www.sphinxsai.com

International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.10 No.10, pp 666-679, 2017

Biosorption of Crystal violet dye by Downy wood mint seeds in aqueous solution

***Aeshah Jamal Al –Timimi, Elham M. AL-Rufaie**

Department of Chemistry, College of Science, Bagdad University, Al-Jadryia, Baghdad, IRAQ

Abstract : In this study, equilibrium, kinetics and thermodynamics of Crystal Violet (CV) adsorption onto Downy wood mint seeds (DWMS) was investigated. Parameters that influence the adsorption process such as pH, adsorbent dose, initial dye concentration, contact time and temperature were studied by batch adsorption process using UV-Visible spectrophotometric. The optimum conditions for removal of CV were found to be pH 7.0, equilibrium time 90 min, biosorbent dosage 1.4 g, initial dye concentration 4 mg L^{-1}.The CV biosorption potential of DWMS increased with increasing temperature. Biosorption data were modeled by Langmuir, Freundlich, Temkin andDubinin– Radushkevich (D–R) isotherms, it seems to fit Freundlich isotherm model with high coefficients of correlation at different temperatures. Kinetics of the adsorption process was tested by pseudo-first-order and pseudo-second-order kinetics, and intraparticle diffusion mechanism. Pseudo-second-order kinetic model provided a better discretion. Thermodynamic parameters suggest that the biosorption process is spontaneous and exothermic in nature.

Keywords : Adsorption; Crystal violet; Downy wood mint seeds; Kinetics; Isotherm; Thermodynamics.

Introduction

Many industries; dyestuff, textile, pharmaceutical, paper, plastic, and tannery, make use of dyes to color their products, the textile industry is the largest consumer of dyes, about 10,000 different textile dyes with an estimated annual production of 7 $x10^5$ metric tons are commercially available worldwide [1].The traditional aim of wastewater treatment is to enable it to be disposed of safely, without being a danger to public health and without polluting watercourses or causing other nuisance. Increasingly another important aim is to recover energy, nutrient, water, and other valuable resources from it. Wastewater management is one of the challenging issues in the world. [2].Hence removal of dyes from wastewaters using economical means has become a real challenge to global scientists [3]. Amongst the numerous techniques of dye removal, adsorption is the procedure of choice and gives the best results as it can be used to remove different types of coloring materials [4,5,6].

Adsorption has been found to be superior for wastewater treatment compared to other physical and chemical techniques, such as flocculation, coagulation, precipitation, and ozonation, as they possess inherent limitations, such as high cost, the formation of hazardous by-products, and intensive energy requirements [7].The crystal violet (CV) dye is a synthetic cationic dye and transmits violet color in aqueous solution. It is also known as Basic Violet 3, gentian violet and methyl violet 10B, belonging to the group of triarylmethane [8]. This dye is used extensively in the textile industries for dyeing cotton, wool, silk, nylon, in the manufacture of printing inks and also the biological stain, a dermatological agent in veterinary medicine [8-9]. The CV is toxic and may be absorbed through the skin causing irritation and is harmful by inhalation and ingestion. In extreme cases, can lead to kidney failure, severe eye irritation leading to permanent blindness and cancer [10-11]. Therefore, removal of this dye from water and wastewater is of great importance.

The present study has been designed to investigate the potential use of Downy wood mint seeds for the removal of crystal violet from aqueous solution. For this purpose, batch adsorption experiments have been carried out under varying experimental conditions such as contact time, the initial concentration of crystal violet solution, pH and temperature of the solution.

Materials and Methods:

Crystal violet solution:

Crystal violet dye was provided from (HIMEDIA) which is of analytical grade and used without further purification. The structure of C.V is given in fig.1.

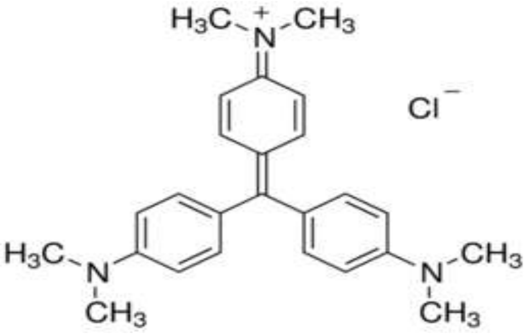

Figure 1.The structure of crystal violet.

A stock solution of 40 mg.L^{-1}was prepared by dissolving 0.01 gm C.V (M.wt=407.9 gm.mol^{-1}) in 250 ml volumetric flask using distilled water as a solvent. Other concentrations needed were prepared by dilution of a stock solution.

Sodium Chloride salt:

1M of a stock solution prepared by dissolving 5.84 gm of NaCl in 100 ml volumetric flask using distal water as a solvent. Other concentrations needed were prepared by dilution of stock solution.

pH adjustment:

A stock solution of 1M standardized NaOH solution and 1M standardized H3PO4 solution were used to adjust the pH of each solution used in our experiments.

The adsorbent:

The Downy Wood Mint seeds (Blephiliaciliate) was used as an adsorbent which was obtained from local market. DWM were thoroughly washed with distilled water several times to remove any impurities if presented on the surface, then soaks in 100 ml distilled water for at least 15 mint fig.2.

(a) (b)

Figure 2. a- dry seeds andb- socked in distilled water for 15 min

Batch adsorption studies:

Batch mode of adsorption studies was used to investigate the effect of different parameters which affects adsorption process and its efficiencies, such as dye concentration (C.V), adsorbent dose (downy wood mint), temperature, pH and contact time.

A solution of a definite concentration of C.V dye and one gm of soaks downy wood mint seeds were taken in 500 ml round bottom flask and agitated in a water bath shaker at predetermined time intervals.

Adsorbate concentration was determined by UV-Vis spectrophotometer (UV-1800 Shimadzu) at its wavelength λmax= 590 nm.

The amount of the adsorbed C.V were calculated by equation 1:

$$q_e = \frac{(C_0 - C_e)\,V}{w} \quad \ldots\ldots \quad (1)$$

q_e= amount of metal ion adsorbed in (mg/g).
C_0= initial metal ion concentrationin (mg/L).
Ce= is the concentration at equilibrium in (mg/L).
V= is the total volume of solution in (L).
w= mass of the adsorben(downy wood mint seeds) used in gram.
The percentage removal were calculated using [12] eq.2:

$$\%R = \frac{C_0 - Ce}{C_0} \times 100 \quad \ldots\ldots \quad (2)$$

Results and Discussion:

Effectof some parameters on Adsorption:

Effect of adsorbent dose:

The adsorbent dose determines the capacity of the adsorbent for a given initial concentration. The adsorption of CV on DWM seeds was studied by changing the quantity of adsorbent (0.2, 0.4, 0.6, 0.8, 1, 1.2, 1.4, 1.6 and 1.8 g) in the test solution while keeping the initial (CV) concentration 5.6 mg/L, temperature (27 ± 2 °C), pH 7.0 and a contact times of 90 min Figure.3. An increase in adsorbent quantities strongly affects the quantities of dye removed from the aqueous solution to certain limit it shows an increase in %R with increase in the adsorbent dose up to 1.4g [13].

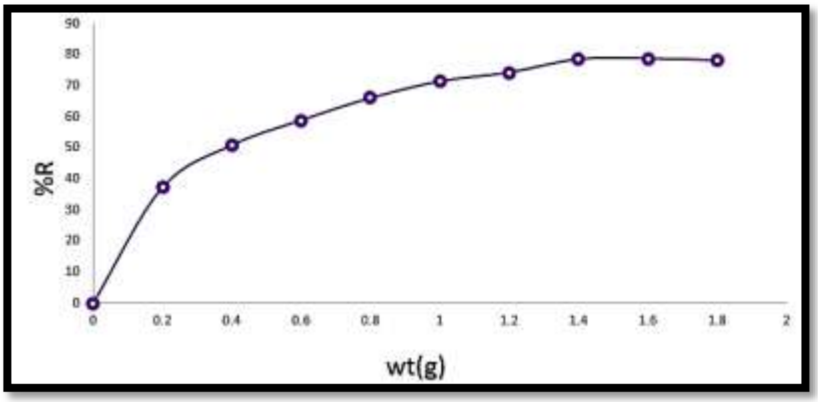

Figure.3.Effect of adsorbent dose on adsorption of CV dye onto DWM seeds.

Effect of contact time:

Figure 4 shows the effect of contact time on the adsorption of CV dye on DWM seeds. In this experiment using different time interval (10, 20, 30, 40, 50, 60, 70, 80 and 90 min) for adsorption of CV dye on (1.4gm) of DWM seeds at room temperature and pH =7. The equilibrium adsorption percent increases with increasing the contact time and approaches equilibrium after about 90 min. Initially, a large number of vacant surface sites is available for adsorption; the adsorption rate is very fast, thus it rapidly increases the amount of adsorbents accumulated on the adsorbent surface mainly within the first hour of adsorption. Adsorption rate decrease after 30 min. and remains constant after 90 min. due to the saturation of the adsorption site and reaches the equilibrium state (adsorption, desorption equilibrium) [14].

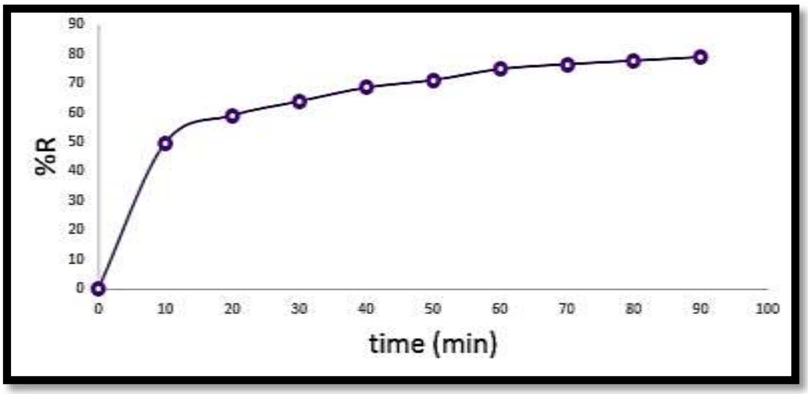

Figure.4. Effect of contact time on adsorption of CV dye onto DWM seeds.

Effect of pH

To study the effect of pH on the adsorption. The range of pH adjusted between 2 and 12. The experimental date indicates that the removal of dye was so effective at pH 7. Figure 5 shows the effect of pH on the removal of Crystal Violet on to DWM [15,16].

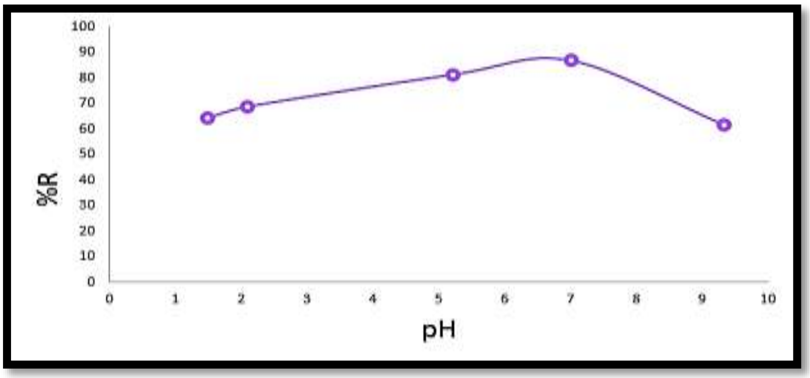

Figure.5. Effect of pH on adsorption of CV dye onto DWM seeds.

Effect of temperature:

Experiments were carried out at different temperature 21, 27, 33, 39, 45, 55 and 65C^0 in conjunction with the optimum other parameters, 90 min contact time, 1.4g adsorbent dose, and pH =7.figure -6 shows that at 65C^0 there are the best Removal % and so this temperature was chosen for further experiments.

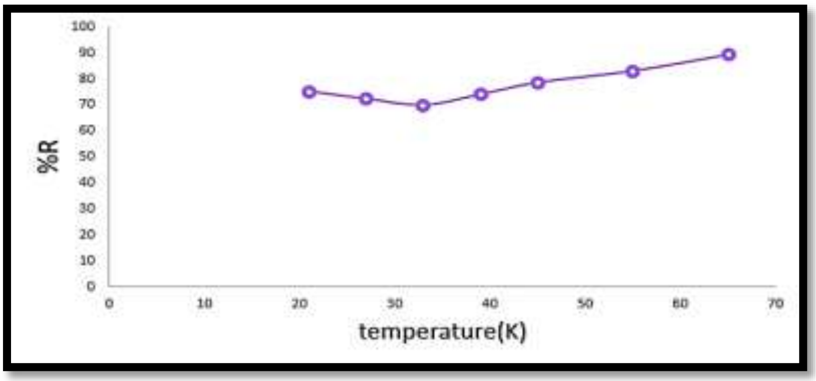

Figure.6. Effect of temperature on adsorption of CV dye onto DWM seeds.

Effect of initial concentration:

The initial concentration provides an important force to overcome all mass transfer resistances of all molecules between the aqueous and solid phase [17].

Figure 7 shows the effect of different initial concentration (4, 4.4, 4.8, 5.6, 6, 6.4 and 6.8 ppm) of CV adsorbed by DWM seeds. The adsorption decreases with the increase of the initial concentration of CV solution. A decrease in R% with increase initial concentration is due to the saturation of the active site on the adsorbent surface.

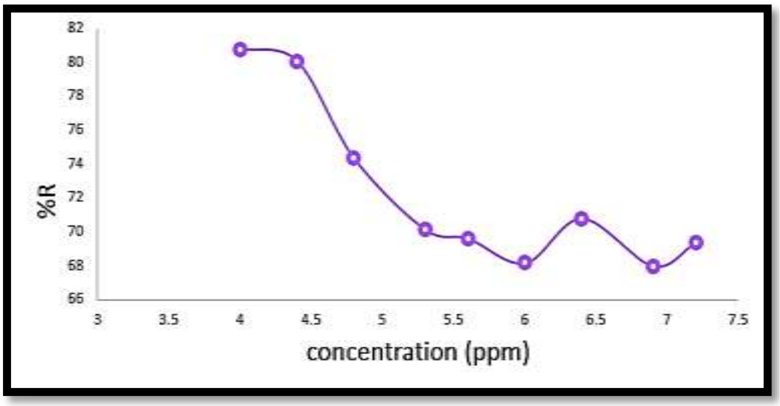

Figure.7. Effect of initial concentration on adsorption of CV dye onto DWM seeds.

Adsorption Isotherm:

Adsorption isotherms play an important role in elucidating the interaction between the adsorbent and further deepen the understanding of the mechanism of adsorption phenomenon.

The distribution ratio of the solute between the liquid and the solid phases is a measure of the position of equilibrium. The preferred form of depicting this distribution is to express the quantity q_e as a function of C_e at a fixed temperature and an expression of this type is termed an adsorption isotherm [18]. The quantity q_e is the amount of solute adsorbed per unit weight of the solid adsorbent, and C_e is the concentration of solute remaining in the solution at equilibrium. The analysis of the isotherm data is important to develop an equation which accurately represents the results and which could be used for design purposes [19].

In the present study, Langmuir, Freundlich, Temkin and Dubinin Radushkevich (*D-R*) models were used to describe the equilibrium data.

Langmuir isotherm:

The Langmuir isotherm assumes that the sorption takes place at specific homogeneous sites within the adsorbent [20]. The linear form of Langmuir isotherm is represented by the Eq. 3:

$$C_e/q_e \quad = \quad 1/q_mK_L \quad + \quad C_e/q_m \qquad \ldots\ldots\ldots \qquad (3)$$

Where C_e is the equilibrium concentration (mg.L^{-1}), q_e the amount adsorbed at equilibrium (mg.g^{-1}), q_mt he adsorption capacity (mg.g^{-1}) and, k_L is the energy of adsorption (Langmuir constant, L mg^{-1}). The values of q_m and k_L were calculated from the slope and intercept of the linear plots C_e/q_e *versus* C_e which give a straight line of slope $1/q_m$ that corresponds to complete monolayer coverage (mg.g^{-1}) and the intercept is $1/q_mk_L$.

Freundlich isotherm:

The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface [21]. The logarithmic form is shown as Eq. 4:

$$\log q_e = \log K_f + 1/n \log C_e \qquad \ldots\ldots\ldots\ldots \qquad (4)$$

where K_f and n are the Freundlich constants related to adsorption capacity and adsorption intensity of adsorbents, respectively. They were calculated from the intercept and slope of the plot of log q_e versus log C_e.

Dubinin–Radushkevich isotherm:

The Dubinin–Radushkevich isotherm (*D-R*) is generally applied to express the adsorption mechanism (physical or chemical) with energy distribution onto a heterogeneous surface [22]. This isotherm model is more general than Langmuir isotherm because it does not assume a homogeneous surface or a constant adsorption potential and is related to the porous structure of the adsorbent. The linear form of *D-R* isotherm equation is represented as:

$\ln q_e = \ln q_s - K_{ad}\,\varepsilon^2$……… (5)

where$q_s$is the theoretical saturation capacity (mg. g^{-1}), K_{ad} is a constant related to the mean free energy of adsorption per mole of the adsorbate ($mol^2\ J^{-2}$), ε is Polanyi potential which is mathematically represented as:

$\varepsilon = RT \ln [1 + 1/C_e]$……… (6)

where$C_e$is the equilibrium concentration of adsorbate in solution (mol L^{-1}), *R* is the gas constant (J $mol^{-1}\ K^{-1}$) and *T* is the absolute temperature (K). The *D-R* model constants, $K_{ad}$and q_s, can be determined from the intercept and slope of thelinear plot of $\ln q_e$versus ε^2, respectively. The constant K_{ad} gives an idea about the mean free energy *E* (kJ mol^{-1}) of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated from the relationship:

$E = 1/(2K_{ad})^{1/2}$ ……………..…..(7)

Temkin isotherm:

Temkin isotherm contains a factor that explicitly taking into account if adsorbent-adsorbate interact and is based on the adsorption that the free energy of adsorption is simply a function of surface coverage.[23]

The linearized Temkin isotherm is shown in equation (8):

$q_e = B \ln k_T + B \ln Ce$……….. (8)

Where B equals to = [RT / b_T] In J/mol corresponding to the energy of adsorption, b_T is the Temkin isotherm constant and k_T (L/g) is the equilibrium binding constant related to the maximum binding energy.Temkin plot of qe versus *ln*Ce at 338K.

Both value of B and K_T computed from the slope and intercept of the plot. The Temkin isotherm parameters B, K_T, b_T and R^2 are listed in Table 1. From the value of R^2 this model is applicable to the description of equilibrium data.

Dimensionless separation factor R_L were calculated from eq :

$R_L = 1 / 1 + K_L\, C_0$…….. (9)

Table 1-Langmuir, Freundlich, Dubinin RadushKvich and Temkin isotherm model parameters and their respective correlation coefficients for the sorption of CV onto DWM biosorbent.

Langmuir isotherm					
	Temperature (K)	**q_m (mg/g)**	**K_L (L/mg)**	**R_L**	**R^2**
Downy Wood Mint Seeds	**306**	3.5536	0.3338	0.4282	0.7355
	312	2.0449	0.9018	0.2170	0.7860
	318	5.0581	0.2751	0.4761	0.6453
	328	4.2955	0.5209	0.3243	0.6787
	338	2.0742	1.4413	0.1478	0.9698

Freundlich isotherm				
	Temperature (K)	**n**	**K_f mg.g^{-1}**	**R^2**
Downy Wood Mint Seeds	**306**	1.3146	0.9585	0.8584
	312	2.1101	0.9667	0.8277
	318	1.0767	1.0886	0.9340
	328	1.3992	1.4743	0.9510
	338	2.1949	1.2125	0.9648

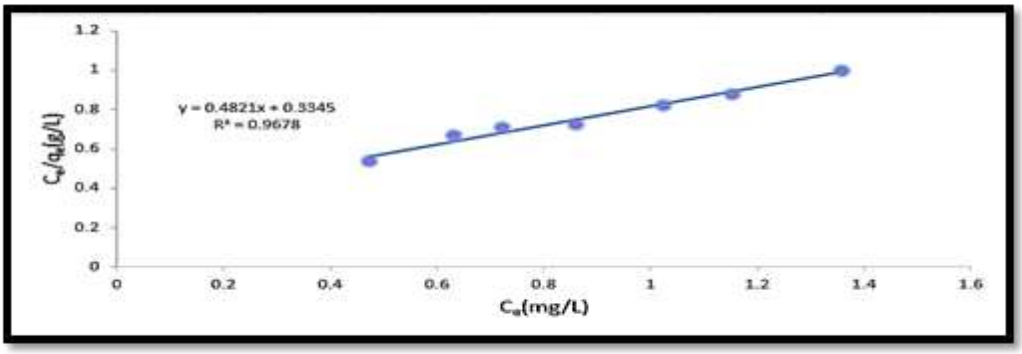

Figure 8- Langmuir's adsorption isotherm for the adsorption of CV onto DWM biosorbent at 338K.

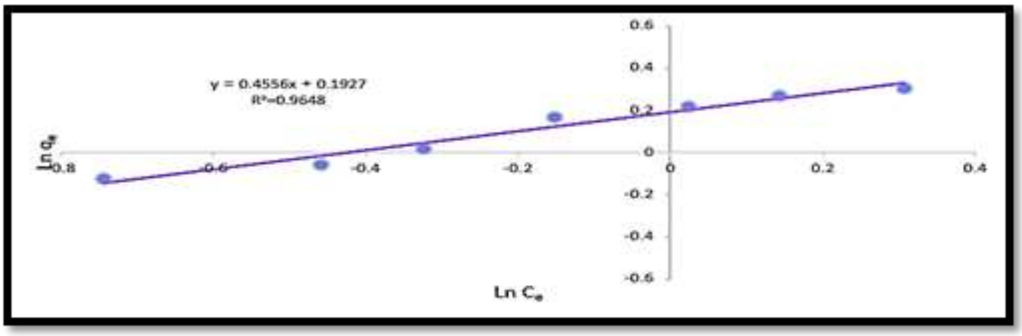

Figure 9- Freundlich adsorption isotherm for the adsorption of CV onto DWM biosorbent at 338K

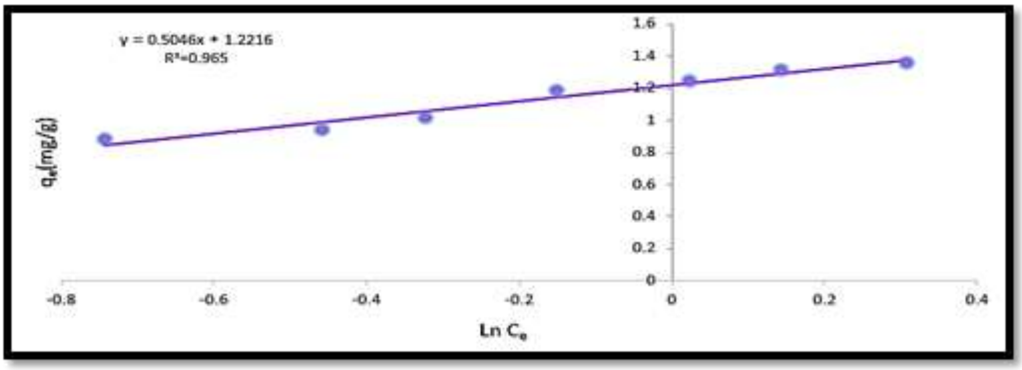

Figure 10- Temkin isotherm model for the adsorption of CV by DWM biomassat 338K.

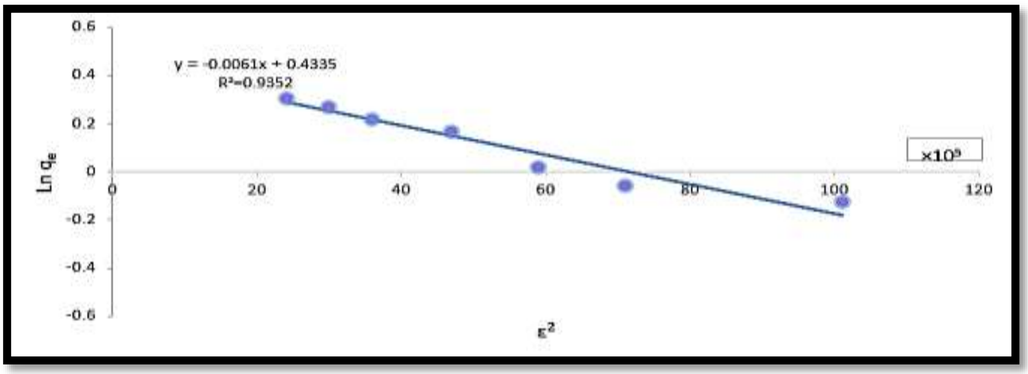

Figure11- D-R isotherm model on the adsorption of CV onto DWM biosorbent at 338K.

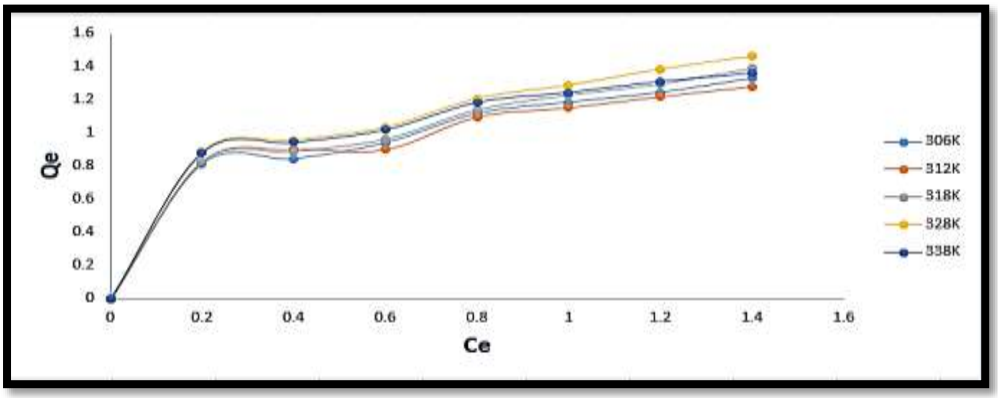

Figure 12- Adsorption isotherm models on the adsorption of CVinto DWM biosotbent at different temperature

Kinetic Adsorption:

In order to understand the controlling mechanism of the adsorption process, the pseudo first-order, the pseudo-second order and intraparticle diffusion models were applied to examine the experimental data.

The pseudo first-order rate expression of Lagergren is given as [24]:

$$\ln (q_e - q_t) = \ln q_e - K_1 t \quad …….. \quad (10)$$

where k_1 (min^{-1}) is the rate constant of the pseudo-first-order adsorption process which is obtained from the slop of the plot of $\ln(q_e-q_t)$ vs time and the intercept gives q_e (equilibrium or maximum adsorption capacity) as shown in fig. 13.

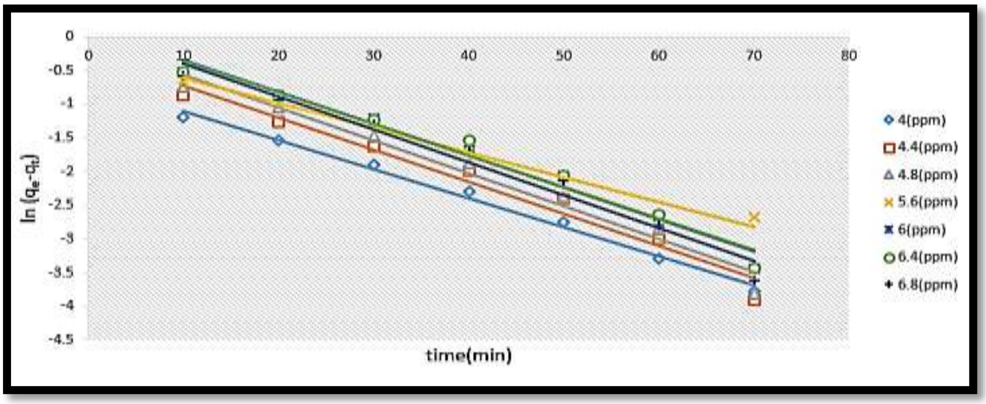

Figure. 13. Pseudo-first-order kinetic model plots for adsorption of CV on DWM seeds at 338K

The pseudo-second-order kinetics given by Ho's equation [25]:

$t/q_t = 1/K_2q_e^2 + t/q_e$……… (11)

where k_2 (gmg^{-1} min^{-1}) is the pseudo-second-order rate constant. The slopes andintercepts of plots of t/qtvs. t were used to the calculatethe second-order rate constant k_2 and q_e.

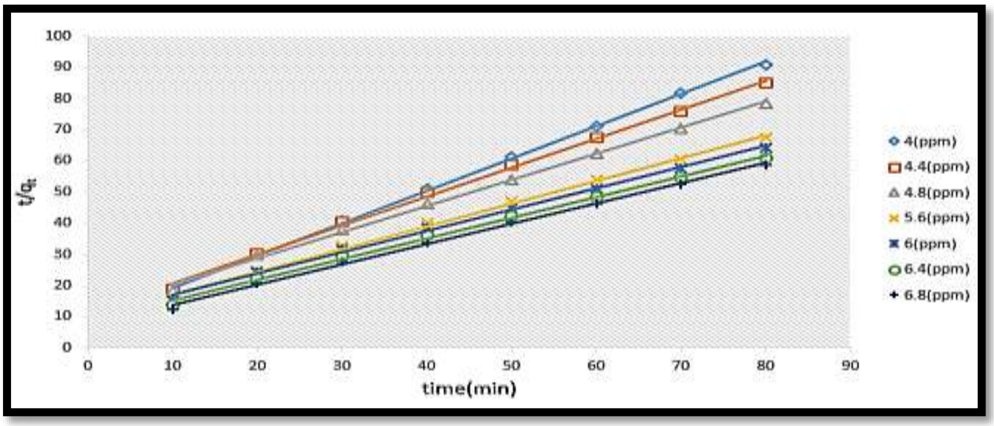

Figure. 14. Pseudo-second-order kinetic model plots for adsorption of CV on DWM seeds at 338K

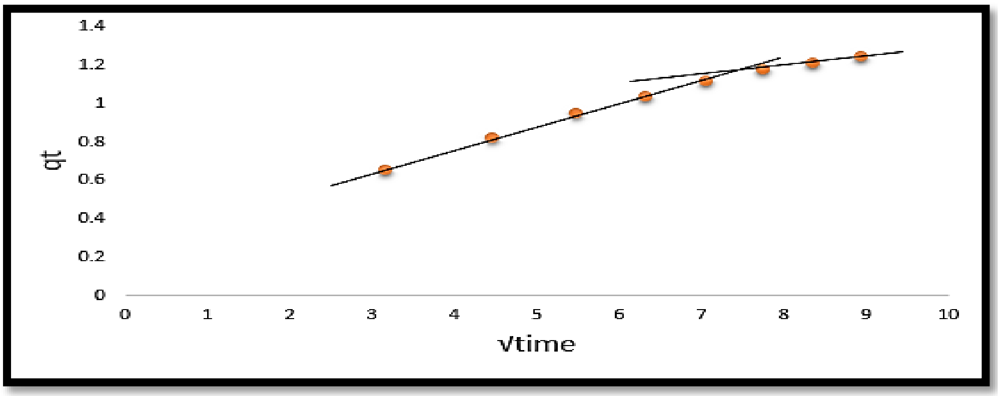

Figure 15 :Intraparticle diffusion model plots for adsorption of CV on DWM of 6 mg/L at 338K

Table2: Kinetic Parameters Of The Adsorption Of C.V Onto DWM Seeds at 6 mg/L

Temp. (K)	First-order			Second-order			Intra-particle diffusion	
	q_e (mg.g^{-1})	K_1 Min^{-1})(	R^2	q_e (mg.g^{-1})	K_2 (mg/g.min)	R^2	Kd (mg/g.min)	R^2
306	0.7936	0.0386	0.9417	1.3199	0.0664	0.9940	0.0801	0.9951
312	0.7626	0.0315	0.9889	1.3065	0.0523	0.9908	0.0883	0.9953
318	1.0788	0.0507	0.9325	1.3943	0.0604	0.9959	0.0878	0.9907
328	0.9881	0.0418	0.9764	1.4747	0.0509	0.9960	0.0981	0.9913
338	1.1387	0.0472	0.9722	1.4649	0.0452	0.9971	0.1039	0.9839

The values of regression coefficient for pseudo-second-order model are greater than those for pseudo-first-order model. Thus the adsorption of CV onto DWM is best explained by the pseudo-second-order kinetic model. Adsorption rate constants and calculated adsorption capacities are summarized in Table 2.

The intra-particle diffusion model equation is given as [26]:

$q_t = K_d\, t^{0.5} + C$ …….. (12)

wherek_d, the intra-particle diffusion rate constant (mg/g min0.5) which can be evaluated from the slope of the linear plot of q_t versus $t^{0.5}$, C represents the thickness of the boundary layer [27]. The intraparticle diffusion plot is shown in fig. 15.

Adsorption Thermodynamics:

Thermodynamics of equilibrium sorption data can give more important information on sorption process. In the present study, the effect of temperature on the adsorption was investigated at different dye concentrations. It showed that the sorption of CV increase with increasing the temperature. The increase in the dye sorption onto DWM biosorbent is due to the deformation of bonds between the dye molecules and the active site of DWM biomass. Thermodynamic parameters were calculated using the following equations (12-14) [28]:

$\Delta G° = -RT ln K_{eq}$…………(13)

Where $\Delta G°$ is standard free energy of adsorption, R is the gas constant, K_{eq} is the distribution coefficient for sorption. The K_{eq} value was calculated from the following equation:

$K_{eq} = q_e / C_e$ ………… (14)

Where q_e and C_e are the equilibrium concentrations of dye ions in the adsorbed phase (mg/g) and in the solution (mg/L), respectively. The standard enthalpy ($\Delta H°$) and entropy ($\Delta S°$) of adsorption can be estimated from Van't Hoff equation:

$ln K_{eq} = \Delta S°/R - \Delta H°/RT$ ……………..(15)

The linear plots of $ln K_{eq}$ vs. $1/T$ (Figure 15) give the numerical values of enthalpy

($\Delta H°$) and entropy ($\Delta S°$) from the slope and intercept, respectively.

The values of the thermodynamic parameters for the sorption of CV onto biosorbent are given in Table 3. The negative value of ΔH^o indicates exothermic nature of adsorption while positive ΔS^o value confirms the increased randomness at the solid-liquid interface during adsorption [29-32]. The degree of the spontaneity of the adsorption process is determined by the Gibbs free energy [33].

The negative values of $\Delta G°$ for the sorption of CV onto DWM biomass are attributed to the spontaneous nature of sorption and it means that the adsorption process is thermodynamically favoured with strong interaction of the dye molecules onto the biosorbent surface.

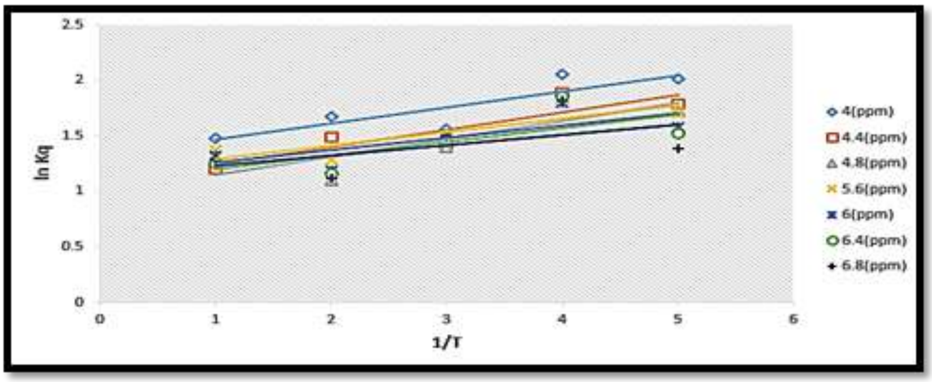

Figure 15- Plot of 1/T vs. lnkq for the adsorption of CV onto DWM biosorbent

Table 3- Thermodynamic parameters of CV adsorption onto the DWM biosorbent at 6mg/L

-ΔH⁰(J/mol)	**ΔS⁰(J/K/MOL)**	**-ΔG⁰(J/mol)**				
931.16	9.5162	**306K**	**312K**	**318K**	**328K**	**338K**
		3372.69	3097.19	3963.93	4911.58	4445.35
		K_{eq}				
		3.7649	3.3003	4.4785	6.0565	4.8641

Conclusion:

DWM seeds were tested and evaluated as a possible biosorbent for removal of CV from its aqueous solution, the removal efficiency approaches 90%. The temperature has a strong influence on the adsorption process and the maximum removal was observed at 338K. experimental equilibrium data provide the best fit with freundlich isotherm with R^2=0.96, which signifies that a heterogeneous adsorption takes place between the dye and the surface pf DWM seeds. The nature of adsorption was physical adsorption as inferred from the Dubinin-Radushkevich isotherm model. The thermodynamic study indicated that this adsorption is spontaneous and exothermic as evidenced by negative values of the changer in Gibbs free energy ΔG^0 and enthalpy ΔH^0. The pseudo-second order equation best describes the kinetics of adsorption system due do it, higher R^2values than that of the pseudo first-order.

References

1. Carmen, Z. and Daniela, S. Textile Organic Dyes: Characteristics, Polluting Effects and Separation/Elimination Procedures from Industrial Effluents: A Critical Overview. In Puzyn, T. andMostrag-Szlichtyng, A. (Eds) *Organic Pollutants Ten Years After the Stockholm Convention: Environmental and Analytical Update*. InTech, Croatia. 2012. P.55

2. Michael T. and David B. An Introduction to Wastewater Treatment, 2011. P. 8-9, ISBN 978-87-7681-843-2
3. Gupta, V.K., Mittal, A., Malviya, A. and Mittal, J. Adsorption of Carmoisine A from Wastewater using Waste Materials—Bottom Ash and Deoiled Soya. Journal of Colloid and Interface Science, 2009. 335, 2433,
4. Derbyshire, F., Jagtoyen, M., Andrews, R., Rao, A., Martin-Gullon, I. and Grulke, E. Carbon Materials in Environmental Applications. In: Radovic, L.R. Ed., Chemistry and Physics of Carbon. Marcel Dekker, New York, 2003.27, 1–66,
5. Ho, Y.S. and McKay, G..Sorption of Dyes and Copper Ions onto Biosorbents, Process Biochemistry, 2003. 38, 1047-1061.
6. Jain, A.K., Gupta, V.K., Bhatnagar, A. and Suhas,. Utilization of industrial waste products as adsorbents for the removal of dyes, Journal of Hazardous Materials, 2003, B101, 31-42.
7. Padmesh, T.V.N., Vijayaraghavan, K., Sekaran, G. and Velan, M..Biosorption of Acid Blue 15 using Fresh Water Macroalga Azolla Filiculoides: Batch and Column Studies, Dyes and Pigments, 2006, 71, 77-82,
8. Adak, A.; Bandyopadhyay, M.; Pal, A. Sep. Purif. Technol. 2005, 44, 139.
9. Ayed, L.; Chaieb, K.; Cheref, A. World J. Microbiol. Biotechnol. 2009, 25, 705.
10. Senthilkumaar, S.; Kalaamani, P.; Subburaam, C. V. J. Hazard. Mater. 2006, 136, 800.
11. Mittal, A.; Mittal, J.; Malviya, A.; Kaur, D.; Gupta, V. K. J. Colloid Interface Sci. 2010, 343, 463.
12. Varga, I., Szebeni, Norbert and Kovács. Determination of trace elements in human liver biopsy samples by ICP–MS and TXRF: hepatic steatosis and nickel accumulation. Analytical and bioanalytical chemistry, 2005. 383(3): p. 476-482.
13. Alam,M. Nadem R. and Jilani,M. I. Pb (II) removal from waste water using pomegranate waste biomass. International Journal of chemical and Biochemical sciences, 2012. 1, pp: 24-29.
14. Srivatava,V. C. . Mall I. D and I. Mishra,M. Equilibrium modeling of single and binary adsorption of cadmium and nickel on to baggase fly ash. *Journal of Chemical Engineering,* 2006. 117, pp: 79-91.
15. Al Khafaji, I. H. and Y. K. Al-Bayati "Synthesis of New Selective Electrodes for the Determination of Metronidazole Benzoate (MNZB) Based on a Molecularly Imprinted Polymer Combined With Poly Vinyl Chloride." 2017.Vol.10 No.3, pp 552-561.
16. Porkodi K, Vasanth Kumar K. Equilibrium, kinetics and mechanism modeling and simulation of basic and acid dyes sorption onto jute fiber carbon: Eosin yellow, malachite green and crystal violet single component systems. J Hazard Mater. 2007. 143:311–27.
17. Ho, Y.S., Chiang, T.H. and Hsueh, Y.M. Removal of basic dye from aqueous solutions using tree fern as a biosorbent. *Process Biochem*. 2005. 40, 119 124.
18. Weber, W. J. JrIn: Weber W.J. Jr (ed). Physicochemical processes for water quality control, New York: Wiley- Interscience.1972.
19. Ho, Y. S.; McKay, G. *Can. J. Chem. Eng.* 1998, *76*, 822.
20. Zou, W.; Zhao, L.; Han, R. *J. Radioanal. Nucl. Chem.* 2011, *288*, 239.
21. Mall, I. D.; Srivastava, V. C.; Agarwal, N.; K.; Mishra, I. M. *Chemosphere* 2005, *61*, 492.
22. Dubinin, M. M.; Radushkevich, L. V. *Proc. Acad. Sci. USSR Phys. Chem. Sect*. 1947, *55*, 331.
23. Jayaraj,R. Thanaraj, P. J. Natarajan S. T. and Prasath,P. M. D. Removal of congo red dye from aqueous solution using acid activated ecofriendly low-cost carbon prepared from marine alagaevoloriabryopsis. Journal of Chemical and Pharmaceutical Research,2011. 3 (3), pp:389-396.
24. Yuh-Shan H.,. Comment on An evaluation of copper biosorption by a brown seaweed under optimized condition's by Antunes, W.M., Luna A. S., Henriques C. A., and da Costa A. C., Electronic Journal of Biotechnology. 2004.
25. Ho YS, McKay G., Pseudo-second order model for sorption processes, 34, Process Biochem, 1999, Volume 34, P 451.
26. Michael T. and David B., An Introduction to Wastewater Treatment, 2011. P. 8-9, ISBN 978-87-7681-843-2
27. Puthiya V. N., Rajan G. Kinetic analysis of crystal violet adsorption on to bottom ash, 36, Turkish J. Eng. Env. Sci, 2012. p- 249 – 262.
28. Chosh, D. and Bhattacharyya,K. G.. Adsorption of methylene blue on kaolinite .*Applied Clay Science*, 200220, pp: 295-300.

29. A. A.Asem, D. M. Ahmed, Y. M. Ahmed. Removal of some hazardous heavy metals from aqueous solution using magnetic chelating resin with iminodiacetate functionality, Separation and Purification Technology, 2008. 61, 348–357,
30. A. M. Sevim, R. Hojiyev, A. Gül, M. S. Celik. An investigation of the kinetics and thermodynamics of the adsorption of a cationic cobalt porphyrazine onto sepiolite, Dyes and Pigments, 2010. xxx 1-14.
31. L. Wang, J. Zhang, R. Zhao, C. Li, Y. Li, C. Zhang. Adsorption of basic dyes on activated carbon prepared from Polygonumorientale Linn: Equilibrium, kinetic and thermodynamic studies, Desalination, 2010.254, 68–74.
32. S. Chegrouche, A. Mellah, M. Barkat. Removal of strontium from aqueous solutions by adsorption onto activated carbon: kinetic and thermodynamic studies, Desalination, 2009235, 306–318.
33. Bouklah, M. Itammouti,B. Thermodynamic characterization of steel corrosion for the corrosion inhibition of steel in sulphuric acid solutions by Artemisia. Portugaliae Electrochemical Acta, 2006.24, pp: 457-468.

*****