models. Nonlinear forms of equations were used to explain the isotherm models as well as the kinetic models. The experimental data were well fitted with Langmuir isotherm model and pseudo second order kinetic model. The 'g' value of the Redlich-Peterson isotherm is found to be one and it is a special case of Langmuir isotherm.

Keywords: Sorption, Methylene blue, Wood apple shell, Isotherms, Pseudo-second order.

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Introduction

Dyes are widely used in textile, paper, carpet, printing, leather and cosmetic industries. Some dyes are used in medicine and biological stains and colouring plastics, oils and waxes. Today more than 3000 dyes are in use worldwide (1). Presence of colour in the wastewater is one of the main problems in textile industries. Colours are easily visible to human eyes even at very low concentration. Removal of dyes from the effluent is a major problem in most of the textile industries. From an environmental point of view, the removal of synthetic dyes is of great concern, because some dyes and their degradation products are carcinogenic and toxic (2). It is very difficult to remove these chemicals by conventional biological treatment methods. One of the most effective methods for removing different types of colour from wastewater is adsorption method using activated carbon and it gives best results (3-5).

Since commercially available activated carbon is very expensive, now the research is focusing on the use of low cost adsorbents derived from agricultural and wood wastes, such as bagasse (6), coir pith (7), banana pith (8),

tree fern (9), rice husk (10) etc., have been used for dye removal from wastewater. Methylene blue dye is one of the frequently used dyes in all industries. It dissociates into cation and chloride ion in aqueous solution. It has stable colour irrespective of the pH of solution when compared with other dyes (11). In sorption studies, it is used as a standard dye to evaluate the sorption capacity of an activated carbon and it gives the rough surface area of the mesoporous carbon. In this work, we used wood apple outer shell (*Feronia limonia*) as a raw material to produce activated carbon to remove the Methylene blue dye from water.

Methodology

The outer rind of the wood apple was crushed into smaller pieces and soaked with concentrated H₂SO₄ at 1:1 ratio (wt of raw material/ volume of acid) for 48 hours and activated at 160°C for 6 hours. The activated carbon was repeatedly washed with distilled water until the pH of the wash water becomes the pH of the distilled water. The carbon obtained from the wood apple shell (WAC) was dried at 105±1°C for 2 hours. All the chemicals used are of analytical grade. The stock solution of 1000 mg/L Methylene blue (MB) was prepared using double distilled water. Solutions of desired concentration were prepared by diluting the stock

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solution. A calibration graph of absorbance verses concentration of MB was obtained using Systronics photometer (model 104) at λ_{\max} 665 nm. Batch experiments were conducted using screw cap closed containers and ORBITEK shaker at 300 rpm. For isotherm studies 100 mg of WAC and 50 mL of different concentrations of MB dye solution in the range of 20 to 100 mg/L were taken in the closed containers after having adjusted for required pH and shaken for 2 hours. The required initial pH of the dye solution was obtained by using HCl (0.1 N, 0.01 N, and 0.001 N) and NaOH (0.1 N, 0.01 N, and 0.001 N). Effect of carbon dose was studied by using 50 mL of 50 mg/L dye solution (pH = 7 ± 0.05) for 2 hours shaking. Effect of contact time was carried out by using 50 mL of different initial concentrations of dye solution (10, 20, 30, and 40 mg/L) with 100 mg of carbon after adjusting the pH (7 ± 0.05). After equilibrium time, the residual concentration of the dye (the activated carbon was separated by using centrifugal machine) was analyzed using spectrophotometer at a wavelength of 665 nm. All the experiments were carried out at 25°C. Non-linear forms of equations were used throughout the study.

Results and Discussion

Carbon Characterization

The IR spectrum of the prepared activated carbon was recorded in the range 4000 to 450 cm^{-1} as KBr pellets and it is given in Figure 1. Due to low temperature carbonization of the wood apple shells, some functional groups may be present on the surface of the carbon.

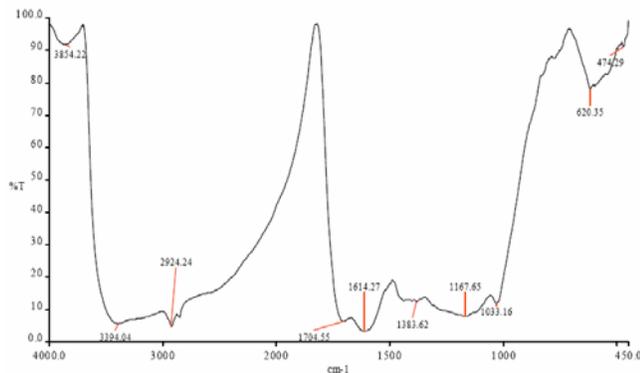


Figure 1. FTIR spectrum of wood apple carbon.

A band at 2924 cm^{-1} is due to the aliphatic CH stretching of methyl group and a sharp band around 1704 and 1614 cm^{-1} is due to stretching frequency of C=O and bending N-H groups respectively. Bands around 1383 and 620 cm^{-1} are due to phenolic OH and $-\text{SO}_3\text{H}$ groups respectively. Scanning Electron Microscope of the surface morphology of WAC is given in Figure 2. The pH of the carbon was found to be 3.91 due to the existence of the functional

groups like phenol, carboxylic acid and sulphuric acid group.

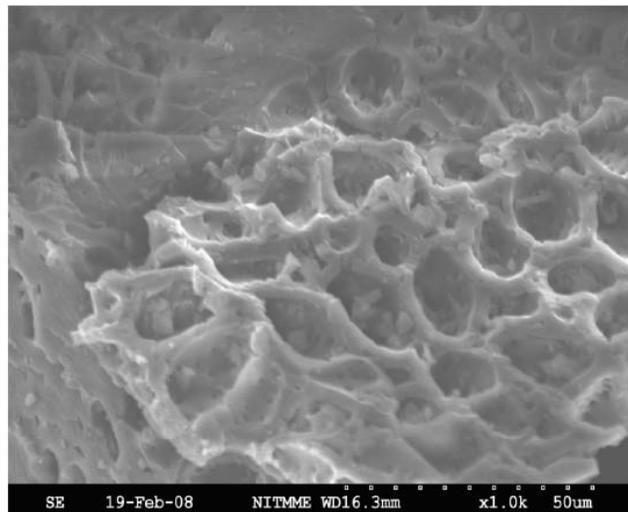


Figure 2. SEM picture of wood apple carbon.

Sorption Isotherm Models

The distribution of dye molecules between the sorbent and the dye solution is an important factor to establish the sorption capacity of WAC. Sorption isotherm is the relationship between the sorbate in the liquid phase and the sorbate sorbed on the surface of the sorbent at equilibrium at constant temperature. The distribution of dye molecules between the liquid phase and the sorbent is a measure of the position of equilibrium in the sorption process and can be generally expressed by the three well known models viz., Freundlich, Langmuir, and Redlich-Peterson. The Langmuir isotherm takes an assumption that the sorption occurs at specific homogeneous sites within the sorbent (12), and the equation is:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

The Freundlich isotherm is an empirical equation (13) employed to describe the heterogeneous system. The equation is given below:

$$q_e = K_F C_e^{1/n}$$

The Redlich-Peterson isotherm model (14) combines both Langmuir isotherm and Freundlich isotherm equation and the mechanism of sorption is a hybrid one and does not follow ideal monolayer sorption. The equation is:

$$q_e = \frac{A C_e}{1 + B C_e^g}$$

In the above equation, 'g' is the exponent, which lies between 0 and 1. If 'g' is equal to one, the equation modifies to Langmuir model, and if 'g' is equal to zero then the equation changes to Henry's law equation.

Effect of Initial Concentration of the Dye Solution

In general, the isotherm studies for solid-liquid systems are carried out by changing the amount of sorbate in the solution. The performance of the sorbents is usually gauged by its uptake (q_m), which can be calculated by fitting the Langmuir isotherm model to the actual experimental data (if it fits). This approach is feasible if q_m reaches a plateau. A high affinity between the sorbent and sorbate results in good uptake values at low concentrations (C_e). This is characterized by a steep rise of the isotherm curve close to its origin. In general a 'good' sorbent is one with high q_m and a steep initial sorption isotherm slope and low values of Langmuir constant (15). In Figure 3, there is a steep rise of the Langmuir isotherm curve shows that there is a strong affinity between WAC and MB dye. The three types of isotherm models (Langmuir, Freundlich and Redlich-Peterson) are shown in that figure. In this sorption system, the 'g' value becomes 1, which shows the overlap of Redlich-Peterson isotherm on Langmuir isotherm.

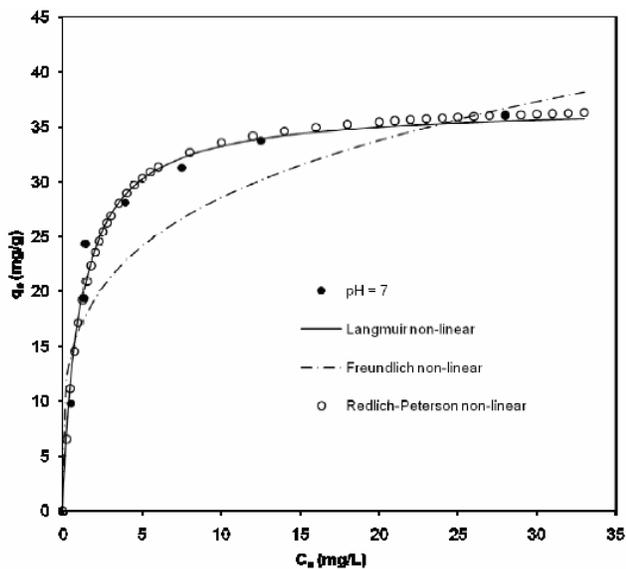


Figure 3. Fitted isotherm models for WAC-MB system.

Figure 4 show the adsorption capacity increases with increasing the pH of the dye solution. The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor K_R (16). The relation between the initial concentration and the K_R values are given in Figure 5 (17). This shows the increase of concentration reduces the K_R value (reaction is more favourable) due to the increase in the number of dye molecules. The increase of pH also lowers the K_R value due to the increase of more negative sites on WAC and

favours the electrostatic attraction between the dye molecules and the negative sites on the surface of the carbon. The Langmuir rate constants K_L increase with increase of pH of the solution. The increase of initial pH of the solution plays an important role in the sorption process.

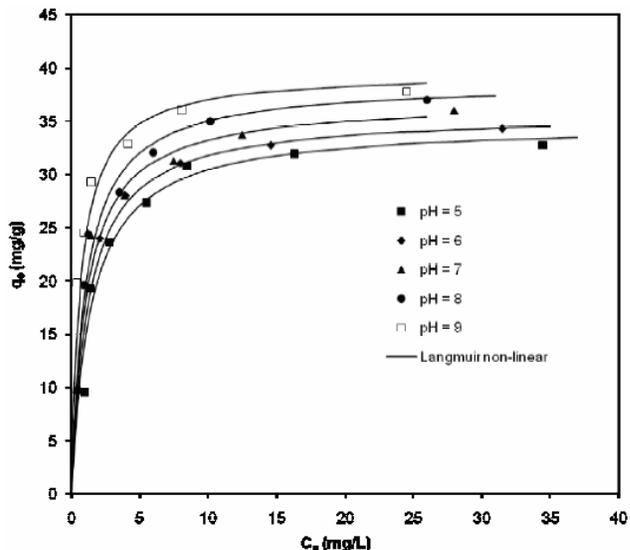


Figure 4. Langmuir isotherms at different initial pH of the MB dye solution.

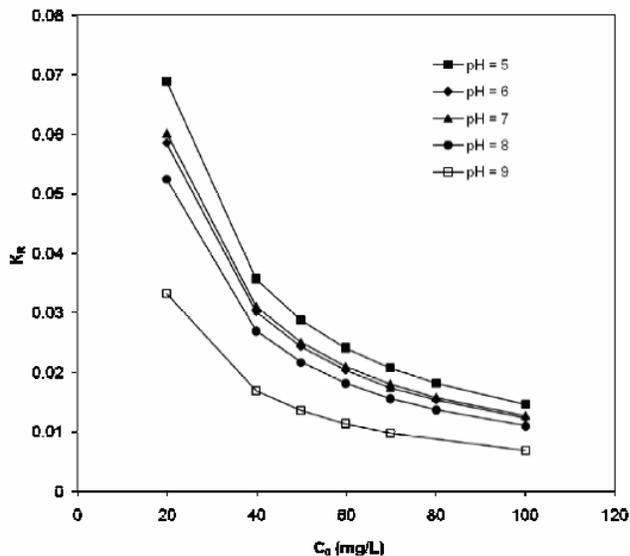


Figure 5. Plot between K_R and initial concentration of MB dye solution at different pH.

Mechanism of the Sorption Process

The pH of the solution is the most important factor, which controls the sorption of dyes on the sorbent material. The kinetics of the sorption strongly depends on the initial pH of the solution. In the present study, the removal of MB increases with increase of pH of the dye solution from 5 to

9. There is a decrease in the pH of the dye solution after the removal of dye from the solution by WAC. This shows there is protons release from the surface of the carbon due to cation exchange between the sorbent and the dye solution (9). This reveals that the increase of pH deprotonate the acidic groups on the surface of the carbon and provides more negative sites for the sorption of cationic form of the dye molecules (18). Whereas at low pH, there would be more number of hydrogen ions in the solution that prevents the negative charge formation on the carbon surface and reduces the uptake of the dye. The aggregation of cationic dyes sorbed on the carbon surface is mainly due to ion exchange mechanism (19). The pH of the MB dye loaded carbon was found to be 4.61 (before sorption pH = 3.91), which shows the strong attachment of dye molecules on the surface of the carbon. At lower C_e , there is no significant difference in the sorption of dye. But at higher C_e there is an appreciable difference in the sorption of dye molecules. The q_m is the maximum sorption and is found to be increased from 34.7 mg/g (pH = 5) to 39.6 mg/g (pH = 9). The q_e values calculated using the nonlinear form of Langmuir, Freundlich and Redlich-Peterson equations were given in Table 1. The Langmuir parameters obtained for this WAC-MB system at different pH of the dye solution were given in Table 2.

Langmuir isotherm		
q_m (mg/g)		36.9
K_L (L/mg)		0.907
r^2		0.954
Freundlich isotherm		
$1/n$		0.243
K_F (L/g)		16.3
r^2		0.766
Redlich-Peterson isotherm		
g		1.00
B (L/mg)		0.839
A (L/g)		31.5
r^2		0.956

pH	q_m (mg/g)	K_L (L/mg)	r^2
5±0.1	34.7	0.704	1.00
6±0.1	35.7	0.803	0.984
7±0.1	36.9	0.907	0.954
8±0.1	38.6	0.963	0.956
9±0.1	39.6	1.44	0.930

Effect of Carbon Dose

The effect of carbon dose for the uptake of MB by WAC was found to be increased by increasing the sorbent dose, due to the introduction of the more activate sites available for sorption. This study will be very useful to find out the optimum amount of carbon required for the removal of dye from the solution (Figure 6). This study showed that a minimum of 100 mg of WAC was required for maximum removal (94%) of dye from 50 mL of MB dye solution (50 mg/L).

Effect of Contact Time

It is necessary to identify the step that governs the overall removal rate in the above sorption process. The pseudo-first order and pseudo-second order kinetic models were tested to fit the experimental data obtained for MB dye uptake by WAC. The kinetic study results were given in Table 3.

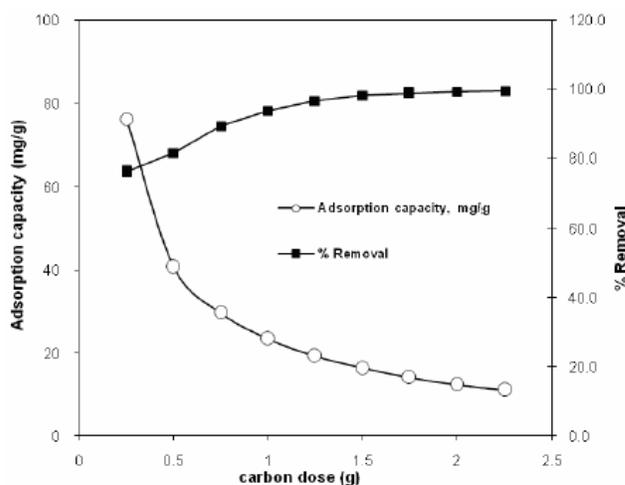


Figure 6. Effect of carbon dose versus adsorption capacity and % removal.

Table 3. Parameters for the fitted kinetic models for the WAC-MB system

C_0	Pseudo-first order model			Pseudo-second order model			
	q_1	k_1	r^2	q_e	k_2	h	r^2
mg/L	mg/g	1/min		mg/g	g/mg min	mg/g min	
10	4.75	0.323	0.852	4.93	0.176	4.27	0.995
20	9.53	0.210	0.926	10.0	0.0415	4.16	0.998
30	14.5	0.125	0.951	15.4	0.0161	3.81	0.991
40	18.8	0.0759	0.977	21.8	0.00456	2.16	0.996

Pseudo-First Order Kinetic Model

A simple kinetic model, which describes the process of sorption, is the pseudo-first order equation suggested by Lagergren (20, 21).

$$q_t = q_e [1 - \exp(-k_1 t)]$$

But this first order equation is applicable only for the initial 20 to 30 min of the sorption process. First order rate constant k_1 and equilibrium capacity q_e values were obtained from slope and intercept of the above plot. The q_e values calculated from the plots are lower than the experimental one. The removal of MB dye using WAC does not follow the pseudo-first order equation.

Pseudo-Second Order Kinetic Model

The pseudo-second order kinetic equation was developed for the sorption process (22). The equations are given below:

$$q_t = q_e \left(\frac{q_e k_2 t}{1 + q_e k_2 t} \right)$$

There are 3 consecutive steps takes place in the sorption of a sorbate by a porous sorbent:

1. transport of the sorbate to the external surface of the sorbent (film diffusion)
2. transport of the sorbate within the pores of the sorbent (particle diffusion)
3. sorption of the sorbate on the interior surface of the sorbent (pore diffusion)

The rate of the reaction is mainly controlled by the first two steps. The plots of time vs. q_t are shown in Figure 7.

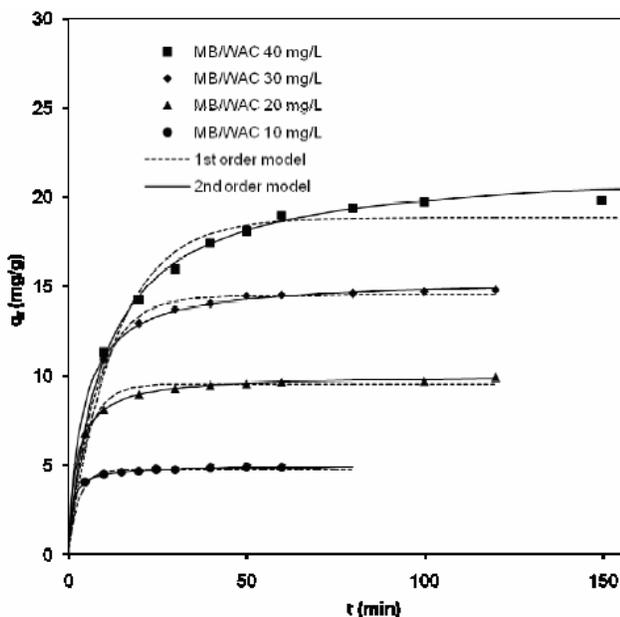


Figure 7. Pseudo-first and second order kinetic model for the uptake of MB and WAC.

The correlation coefficients (r^2) for the non-linear plots of pseudo-second order plots are better (0.993, 0.998, 0.991, and 0.996 for 10, 20, 30, and 40 mg/L dye solution respectively) than the pseudo-first order reaction plots (0.852, 0.926, 0.951, and 0.977). This shows that the pseudo-second order kinetic model explains the sorption in better way. The pseudo-second order model is based on the assumption that the rate determining step may be a chemical sorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate (23). Increase in the initial dye concentration from 10 to 40 mg/L increases the sorption capacity from 5 to 22 mg/g. The plot of rate constant values versus the corresponding metal concentrations (Figure 8) shows that intraparticle/pore diffusion is involved in the overall rate of MB sorption on WAC.

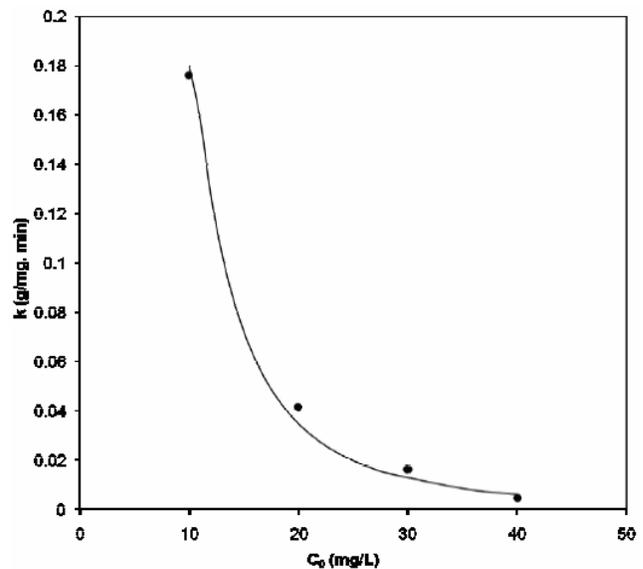


Figure 8. Relation between pseudo second order rate constant (k) and initial concentration of the MB dye solution (C_0).

When pore diffusion limits the rate of sorption process, the relation between initial concentration of the dye solution and the rate of the reaction will not be linear (24). Increase of initial dye concentration from 10 to 40 mg/L decreases the initial rate constant 'h' from 4.27 to 2.16 mg/g.min and the pseudo second order rate constant value k_2 from 0.176 to 0.00456 g/mg.min. This is due to the decrease in the readily available vacant adsorption sites as the dye concentration is increased. In other words, once the easily available sites are occupied the excess dye molecules in solution find remote adsorption sites inside the pores of the carbon with difficulty.

Conclusion

The sorption kinetics and isotherm of MB removal using WAC was carried out in batch experimental system. The

following conclusions were drawn based on the above study:

- 1) the waste biomass from wood apple shell is converted into activated carbon using concentrated sulphuric acid;
- 2) the sorption was found to be dependent on initial MB dye concentration, pH and the contact time;
- 3) the rate of sorption follows pseudo-second order rate equation;
- 4) the above experimental data were fitted with the Langmuir model and Redlich-Peterson model; and
- 5) increase in pH of the initial concentration of dye solution and carbon dose increases the rate of the reaction. The increase in pH of the initial concentration of dye solution plays a major role in the sorption process.

The present study has demonstrated that the carbon derived from wood apple rind can be employed for the removal of MB from water. The experimental results obtained by the batch experiments can be useful for the environmental engineers in designing the batch experimental set up for removal of MB from water using WAC.

References

1. Barnes D, Forstery CF, Hrudey SE, eds. (1987) Surveys in Industrial waste water treatment-Petroleum and organic chemicals industries, Longman scientific and technical, Longman group, UK.
2. Lorenc-Grabowska E, Gryglewicz G, (2007) Adsorption characteristics of Congo Red on coal based mesoporous activated carbon. *Dyes Pigments*; 74:34-40.
3. Jain AK, Gupta VK, Bhatnagar A, Suhas, (2003) Utilization of industrial waste products as adsorbents for the removal of dyes. *J Hazard Mater*; 101:31-42.
4. Ho YS, McKay G, (2003) Sorption of dyes and copper ions onto biosorbents. *Process Biochem*;38:1047-61.
5. Derbyshire F, Jagtoyen M, Andrews R, Rao A, Martin-Gullon I, Grulke E, (2001) Carbon materials in environmental applications. In: Radovic, L.R. (Ed.), *Chemistry and Physics of Carbon*, Vol. 27. Marcel Dekker, New York, pp. 1-66.
6. Valix M, Cheung WH, McKay G, (2004) Preparation of activated carbon using low temperature carbonisation and physical activation of high ash raw bagasse for acid dye adsorption. *Chemosphere*;56:493-501.
7. Namasivayam C, Kavitha D, (2002) Removal of Congo red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste. *Dyes Pigments*;54:47-58.
8. Kadirvelu K, Kavipriya M, Karthika C, Radhika M, Vennilamani N, Pattabhi S, (2003) Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions. *Bioresource Technol*;87:129-32.
9. Ho YS (2005) Effect of pH on lead removal from water using tree fern as the sorbent. *Bioresource Technol*; 96:1292-96
10. Malik PK, (2003) Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: A case study of acid yellow 36. *Dyes Pigments*; 56:239-49.
11. Tor A, Cengeloglu Y, (2006) Removal of Congo red from aqueous solution by adsorption onto acid activated red mud. *J Hazard Mater*; 138:409-15.
12. Langmuir I, (1918) The adsorption of gases on plane surfaces of glass, mica and platinum. *J Am Chem Soc*; 40:1361-403.
13. Freundlich HZ, (1906) Over the adsorption in solution. *J Phys Chem*; 57A:385-470.
14. Redlich O, Peterson DL (1959) A useful adsorption isotherm. *J Phys Chem*; 63:1024.
15. Holan ZR, Volesky B, Prasetyo I, (1993) Biosorption of cadmium by biomass of marine algae. *Biotechnol Bioeng*; 41:819-25.
16. Hall KR, Eagleton LC, Acrivos A, Vermeulen T, (1966) Pore- and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions. *Ind Eng Chem Fund*; 5:212-23.
17. Ho YS, Huang CT, Huang HW, (2002) Equilibrium sorption isotherm for metal ions on tree fern. *Process Biochem*; 37:1421-30.
18. Adler E, Lundquist K, (1963) Spectrochemical estimation of phenylcoumaran elements in lignin. *Acta Chem Scand*; 17:13-26.
19. Giles CH, Easton IA, McKay RB, (1964) Mechanism of adsorption of cationic dyes by alumina, and a note on heat changes in solution adsorption. *J Chem Soc*; NOV: 4495-503.
20. Lagergren S, (1898) About the theory of so-called adsorption of soluble substances. *K. Sven. Vetenskapsakad. Handl.*;24:1-39.

21. Ho YS (2004), Citation review of Lagergren kinetic rate equation on adsorption reactions. *Scientometrics*; 59:171-7.
22. Ho YS, McKay G, (2000) The kinetics of sorption of divalent metal ions onto sphagnum moss peat. *Water Res*; 34:735-42.
23. Ho YS (2006), Second-order kinetic model for the sorption of cadmium onto tree fern: A comparison of linear and non-linear methods. *Water Res*; 40:119-25.
24. Komoto M (1956), *Seito Gijutusu kenkyukasishi*; 5:49: Chem. Abst., 1958, 52,12371e.