Research Journal of Chemical Sciences ISSN 2231-606X
Vol. **4(7),** 36-42, July (**2014**) *Res. J. Chem. Sci.*

Adsorption of Methylene Blue onto Microwave Assisted Zinc Chloride Activated Carbon Prepared from *Delonix Regia* Pods - Isotherm and Thermodynamic Studies

K. Ramesh[1], A. Rajappa[2] and V. Nandhakumar[3*]
[1]Department of Chemistry, Arasu Engineering College, Kumbakonam, Tamilnadu, INDIA
[2]Department of Chemistry, Sri Manakula Vinayagar Engineering College, Pondicherry, INDIA
[3]Department of Chemistry, A.V.V.M Sri Pushpam College, Poondi, Tamilnadu, INDIA

Available online at: www.isca.in, www.isca.me
Received 18th May 2014, revised 9th June 2014, accepted 7th July 2014

Abstract

Delonix regia (Flame tree) pods were utilized to prepare activated carbon by using orthogonal array experimental design method with the parameters such as microwave radiation power, radiation time, concentration of $ZnCl_2$ solution and impregnation time. Optimized conditions were found to be radiation power 850 W, radiation time 12 min, 60 % of $ZnCl_2$ and impregnation time 24 hours. Carbon prepared was designated as MWZAC (Microwave assisted Zinc chloride Activated Carbon). The characteristics of the MWZAC were determined by BET analysis and pH_{ZPC}. MWZAC was used to remove Methylene blue dye from aqueous solution by batch mode adsorption technique. Influence of the parameters such as initial dye concentration and temperature on adsorption was studied. Equilibrium data were fitted with Langmuir, Freundlich, Tempkin, Dubinin-Raduskevich, Harkins - Jura and Sips isotherms. The order of best describing isotherms was given based on R^2 value. Various thermodynamic parameters such as ΔH°, ΔS°, and ΔG° have been evaluated using Vant Hoff plots.. Analysis of these values inferred that this adsorption was endothermic, spontaneous and proceeded with increased randomness.

Keywords: Adsorption, $ZnCl_2$ activated microwave carbon, isotherms, Methylene blue dye.

Introduction

Discharged wastewater by some industries under uncontrolled and unsuitable conditions is causing significant environmental problems. Natural water bodies such as ponds, lakes, rivers and their watershed will be subjected to serious environmental issue, if untreated effluent is discharged into them as such. Researchers have investigated the removal of dyes from the effluent water which was released by large tiny printing and dyeing units, using activated charcoal as adsorbent[1]. Adsorption process is the most powerful technique and used for separating organic and inorganic pollutants from water and waste water and it is embodied in carbon adsorption systems and ion exchangers[2].

Activated carbon is the most common adsorbent for the removal of many organic contaminants. The adsorption process of activated carbon, however, is prohibitively expensive, which limits its application. Therefore, there is a need to produce activated carbon from cheaper and readily available materials. In the past years, several investigations have been reported the removal of dyes using activated carbons developed from industrial or agricultural wastes[3]. Also several studies of dye removal were carried out using adsorbents developed from natural materials[4,5].

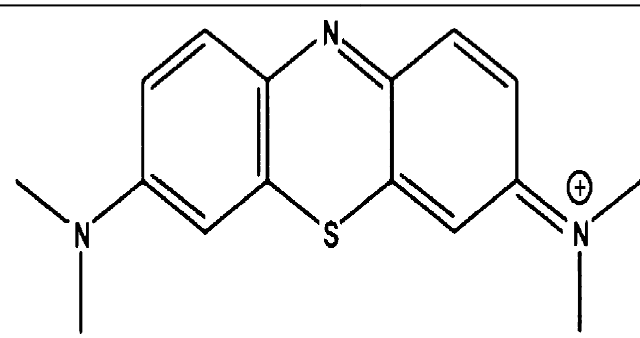

Figure-1
Structure of MB

In the present study, an attempt has been made to prepare carbon from *Delonix regia* (flame tree) pods by microwave irradiation technique. The above mentioned plant belongs to royal Poinciana or flamboyant which is a member of bean family and produces brown woody seed pods purely a waste material[6].

Recently, microwave energy has been widely used in research and industrial processes[7]. The microwave irradiation technique has the following advantages rather than conventional heating techniques[8, 9]. i. Interior heating, ii. selection of heating, iii. Extensive heating rates, iv. Good control of heating process, v. Small equipment size, vi. Reduced wastage production, vii. No direct contact between heating source and heating materials.

Table-1
Nomenclature

Nomenclature			
C_i, C_t and C_e	Initial Concentration, at the time 't' and at equilibrium respectively	ε	Polanyi potential
q_e and q_t	Quantity adsorbed at the time 't' and at equilibrium respectively	E	Mean free energy of adsorption
V	Volume of the dye solution in liter (L)	R	Gas Constant
W	Mass of the adsorbent in gram (g)	T	Temperature (K)
Q_e	Amount of solute adsorbed per unit weight of adsorbent (mg/g)	h	Initial adsorption rate (mg/g min)
Q_0	Adsorption efficiency	a_T	Equilibrium binding constant
b	Adsorption energy	q_m	Constant related to adsorption capacity (mg/g)
R_L	Separation factor	B and A	Isotherm constants
K_f and n	The constants incorporating all factors affecting the adsorption capacity and intensity of adsorption respectively	q_D	Theoretical saturation capacity (mg/g)
b_T	Tempkin constant related to heat of sorption (J/mg)	B	Constant related to the mean free energy
K_c	Equilibrium constant	ΔS°	Entropy of adsorption
ΔG°	Standard free energy	ΔH°	Enthalpy of adsorption

Methodology

Preparation of Adsorbents: The air dried pods were cut into small pieces and powdered in a pulveriser. Taguchi experimental design method was used to prepare and to determine optimal parameters to prepare efficient carbon[6,10].

20 g of the crushed and ground pods was admixed with 75 mL $ZnCl_2$ solution of desired strength (20, 40 and 60 %). The slurry was then allowed to stand as such at ordinary conditions of temperature and pressure for a day (24 hours) to ensure the access of the $ZnCl_2$ to the *Delonix Regia* pods. Then the slurry was subjected to microwave heating of pre- determined power (450, 600, 850 watts) for pre- determined duration (8, 10, 12 minutes). Thus the carbonized samples were washed with 0.5 M HCl followed with hot distilled water and cold distilled water until the pH of the washings reach 7. Then the carbon was filtered and dried at 423 K. Totally 27 number of carbons were prepared by varying parameters such as concentration of $ZnCl_2$ solution, Microwave heating watts power and radiation times[11].

Preparation of stock Solution: The stock solution of dye was prepared by dissolving appropriate amount of exactly weighed dye in double distilled water to a concentration of 1000 mg/L. The experimental solutions were prepared from the stock solution by proper dilutions.

Characterization of MWZAC: Particle size (µm), Surface area (m^2/g), Pore volume (cm^3/g), Pore size or Pore width (nm), Bulk density (g/mL), Fixed Carbon (%), Moisture content (%) and pH_{zpc} were determined.

Adsorption experiments: The effect of parameters such as initial concentration of dye solution, adsorbent dose, pH of the solution and contact time was studied by batch mode technique because of its simplicity. Pre-determined dose of the adsorbent was taken in 250 mL iodine flask and 50 mL and pre - determined concentration of the dye solution was poured into the flask. Then the content flask was agitated using rotary shaker with 180 rpm for pre- determined duration. Then the aliquot was centrifuged. Concentration of the centrifugate was measured after proper dilution using Systronics Double Beam UV-visible Spectrophotometer: 2202 at the wave length of 680 nm.

Effect of pH was studied by bringing the desired pH of the solutions by adding concentrated HCl acid / 1N NaOH solution. The kinetics experiments were performed with the working pH 7 and for contact times 5, 10, 20, 40, 60, 80, 100, 120, 140 and 160 minutes[12].

Results and Discussion

Optimization of adsorbent preparation parameters: Efficiency of the prepared samples to remove MB dye from the aqueous solution were accessed with 20 mg of the adsorbent , 50 mL of MB dye solution of concentrations of 100, 150 and 200 mgL^{-1} and 1 hour agitation time.

The results inferred that percentage of removal of MB dye increased with the increase of radiation time, radiation power and concentration of $ZnCl_2$ solution. Hence carbon prepared using 60 % $ZnCl_2$ solutions, radiation power 850 watts, radiation time 12 minutes and impregnation time 24 hours was chosen with the dosage of 20 mg/50 mL for further studies.

Physico-chemical characteristics of MWZAC: Physico-chemical characteristics of MWZAC were collected in the table 3. Percentage of fixed carbon, surface area, pH_{zpc} and other values are reasonable to function as a good adsorbent.

Table-2
Data Processing Tools

S. No.	Parameters		Formulae
1.	**Mass balance relationships**	% of Removal	$(C_i - C_t)\times V/C_i$
		Quantity adsorbed at equilibrium, q_e	$(C_i - C_e)\times V/W$
		Quantity adsorbed at the time t, q_t	$(C_i - C_t)\times V/W$
2.	**Isotherms**	Langmuir Separation factor	$C_e/Q_e = 1/Q_0b + C_e/Q_0$ $R_L = 1/(1+ bC_0)$
		Freundlich	$\log Q_e = \log K_f + 1/n \log C_e$
		Tempkin	$q_e = RT/b_T \ln a_T + RT/b_T \ln C_e$
		Sips	$C_e^{1/n}/q_e = 1/q_m.b + 1/q_m C_e^{1/n}$
		Harkins – Jura	$1/q_e^2 = [B/A]-[1/A] \log C_e$
		Dubinin – Raduskevich, Polanyi potential Mean free energy of adsorption	$\ln q_e = \ln q_D - B\varepsilon^2$ $\varepsilon = RT \ln(1+1/C_e)$ $E = 1/(2B)^{1/2}$
3.	**Thermodynamic Parameters**	Standard Free energy Change	$\Delta G° = -RT \ln K_c$
		Van't Hoff equation	$\ln K_c = \Delta S°/R - \Delta H°/RT$

Table-3
Physico-chemical characteristics of MWZAC

Properties	Values	Properties	Values
pHzpc	7.01	Pore size (Pore width), nm	2.7174
Particle size, µm	53 - 90	Bulk density, g/mL	0.52
Surface area (BET), m^2/g	586	Fixed Carbon, %	71.11
Pore volume, cm^3/g	0.3986	Moisture content, %	4.36

Effect of temperature on adsorption: Percentage of removal increased with the increase of temperature of the solution for all studied initial concentrations of the dye. It is further noticed that percentage of removal was found to be high when the initial concentration of the dye solution was high.

Isotherm studies: The presence of equilibrium between two phases (liquid and solid phase) is rationalized by adsorption isotherm. The data pertaining to equilibrium have been obtained at different temperatures then made such as Langmuir, Freundlich, Tempkin, sips, Harkins - jura, and Dubinin-Raduskevich adsorption isotherm models[13]. These isotherms are depicted in figure 2. Results of various isotherms are collected in table 4.

Langmuir isotherm: The Langmuir adsorption isotherm was developed to explain the adsorption of gas on to solid surface. It evidences the existence of monolayer and also the surface is energetically homogeneous[14], where, Q_0 is a constant related to adsorption capacity (mg/g) and b is Langmuir constant related to energy of adsorption. The essential characteristics of Langmuir isotherm can be expressed by dimensionless separation factor, R_L[15]. The R_L values of this adsorption process were in between 0 and 1 indicates favourable adsorption.

Freundlich isotherm: It is a most popular model for a single solute system, based on the distribution of solute between the solid phase and aqueous phase at equilibrium. The Freundlich model describes the adsorption within a restricted range only[16]. The 'n' values are in between 1 and 10 which represent favourable adsorption[15].

Tempkin isotherm: The Tempkin isotherm assumes that the heat of sorption in the layer would decrease linearly with coverage due to sorbate/sorbent interactions. Further the fall in the heat of adsorption is not logarithmic as stated in Freundlich expression. 'b_T' is the Tempkin constant related to heat of sorption (J/mg) and 'a_T' is the equilibrium binding constant corresponding to the maximum binding energy (L/g) [17].

Sips isotherm: Sips isotherm describes the characteristics of Freundlich and Langmuir isotherm with respect to concentration of adsorbate. At low concentration of the adsorbate, it turns into Freundlich isotherm and at high concentration of adsorbate; it predicts a monolayer adsorption capacity characteristic of Langmuir isotherm [18]. 'q_m' is a constant related to adsorption capacity (mg/g) and 'b_L' is Langmuir constant related to energy of adsorption (L/mg).

Harkins – Jura isotherm: The Harkins-Jura adsorption isotherm explains multilayer adsorption and can be accounted with the existence of heterogeneous pore distribution[19].

Dubinin – Raduskevich isotherm: In Dubinin-Radushkevich isotherm, '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) and ε is Polanyi potential. The energy of activation from this reaction accounts for the adsorption. The adsorption will be physisorption if energy of activation is less than 8 kJ/mol and will be chemisorption and if it is lie between 8–16 kJ/mol[20].

Analysis of isotherm results: In this present study Q_0 value ranged from 364.61 to 370.37, hence it indicates that the surface area of the adsorbent is carried by the monolayer of the adsorbate. The R_L value was ranged from 0.07 to 0.17, hence is indicate favourable adsorption. A value of 1/n below one is indicates a normal Langmuir isotherm, while n value from 2.98 to 3.64 hence is indicative of cooperative adsorption. R^2 values of these isotherm plots reveal that Harkins – Jura isotherm well describes the present system that is the existence of heterogeneous pore distribution. The B value of Dubinin-Raduskevich isotherm was ranged from 0.028 to 0.016 hence is indicating the adsorption physisorption in nature. The adsorption capacities (mg/g) obtained from these isotherms indicate that MWZAC is a potential adsorbent when compared to the adsorption capacities of adsorbents prepared from plant bio masses which are given in the table 5.

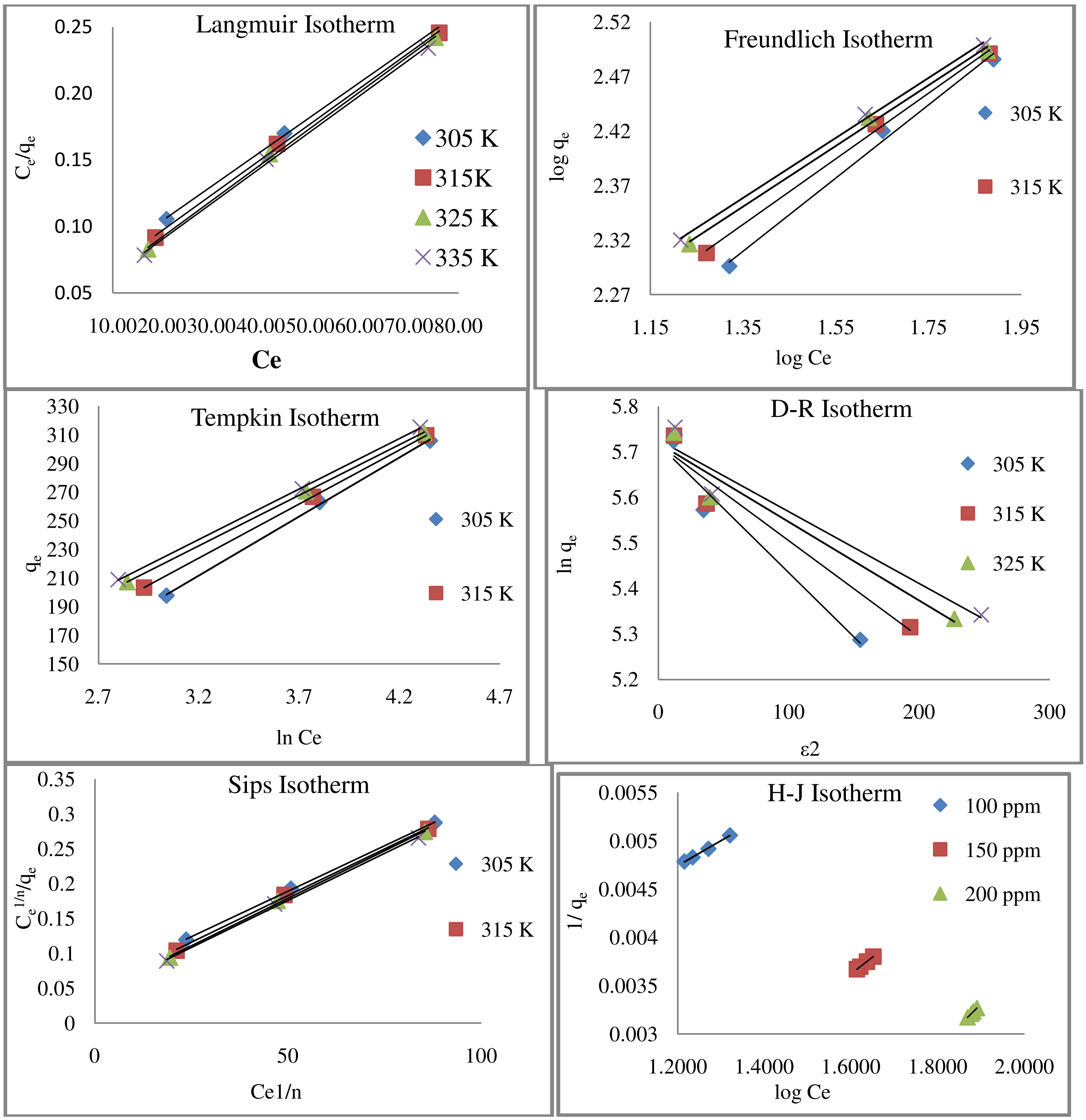

Figure-2
Adsorption Isotherm

Table-4
Isotherm parameters for removal of Methylene blue by MWZAC

Temperature (K)	Langmuir Isotherm Q_0 (mg/g)	b (L/mg)	R_L 100 ppm	R_L 150 ppm	R_L 200 ppm	R^2	Dubinin Raduskevich q_D (mg/g)	B×10^{-4} (mol^2/J^2)	E (kJ/mol)	R^2
305	364.61	0.05	0.17	0.12	0.09	0.999	303.65	0.028	0.01337	0.961
315	370.37	0.062	0.12	0.09	0.14	0.999	303.53	0.021	0.01543	0.948
325	370.37	0.071	0.09	0.14	0.10	0.999	304.29	0.017	0.01715	0.947
335	**370.37**	0.075	0.14	0.10	0.07	0.998	306.45	0.016	0.01768	0.939

Temperature (K)	Freundlich Isotherm n	k_f (mg$^{1-1/n}$.L$^{1/n}$.g^{-1})	R^2	Sips Isotherm n	b (L/mg)	q_m (mg/g)	R^2
305	2.98	71.95	0.993	2.98	0.044	384.61	0.999
315	3.32	84.72	0.997	3.32	0.054	370.37	0.998
325	3.59	94.41	0.996	3.59	0.063	370.37	0.999
335	3.64	97.05	0.998	3.64	0.065	370.37	0.998

Temperature (K)	Tempkin Isotherm b_T (J/mg)	a_T (L/g)	R^2	Harkins – Jura Isotherm Concentration (ppm)	A	B	R^2
305	3.22	0.53	0.999				
315	4.62	0.79	1.000	100	384.61	- 0.061	0.997
325	6.12	1.09	1.000	150	294.12	0.558	0.999
335	7.31	1.17	0.999	200	222.22	1.177	0.999

Table-5
Adsorption capacities of few adsorbents prepared from plant bio masses

Adsorbent	Adsorption capacity(mg/g)	Reference
Bamboo-based activated carbon	Q_0=454.2	B.H. Hameed, et al, 2006
Bark	Q_0 = 914.59	McKay et al, 1999
Rice husk – H3PO4 impregnated	Q_0=333.33	Singh and Srivastava, 2001
Coal	Q_0=323.68	McKay et al, 1999
Rice husk	Q_0=312.26	McKay et al, 1999
Cotton Waste	Q_0=277.78	McKay et al, 1999
NaOH treated Raw Clay	Q_0=204.0	Ghosh and Bhattacharyya, 2001
Tree Leaves	Q_0=133.33	Singh and Srivastava, 1999
Saw dust	Q_0=32.26	De and Basu, 1998
Raw Clay	Q_0=27.49	Ghosh and Bhattacharyya, 2001
MWZAC	**Q_0=370.37**	**Present Study**

Thermodynamics studies: Various Thermodynamic parameters such as ΔH°, ΔS° and ΔG° have been determined using Van't Hoff's plot. The thermo dynamical parameters calculated are presented in table 6. Negative standard free energy of adsorption indicates that the adsorption process is spontaneous in nature. The positive ΔH° values infer that the adsorption is endothermic nature, which was supported by the experimental data i.e., adsorption capacity increased with the increase of temperature, as shown in the table. 6. Since ΔH° values are small the bonding between MB and MWZAC surface should be very weak. Positive value of ΔS° suggests that the adsorption proceeds with increased randomness [21].

Table-6
Thermodynamic Parameters and their results

Concentration (ppm)	Temperature (K)	k_d	ΔG° kJ/mol	ΔH° kJ/mol	ΔS° kJ/mol
100	305	9.4617	-5.6995	8.4553	46.5750
	315	10.8976	-6.2565		
	325	12.0688	-6.7310		
	335	12.7253	-7.0857		
150	305	5.8761	-4.4914	3.5218	26.2971
	315	6.1645	-4.7642		
	325	6.4734	-5.0475		
	335	6.6352	-5.2716		
200	305	2.3319	-2.1473	2.7045	15.913
	315	2.4264	-2.3219		
	325	2.4755	-2.4496		
	335	2.5758	-2.6357		

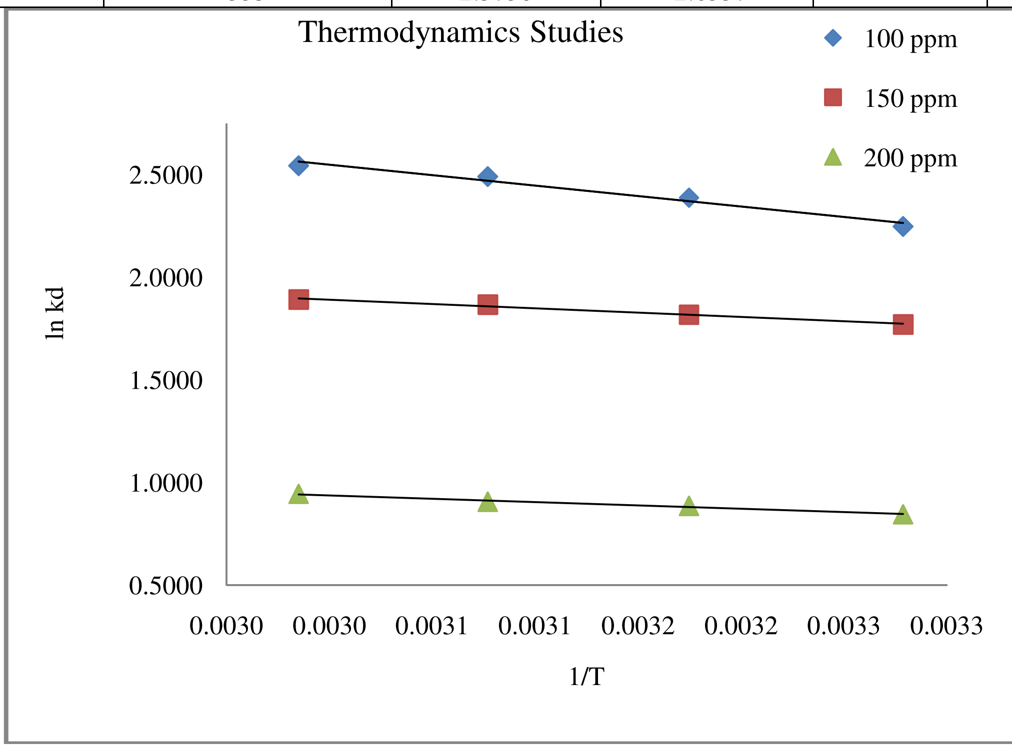

Figure-3
Thermodynamics Studies

Conclusion

Microwave assisted zinc chloride activated carbon (MWZAC) was prepared from *Delonix regia* (Flame tree) pods found to have good capacity of adsorption. Experimental data indicated that MWZAC was effective in removing MB dye from aqueous solution. Equilibrium adsorption was achieved in about 60 minutes for the dosage of 20 mg/50 mL of solution at room temperature of 305 K for the initial concentration of dye solutions ranging from 100 to 200 mg/L. Tempkin isotherm represents the equilibrium adsorption data well when compared to other isotherms studied. The adsorption data was also fitted with Langmuir adsorption model. The fitness of Langmuir's model indicated the formation of monolayer coverage of the sorbate on the surface of the adsorbent. The R_L values of Langmuir isotherms were in between 0 to 1 indicating the favourable adsorption. The B value was ranged from 0.028 to 0.016 hence is indicate the adsorption physisorption in nature.

Extensive study on thermodynamics with the help of thermodynamic parameters reveals that the adsorption system was spontaneous, endothermic with increased randomness.

References

1. Moreno-Castilla C., Adsorption of organic molecules from aqueous solutions on carbon materials, *Carbon,* **42,** 83-94, (**2004**).
2. Abechi E.S., Gimba C.E., Uzairu A. and Kagbu J.A., Kinetics of adsorption of Methylene blue onto activated carbon prepared from palm kernel shell, *Arch. Appl. Sci. Res.* **3** (**1**), 154-164 **(2011)**
3. Salleh M.A.M., Mahmoud D.K., Karim W.A. and Idris A., Cationic and Anionic Dye Adsorption by Agricul- tural Solid Wastes: A Comprehensive Review, *Desalination,* **280(1-3)**, 1-13 **(2011)**
4. Wang J., C. Chen., Biosorption of heavy metals by Saccharomyces cerevisiae: A review, *Biotechnol. Adv*. **24**: 427-451 **(2006)**.
5. Mahvi A.H., D. Naghipour, F. Vaezi and S. Nazmara., Tea waste as an adsorbent for heavy metal removal from industrial wastewaters, *Am. J. Appl. Sci.,* **2,** 372-375 **(2005)**
6. Yuh-Shan Ho, R., Malarvizhi, Sulochana N., Equilibrium Isotherm Studies of Methylene Blue Adsorption onto Activated Carbon Prepared from Delonix regia Pods. *Journal of Environmental Protection Science,* **3**, 111–116 **(2009)**
7. Yagmur E., Ozmak M., Aktas Z., A Novel method for production of activated carbon from waste tea by chemical activation with microwave energy, *Fuel.,* **87,** 3278-3285 **(2008)**
8. Bykov YV., Rybakov KI., Semenov VE., High-temperature microwave processing of materials, *J Phys.,* **34,** 55 **(2001)**
9. Foo Keng Yuen, Hameed B.H., Recent developments in the preparation and regeneration of activated carbons by microwaves, *Advances in Colloid and Interface Science*. **149**, 19–27 **(2009)**
10. Makeswari M., Santhi T., Optimization of preparation of activated carbon from *Ricinus communis* leaves by microwave – Assisted Zinc Chloride chemical activation: Competitive adsorption of Ni2+ ions from aqueous solution, *Journal of chemistry,* 2013, 1-12 **(2013)**.
11. Namasivayam C. and Sangeetha D., Equilibrium and kinetic studies of adsorption of phosphate onto ZnCl2 activated coir pith carbon, *J. Colloid and Interface Science,* **280**, 359–365 **(2004)**
12. Venkatraman B.R., Hema K., Nandhakumar V., Arivoli S., Adsorption Thermodynamics of Malachite Green Dye onto Acid Activated Low Cost Carbon, *J. Chem. Pharm. Res.,* **3**(**2**), 637-649 **(2011)**
13. Sivakumar, P., Palanisamy, P.N., Adsorption studies of basic red 29 by a nonconventional activated carbon prepared from *Euphorbia Antiquorum L. Int.J. ChemTech Res*., **Vol.1, No.3** , pp 502-510 **(2009)**
14. Perez-Marin, A. B., Zapata, V., Meseguer., Ortuno, J. F., Aguilar, M., Saez, J., Llorens, M., Removal of cadmium from aqueous solutions by adsorption onto orange waste. *J. Haz. Mat*., **139**(**1**), 122-131 (**2007**).
15. Arivoli S., Nandhakumar V., Saravanan S., Sulochana Nadarajan., Adsorption Dynamics of Copper ion by Low Cost Activated Carbon, *The Arabian Journal for Science and Engineering,* **34**(1A), January **(2009)**.
16. Taty-Costodes V.C., Fauduet H., Porte C., Delacroix A., Removal of Cd(II) and Pb(II) ions from aqueous solutions by adsorption onto sawdust of pinus sylvestris, *J. Hazard. Mater*., **B105**, 121-142 **(2003)**.
17. Teles de Vasconcelos L.A., Gonzalez Beca, C.G., Adsorption equilibria between pine bark and several ions in aqueous solution Cd(II), Cr(III) and Hg(II), *Eur. Water Pollut. Control*., **3(6)**, 29-39 **(1993)**
18. Ho Y.S., Porte RJ.F. and Mckay G., Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: copper, nickel and lead single component systems. *Water, Air, and Soil Pollution*. **141**, 1–33 **(2002)**
19. Basar, C.A., Removal of direct blue-106 dye from aqueous solution using new activated carbons developed from pomegranate peel: Adsorption equilibrium and kinetics, *J. Hazard. Mater*., **B135,** 232-241 **(2006)**
20. Vikrant Sarin, Tony Sarvinder Singh, Pant K.K., Thermodynamic and break through column studies for the selective sorption of chromium from industrial effluent on activated eucalyptus bark. Bioresource Technology. **97(16)**, 1986 – 1993 **(2006)**
21. Weber Jr, W.J., Morris, J.C., Kinetics of adsorption on carbon from solution, *J. Sanit. Eng. Div. ASCE*. **89 (SA2)**, 31–59 **(1963)**.
22. Roopa V, Ramesh K, Rajappa A and Nandhakumar V., Equilibrium and isotherm studies on the adsorption of Rhodamine B onto activated carbon prepared from bark of *Eryth rina Indica, Int.J.Curr.Res.Chem.Pharma.Sci.,* **1(2),** 23-29 **(2014)**