International Journal of Applied Engineering Research ISSN 0973-4562 Volume 10, Number 17 (2015) pp 38470-38476
© Research India Publications. http://www.ripublication.com

Determination of Equilibrium and Kinetics Modeling for the Adsorption of Acid Orange 7 onto Activated Carbon prepared from *Leucaena leucocephala* Seed Shell Waste

A.Babu Rajendran[1],

[1]*Department of Chemistry, Govt. Hr. Sec. School, Kannivadi, Tirupur, TN, India.*

K. Sakthivel[2],

[2] *Department of Chemistry, Periyar University, Salem, TN, India.*

K. Jothivenkatachalam [3],

[3]*Department of Chemistry, Anna University, BIT Campus, Tiruchirappalli, TN, India.*

S. Karthikeyan[4],

[4]*Department of Chemistry, Chikkanna Govt. Arts College, Tirupur, TN, India.*
Email: skmush@rediffmail.com

Abstract

In the present study *Leucaena leucocephala* Seed Shell Waste used as a precursor for the preparation of activated carbon. The characteristic of the prepared activated were analysed using SEM, FTIR and XRD analysis. The equilibrium studies were carried by isotherm models namely, Langmuir and Freundlich model. The equilibrium adsorption result was best fitted with Langmuir isotherm model and its maximum monolayer adsorption capacity was 72.34 mg/g for acid orange 7. Adsorption kinetics studies showed that the pseudo second-order kinetic model yield the best fit. An intraparticle diffusion model suggested that the intraparticle diffusion was not rate-controlling step. Thermodynamics studies revealed that the spontaneous and exothermic nature of the sorption process. The results indicate that the *Leucaena leucocephala* seed shells could be utilized as a potential adsorbent for the adsorption of acid orange 7.

Keywords: Acid orange 7; *Leucaena leucocephala* activated carbon; Isotherm models; Kinetic models; Thermodynamic studies.

Introduction

Water pollution due to the discharge of dying and textile industry effluent is a major problem unfavorably affects the environment due to its high toxicity and non-biodegradable nature. Unreacted or partially treated effluents from industries namely, paper, leather, plastic, food, woolen, cosmetic and carpet contributes to pollution load. The presence of small concentrations of dyes, are easily detectable [1] and effect the process of photosynthesis and thus affect aquatic ecosystem.

Hence the removal of dyes from textile industries is the major environmental concern these days [2, 3]. Various methods have been employed in the past for the removal of dye from waste water [1, 4-7]. Most of the conventional techniques are expensive [7]. But adsorption process has been found to be more effective method for treating effluents [8-14]. Though the activated carbon [15] is most effective for adsorption of dyes, but quite expensive and hence there is an increasing need for effective but cheaper sorbents. In recent years, many naturally occurring waste materials have been investigated to evaluate their suitability and ability to be used as an adsorbent. Recently some agricultural wastes and forestry products have been developed as adsorbents. The costs of these biomaterials are negligible when compared to the cost of commercial activated carbon and also renewable sources of raw materials for the production of activated carbon. Activated carbon prepared from different materials like agricultural wastes [16], sago waste [17], pine saw dust [18], sugar cane dust [19], coir pith [20], oil palm waste [21], coconut shell waste [22], tropical wood [23], saw dust [24], *pinus pinaster* bark [25], corncob [26], eucalyptus bark [27], pistachio shells [28], babool wood [29], *Feronia limonia* [30], *Leucaena leucocephala* seed shell [31], *Pongamia pinnata* [32], *Jatropha curcas* [33].

In the present study reveals that the activated carbon prepared from *Leucaena leucocephala* seed shell waste as an agricultural adsorbent and the adsorption of Acid orange 7 was investigated. The isotherm, kinetic and thermodynamic modeling studies were carried out and they have been discussed elaborately.

Materials and methods

Leucaena leucocephala seed shell waste is collected and it was dried and broken into small pieces. The pieces were then impregnated with 10% phosphoric acid solution for 2 hours and soaked in the same solution for 24 hours. The excess solution was decanted off and air dried. Then the material was carbonized in muffle furnace carbonized at 120-130 °C. The dried material was powdered and activated in a muffle furnace at 800 °C for a period of 60 minutes. Then the material was washed with large volume of water to remove residual acid, dried and powdered.

The prepared activated carbon morphological study was characterized by Scanning Electron Microscopy SEM. The functional groups character was determined by FTIR analysis.

Dye Adsorption Measurements

All reagents used were of AR-grade (E-merk). Different concentration of dye solution of Acid Orange 7 was prepared with distilled water. Batch mode adsorption studies were carried by adding 50 mg of the adsorbent and 50 mL of dye solution of certain concentrations, varying pH and temperatures in a thermostated water bath shaker. The samples were withdrawn from the shaker at predetermined time intervals and the solutions were separated from the adsorbent by centrifugation. The concentrations of dyes in the solutions were determined before and after adsorption using Elico UV visible spectrophotometer. The pH of the dye solution was adjusted by using 0.1N NaOH or HCl solution. The adsorption studies were carried out at different temperatures. The amount of dye adsorbed q (mg/g) and adsorption efficiency was calculated as follows:

$$q = \frac{C_0 - C_e}{m} \text{ x } V \qquad (1)$$

$$\text{Adsorption Efficiency (\%)} = \frac{(C_0 - C_e)}{C_0} \text{ x } 100 \qquad (2)$$

where, C_o = initial dye concentration (mg/L)
C_e = equilibrium concentration (mg/L)
V = volume of solution (ml)
m = mass of adsorbent (g)
C = residual dye concentration (mg/L)
q = amount of dye adsorbed (mg/g)

Results and discussion

SEM analysis

Scanning electron micrographs (SEM) of the prepared carbon samples with two different magnifications are shown in Figure 1 and 2. The SEM images clearly indicated that the external surfaces of the sample was rough and contained pores of various sizes and shapes like honeycomb structure. The surface had narrow elongated pores, which are consistent with the well-developed porosity. The micrographs revealed that the cavities on the surfaces of the carbon sample resulted from the evaporation of the H_3PO_4 during activation at moderate temperatures, creating an empty space. During impregnation, the molecules of the chemical impregnating agent diffused into the texture of the lignocellulosic material.

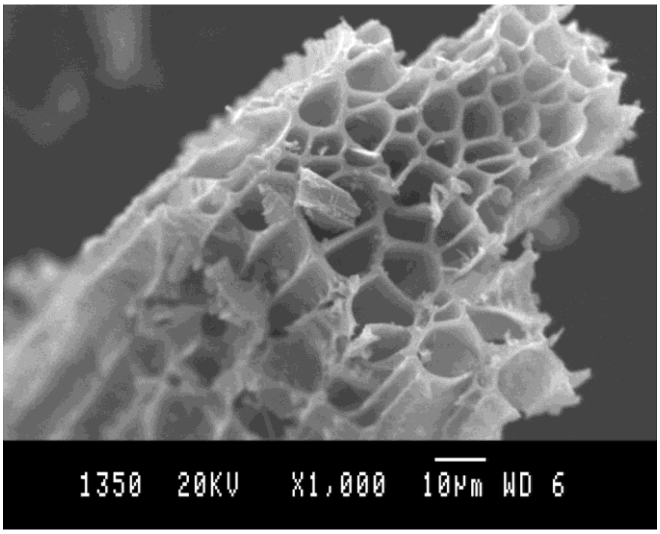

Fig.1. SEM image of LSAC at X1000

Chemical surface characterization

Surface functional groups within activated carbon contribute significantly to its adsorption ability, as ion exchangers, adsorbents, catalysts, and catalyst supports. Fourier transform infrared spectroscopy (FTIR) spectra of the precursor and LSAC are presented in Figure 3. The precursor had a peak at 2800-3000 cm^{-1} which was attributed to the C–H, yet there was a decrease in the spectrum of LSAC. Significant differences occurred at the bands from 1400–1700 cm^{-1}. For the spectrum of the precursor, the band at 1616 cm^{-1} is ascribed to C=O. The changes in the FT-IR spectrum of LSAC were evidence of the formation of structures containing multiple Carbon-Carbon bonds as well as the elimination of originally present oxygen and hydrogen atoms.

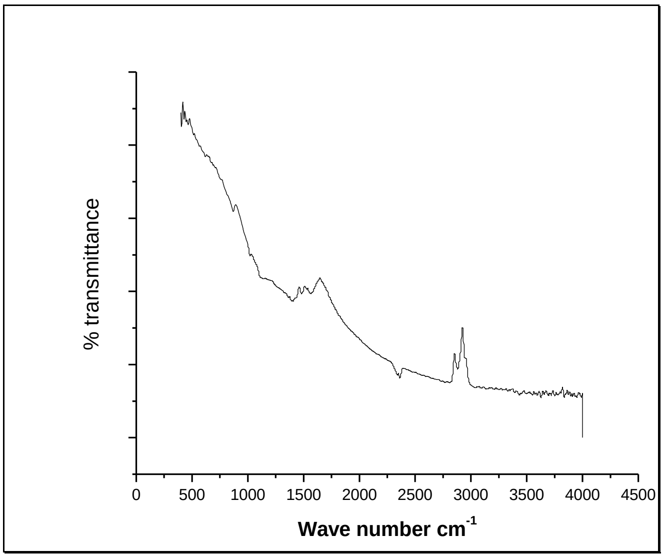

Fig.3. FTIR Spectra for LSAC

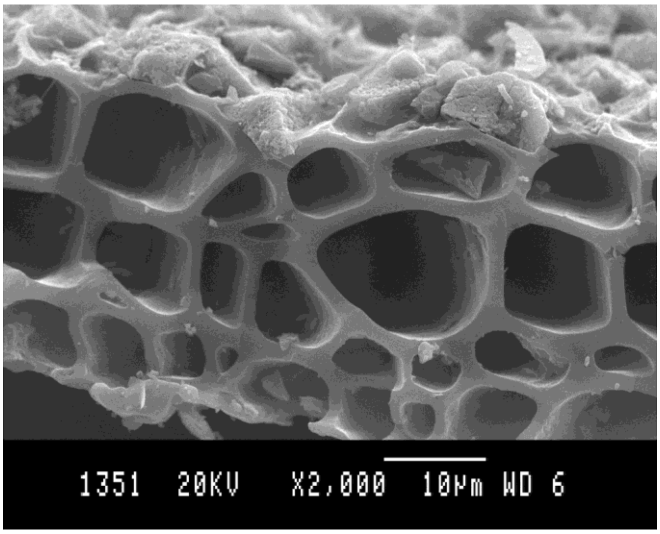

Fig.2. SEM image of LSAC at X2000

XRD analysis

The result of XRD measurements Figure 4 confirms that AC material produced from *Leuceana leucocephala* is characterized by a significant content of amorphous phase in the structure of carbon surface. The peak from 2 theta value in the range of 27-30º indicate the presence of carbon from the graphitic layers spaced inplane of ca. in consequence, its porous structure rather free of slit-shaped micropores with dominant orientation and hence significant content of amorphous phase.

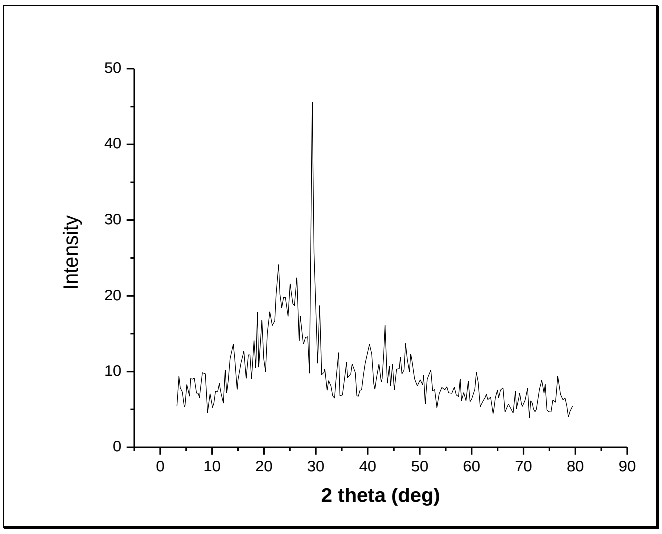

Fig.4. XRD pattern for LSAC

Adsorption Kinetics

The kinetic of adsorption have been studied for Acid Orange 7 at pH 6.5 up to 240 min by varying the initial dye concentration. Three kinetic models were applied to adsorption kinetic data in order to investigate the behavior of adsorption process of Acid Orange 7 onto LSAC: the pseudo-first-order, the pseudo second order and the intra particle diffusion models. A simple kinetic analysis of adsorption, the pseudo first order kinetics and its integrated form, is given by Lagergren [34].

$$\log\ (q_e - q_t) = \log\ q_e\ \frac{k_L}{2.303}\ t \qquad (3)$$

where k_L is the pseudo first order rate constant.
A plot of log $(q_e\text{-}q_t)$ vs time for Acid Orange 7 adsorption onto LSAC enables calculation of the rate constant k_1 and q_e from the slope and intercept of the plot Figure (5).

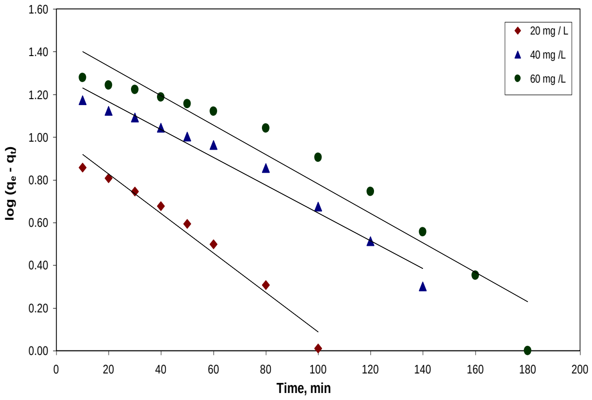

Fig.5. Effect of pseudo first order plot for the adsorption of acid orange 7 onto LSAC

To describe dye adsorption, the modified pseudo second order kinetic equation [35] is expressed as

$$t / q_t = \frac{t}{k_2 q_e^{2}} + \frac{1}{q_e} t \qquad (4)$$

where, k_2 is the pseudo second order rate constant. A plot of t/q_t Vs t for Acid Orange 7 adsorption onto LSAC is shown in Figure (6), which enables calculation of the rate constant k_2 which in turn is used to calculate the initial sorption rate h as follows

$$h = k_2 q_e^2 \qquad (5)$$

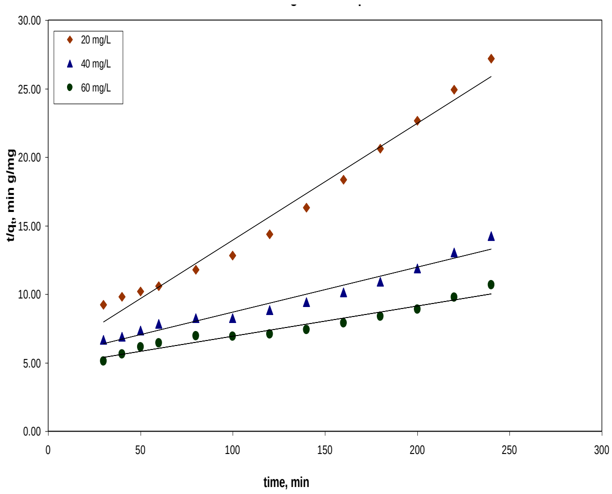

Fig.6. Effect of pseudo second order plot for the adsorption of acid orange 7 onto LSAC

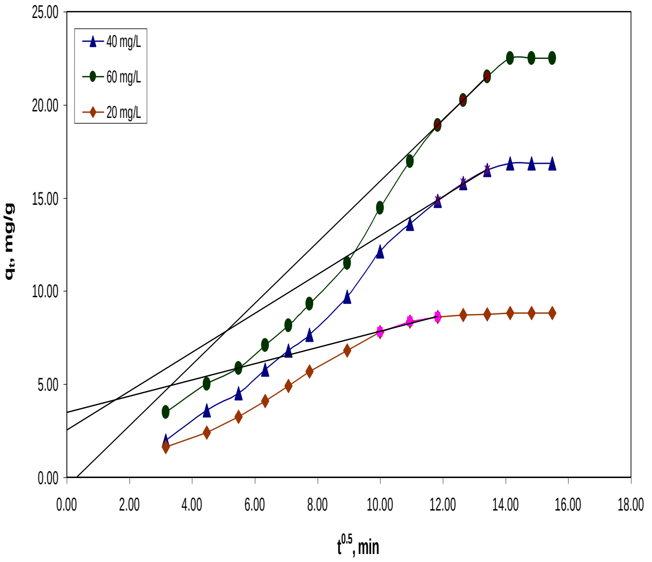

Fig.7. Effect of intraparticle diffusion plot for the adsorption of acid orange 7 onto LSAC

For a solid – liquid adsorption process, the solute transfer is normally characterized by external mass transfer or intra-particle diffusion or both. The intra-particle diffusion model proposed by Weber and Morris [36] was used to identify the mechanism involved in the adsorption process.

$$q_t = k_{id}t^{0.5} + C \qquad (6)$$

where k_{id} (mg/g $min^{0.5}$) is the rate constant of the intra-particle diffusion model and C (mg/g) reflects the boundary layer effect. The k_{id} and C can be determined from the slope and intercept of the plot q_t Vs $t^{0.5}$ and is shown in Figure (7) for Acid Orange 7 adsorption.

The parameters of the pseudo-first order, pseudo-second order and intraparticle diffusion models are shown in Table 1. The results indicated that among these three models, the pseudo-second order kinetic equations had higher R^2 values and experimental q_e values that agree well with the calculated values. The low R^2 values for the pseudo-first order model indicated that these models did not fit the data well. Furthermore, for the pseudo-first order kinetic model, the experimental q_e was not in good agreement with the calculated q_e. Therefore, the pseudo-second order kinetic model provided the best description of the Acid Orange 7 adsorption mechanism. The pseudo first order and second order rate constant decreased with increasing the dye concentration. According to the intra particle diffusion model, the plot of uptake should be linear if intra particle diffusion is involved in the adsorption process and if the line passes through the origin then intra particle diffusion is the rate controlling step. When the plot doesn't pass through the origin, this is an indicative of boundary layer control. This shows that the intra particle diffusion alone is not the rate limiting step, but also other kinetic models may control the rate of adsorption, all of which may be operating simultaneously.

TABLE. 1. Kinetic parameters for the adsorption of Acid Orange 7 onto LSAC

Model	Parameters	Concentration		
		20 mg/L	40 mg/L	60 mg/L
Pseudo first order	K_1	0.0133	0.0091	0.0073
	R^2	0.9312	0.9682	0.9718
Pseudo second order	K_2	0.0398	0.0060	0.0027
	h	5.6446	5.1879	4.1046
	q_e	11.8951	29.1933	38.7265
	R^2	0.9897	0.9921	0.9901
Weber Morris	K_{id}	0.6333	1.3604	1.7867
	R^2	1.000	0.9952	0.9578

Adsorption Isotherms

In this work, adsorption isotherm data of Acid Orange 7 dye were fitted with the Langmuir and Freundlich models, for variation in Activated carbon (LSAC) dosage, which are most widely used. The isotherm fits were compared through the coefficient of correlation (R^2) and were reported in Table (1 & 2).

The Langmuir model [37] assumes that the solid surface carries a limited number of sites that are characterized by equal energy of adsorption, independent of the degree of coverage and thus indicating a monolayer adsorption. The linearized form of the Langmuir equation is described

$$\frac{1}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_e} \qquad (7)$$

where, Q_o is the maximum adsorption capacity, b is the Langmuir binding energy coefficient. The b and Q_o can be calculated from the intercept and slope of the linear plot of C_e/q_e against C_e as shown in Figure (8).

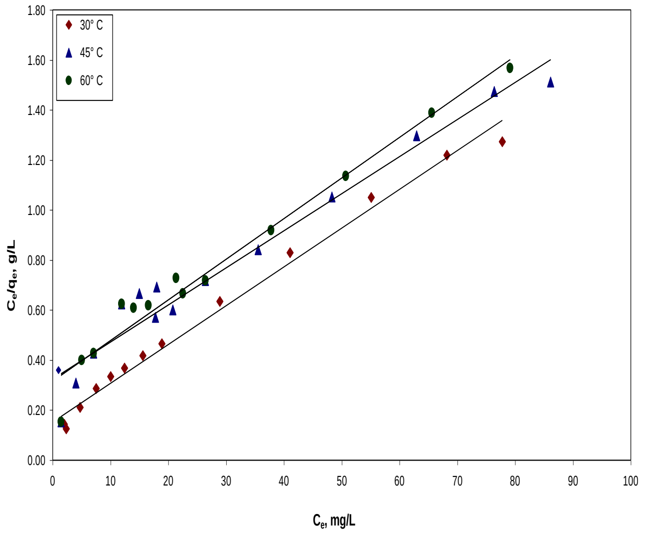

Fig.8. Effect of langmuir plot for the adsorption of acid orange 7 onto LSAC

It is evident that the Langmuir adsorption isotherm is more fitted to describe the adsorption equilibrium ($R^2 > 0.99$). Therefore, monolayer coverage of Acid Orange 7 onto LSAC particles are taken up with the maximum adsorption capacity was obtained 64.56, 72.34 and 67.45 mg/g at 30, 45 and 60 °C. The adsorption capacity was increased 30 and 45 °C due to the available sites present in the surface of the carbon, then it was decreased 60 °C due to the non availability of the sites or desorption will takes place. The K_L values was decreased with increasing temperature.

The Freundlich isotherm [38] is an empirical equation and is one of the most widely used isotherms for the description of multi-site adsorption. The linear form as follows:

$$\log q_e = 1/n \log C_e + \log k_f \tag{8}$$

where K_f and n are the Freundlich isotherm constants indicating the adsorption capacity and adsorption intensity respectively. The K_f and n can be calculated from the intercept and slope of the linear plot of log q_e against log C_e Figure (9). The value of n indicates favorable adsorption of Acid Orange 7 onto LSAC.

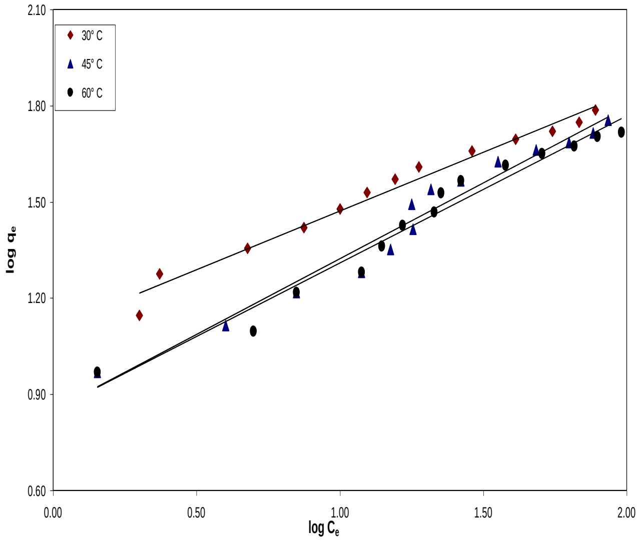

Fig.9. Effect of Freundlich plot for the adsorption of acid orange 7 onto LSAC

Table. 2. Isotherm parameters for the adsorption of Acid Orange 7 onto LSAC

Temp	Langmuir			Freundlich		
	Q_0(mg/g)	KL (L/mg)	R^2	Kf	n	R^2
30 °C	64.5622	6.5071	0.9900	8.9866	2.1015	0.9772
45 °C	72.3471	3.8143	0.9895	6.3363	1.9771	0.9663
60 °C	67.4544	3.0818	0.9921	6.3107	2.0277	0.9663

Adsorption thermodynamics

The thermodynamic parameters such as free energy (Δ*G*), enthalpy (Δ*H*), and entropy (Δ*S*) give a description of adsorption behavior related to temperature. Parameters can be calculated from

$$\Delta G = - RT\ln K_L \tag{9}$$

$$\ln K_L = (\Delta S/R) - (\Delta H/RT) \tag{10}$$

where K_L (L/mol) is from Langmuir equation, *R* is the gas constant (8.314 J/(mol.K), and *T* (K) is the temperature in Kelvin. As can be seen from Table 3, the values of Δ*G* were consistently negative at all temperatures measured, which revealed the adsorption process was feasible and spontaneous in nature. Furthermore, the absolute values of Δ*G* indicating that the sorption process is more favorable at low temperature. The negative value of Δ*H* was indicative of the exothermic nature of the adsorption process. The negative value of Δ*S* suggested the decreased randomness at the solid-solute adsorption systems, which indicated that gain of entropy caused by the water molecules displaced is less than that lost by the Acid orange 7 molecules.

Table. 3. Thermodynamic parameters for the adsorption of Acid Orange 7 onto LSAC

Δ*H* (kJ/mol)	Δ*S* (J/(molK))	Δ*G* (kJ/mol)		
		303K	318K	333K
-20.9307	-52.2668	-5075.8268	-4144.3816	-3188.3933

Conclusions

In the present study, *Leucaena leucocephala* seed shell was modified by using H_3PO_4 in a activation method at relatively low energy consumption. The kinetic adsorption complied well with the pseudo-second-order model. The results of the intraparticle diffusion model suggest that intraparticle diffusion was not the sole rate determining step. It was found that the Langmuir isotherm model yielded the best for equilibrium data with the maximum monolayer adsorption of 72.34 mg/g for Acid Orange 7. Thermodynamics studies indicated the spontaneous and exothermic nature of the sorption process.

Acknowledgement

We acknowledge the Principal and Head of the Department of Chemistry, Chikkanna Government Arts College, Tirupur and Institute for Environmental Nanotechnology for their kind cooperation and support to complete this work.

References

[1] P. Nigam, G. Armour, M.I. Banat, D. Singhand, and R. Marchant, “Physical Removal of Textile dyes from Effluents and Solid-State Fermentation of Dye-Adsorbed Agricultural Residues”, Bioresour.Technol., vol. 72, pp. 219-226, 2000.

[2] G. McKay, M.S. Otterburn and A.G. Sweeney, “Fullers earth and fired clay as adsorbents for dye stuffs-equilibrium and rate studies”, Water Air soil Pollut., vol. 24, pp. 147-161, 1985.

[3] F.C. Wu, R.L. Tseng and R.S. Juang, “Adsorption of Dyes and Phenol from Water on the Activated Carbon Prepared from Corncob Wastes”, Environ. Technol., vol. 22, pp. 205-213, 2001.

[4] G. McMullan, C. Meehan, A. Kirby, T. Robinson, P. Nigam, I.M. Banat, R. Marchan and W.F. Smyth, “Microbial Decolorisation and Degradation”, Appl. Microbiol. Biotechnol., vol. 56, pp. 81-87, 2001.

[5] E. Weber and N.L. Wolfe, “Studies of Reduction of Aromatic Azo Compounds in Anaerobic Sediment/Water Systems”, Environ. Toxicol. Chem., vol. 6, pp. 911-920, 1987.

[6] A. Bozdogan and H. Goknuil, “The Removal of Colour of Textile dyes in Wastewaters by the use of Recycled Coagulant, M U Fena Billimleri Dergisi”, Sayi, vol. 4, pp. 83-96, 1987.

[7] T. Robinson, G. McMullan, R. Marchant and P. Nigam, “Remediation of dyes in Textile Effluent; A Critical Review on Current Treatment Technologies with a Proposed Alternative”, Biores. Technol., vol. 77, pp. 247, 2001.

[8] S.D. Khattri and M.K. Singh, “Colour Removal from Synthetic dye Wastewater using a Bioadsorbent”, Water Air Soil Pollut., vol. 120, pp. 283-294, 2000.

[9] K.S. Low, C.K. Lee and B.F. Tan, “Quanternised wood as Sorbent for Reactive dyes” , Appl. Biotechnol., vol. 87, pp. 233-245, 2000.

[10] R.M. Liversidge, G.J. Lioyd, D.A.J. Wase, and C. F Forster, “Removal of Basic 41dye from Aqueous solution by Linseed Cake”, Proc. Biochem., vol. 32, pp. 473, 1997.

[11] N.M. Nasser and M. El-Geundi, “Comparative cost of Colour Removal from Textile effluents using Natural Adsorbents”, J. Chem. Technol. Biotechnol., vol. 50, pp. 257, 1991.

[12] M.M. Kamel, M. Magda, B.M. Kamel and A. Youssef Waly, “Adsorption of Direct dyes by Cellulose derivatives”, Am. Dye Rep., vol. 4, pp. 34, 1991.

[13] K.H.C. Keith, M. Gordon and F.P. John, “Sorption acid dyes from Effluent using Activated Carbon”, Res. Conserv. Recycl., vol. 27, pp. 57-71, 1999.

[14] G. Mckay, “Design models for Adsorption systems in Wastewater Treatment”, J. Chem. Technol. Biotechnol., vol. 31, pp. 717-731, 1981.

[15] Ruth Yu-Li Yeh, and A. Thomas, “Color Removal from dye Wastewater by Adsorption using Powdered Activated carbon: Mass transfer studies”, J. Chem. Tech. Biotechnol., vol. 63, pp. 48-54, 1995.

[16] K. Kadirvelu, M. Kavipriya, C. Karthika, M. Radhika, N, Vennilamani and S. Pattabhi, “Utilization of Various Agricultural wastes for Activated carbon Preparation and Application for the Removal of dyes and Metal ions from Aqueous solution” Biores. Technol., vol. 87, pp. 129-132, 2003.

[17] K, Kathirvelu, C. Karthika, N. Vennilamani and S. Pattabhi, “Activated carbon from Industrial solid waste as an Adsorbent for the Removal of Rhodamine-B from Aqueous solution: Kinetic and Equilibrium studies”, Chemosphere, vol. 60, pp. 1009, 2005.

[18] M. Ozacar and A.I. Sengal, “Adsorption of Metal complex dyes from Aquoues solutions by Pine Sawdust”,Bioresource Technol., vol. 96, pp. 791, 2005.

[19] M. K. Khattri Vand Singh, “Colour removal from Dye Wastewater using sugar cane dust as an adsorbent”, Adsorption Sci.Technol., vol. 17, pp. 269, 1999.

[20] K. Kairivelu, K. Thamaraiselvi and C. Namasivayam, “Adsorption of Nickel(II) from Aqueous solution onto Activated carbon prepared from Coirpith”, Sep. and Pur. Technol., vol. 24, pp. 497, 2001.

[21] C.A. Lua and J. Guo, “Preparation and Characterisation of Chars from Oil palm waste”, Carbon, vol. 36, pp. 1663–1670, 1998.

[22] C.J. Kirubakaran and S.K. Krishnaiah Seshadri, “Experimental study of the production of Activated carbon from Coconut shells in A Fluidised Bed Reactor”, Ind. Eng. Chem. Res., vol. 27, pp. 2411–2416, 1991.

[23] K. Maniatis and M. Nurmala, “Activated carbon production from Biomass”, Biomass Energy Ind. Environ., vol. 274, pp. 1034, 1992.

[24] V.C. Taty-Costodes, H. Fauduet, C. Porte and A. Delaccroix, “Removal of Cd(II) and Pb(II) ions from Aqueous solutions by Adsorption onto Sawdust of Pinus Sylvestris”, J. Hazard. Mater., vol. B 105, pp. 121-142, 2003.

[25] L.A. Teles de Vasconcelos and C.G. Gonzalez Beca, “Adsorption Equilibria between Pine Bark and Several ions in Aqueous solution Cd(II), Cr(III) and Hg(II)”, Eur. Water Pollut. Control, vol. 3, no. 6, pp. 29-39, 1993.

[26] T. Vaughan, C.E. Seo and W.E. Marshall, “Removal of Selected metal ions from Aqueous solution using Modified corncobs”, Biores. Technol., vol. 78, pp. 133-139, 2001.

[27] Vikrant Sarin, Tony Sarvinder Singh and K.K. Pant, "Thermodynamic and Breakthrough column studies for the Selective sorption of chromium from Industrial effluent on Activated eucalyptus bark”, Biores. Technol., vol. 97, pp. 1986–1993, 2006.

[28] Feng-chin Wu, Ru-Ling Tseng and Chi-Chang Hu, “Comparisions of Pore properties and Adsorption performance of KOH-activated and Steamactivated carbons”, Micropor. Mesopor. Mater., vol. 80, pp. 95-106, 2005.

[29] Satish Manocha, B. Vanraj Chauhan, and L.M. Manocha, “Porosity development on Activation of Char from dry and Wet babool wood”, Carbon Science, vol. 3, no. 3, pp. 133-141, 2002.

[30] S. Karthikeyan and P. Sivakumar, “The Effect of Activating agents on the Activated carbon prepared

from Feronia limonia (L.) swingle (Wood Apple) shell", J. Environ. Nanotechnol., vol. 1, pp. 5, 2012.

[31] S. Karthikeyan and A. Baburajendran, "Adsorption of Basic Dye (Rhodamine B) by a Low Cost Activated Carbon from Agricultural Solid Waste: Leucaena leucocephala Seed Shell Waste", Nature Environ. Pollut. Technol., vol. 9, pp. 461, 2010.

[32] S. Karthikeyan, B. Sivakumar and N. Sivakumar, "Film and Pore Diffusion Modeling for Adsorption of Reactive Red 2 from Aqueous Solutin on to Activated Carbon Prepared from Bio-Diesel Industrial Waste", J. Chem., vol. 7, pp. 175, 2010.

[33] S. Karthikeyan, K. Sakthivel and C. Kannan, "Sorption dynamics and Equilibrium uptake of basic dye (basic brown 4) using Jatroha curcas stem activated Carbon", Rasayan J. Chem., vol. 4, pp. 519, 2011.

[34] S. Lagergren, "ZurTheorie Der Sogennten Adsorption GelosterStoffe", Hand linger, vol. 24, pp. 1, 1898.

[35] Y.S. Ho and G. Mckay, Adsorpt. Sci. Technol., vol. 18, pp. 639, 2000.

[36] W. Weber and J. Morris, "Kinetics of Adsorption of Carbon from Solution", J. Sanit-Eng.Div. Am. Soc. Civ. Eng., vol. 89, pp. 31, 1963.

[37] R. Akkaya and U. Ulusoy, "Adsorptive features of chitosan entrapped in polyacrylamide hydrogel for Pb^{2+}, UO_2^{2+} and Th^{4+}", J. Hazard. Mater., vol. 151, pp. 380-388, 2008.

[38] C. Kannan, B. Sivakumar, P. Nithya and S. Karthikeyan, "Thermodynamic, Kinetic and Equilibrium Studies on the sorption of reactive blue-2 from aqueous solution in the Balsamodendron Caudatum Wood waste", Ind. J. Sci., vol. 4, no. 11, pp. 45, 2013.