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Adsorption Studies of Crystal Violet from Aqueous Solution onto Pterocarpus Marsupium Spent

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Abstract: The feasibility of using nutraceutical industrial Pterocarpus Marsupium spent (PMS) as a cheap biosorbent to adsorb Crystal violet (CV), a cationic dye, from aqueous solution. The influence of initial dye concentration, pH, temperature, adsorbent dosage and particle size on dye adsorption was studied. The experimental equilibrium data obtained were analyzed by isotherm models of Langmuir, Freundlich. The pseudo-first order, pseudo-second order, models were applied for adsorption kinetic studies. The experimental value of the adsorption capacity, q_e was 60 mg/g. The kinetic data fitted well to a pseudo-second order model. The thermodynamic parameter values like ΔG^o, ΔH^o and ΔS^o proved that the process of adsorption was exothermic. The FTIR spectra and images of SEM proved the CV being adsorbed onto PMS. Possible interaction that occurred in the CV-PMS system is discussed. PMS is an effective adsorbent to remove CV dye from aqueous solution.

Keywords: Pterocarpus Marsupium Spent; Adsorption, Isotherms, Kinetics

I. INTRODUCTION

Dyes are an important class of synthetic organic compounds used extensively in textile industries. Textile industries are facing a challenge in the field of quality and productivity due to the globalization of the world market. The large-scale production and extensive application of synthetic dyes is causing environmental pollution leading to a serious public concern. Large amounts of dyeing wastewater containing a sizeable amount of residual dye [1] have led to the rigid legislation on the limits of color discharge. The presence of small amount of dyes is highly visible and undesirable. Thus, the necessity for dye-containing water to undergo treatment before disposal into the environment is highly imperative [2, 3]. Conventional waste water treatment methods for removing dyes include physicochemical, chemical and biological methods, such as coagulation and flocculation, ozonation, electrochemical techniques, fungal decolorization and others techniques [4,5]. But these processes are not always effective and economic where the solute concentrations are very low. Besides, most of the dyes undergo very slow biodegradation. Actually, the adsorption technique has been proven to be an effective and attractive process for the treatment of dye-containing waste water [6]. In recent years, biosorption has been strongly recommended as an economically viable sustainable technology for the treatment of waste water streams [7]. The importance and usefulness of biosorption in wastewater treatment is well established [8]. Biosorption is now in the focus owing to its low initial cost, simplicity of design, ease of operation, insensitivity to toxic substances and complete removal of pollutants even from dilute solutions [9,10].

Pterocarpus marsupiumRoxb. (Fabaceae), commonly known as Bijasaland or Vijaysaris one of the valuable multipurpose forest trees belonging to a group called Rasayana in Ayurvedic system of medicine. These Rasayana drugs are immunomodulators and relieve stress in the body. The wood is used as an ointment to astringent, bitter, acrid, cooling, anti-inflammatory, union promoter, depurative, urinary astringent, haemostatic, asthelmintic, constipating, anodyne alterant and rejuvenation. It is also useful in elephantiasis, inflammations, fractures bruises, leprosy, skin disease, leucoderma, erysipelas urethrorrhoea, diabetes, rectalgia, rectitis, opthalmopathy, diarrhea, dysentery, cough, asthma, bronchitis and greyness of hair. The leaf paste is used as an ointment to treat skin diseases, sores and boils, while, the flower is used as appetizing and febrifuge and also taken to treat anorexia and fever. The gum-resin is useful in spasmodic gastralgia, boils, gleet, urethrorrhoea, odontalgia, diarrhea, psoriasis, wound and ulcers, helminthasis, fevers, hepatopathy and ophthalmia. Besides, it has some unique and unidentified features in protecting the pancreatic beta cells and their regeneration [11,12].

The bioactive compounds of Vijaysar like (−) epicatechin (a flavonoid), marsupin (benzofuranone), and pterosupin (adihydrochalcone) have been shown to decrease blood glucose level in diabetics comparable to the effect of metformin [13,14].This study is to investigate adsorption of crystal violet (CV) from aqueous solution using pterocarpus marsupium spent (PMS) as low cost biosorbent. The spent in the present context is the material left after extraction of the principle component(s). The process involves thermal, mechanical and chemical steps. The equilibrium sorption isotherm is fundamentally important in the design of sorption systems. Equilibrium studies give the capacity of the

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sorbent and describe the sorption isotherm by constants whose values express the surface properties and affinity of the sorbent. Equilibrium relationships between sorbent and sorbate are described by sorption isotherms, usually the ratio between the quantity sorbed and that remaining in the solution at a fixed temperature at equilibrium. [15, 7].

In order to understand the nature of the adsorption: at first we conducted an optimization of the parameters of adsorption such as pH effect, mass effect and the effect of initial concentrations of PMS, and on the other hand kinetics and equilibrium isotherms have been evaluated. Also, we characterized mint waste biomass samples before and after MB adsorption by FTIR.

II. MATERIALS AND METHOD

A. Materials

Crystal violet (CV),(tris(4-(dimethylamino)phenyl)methyliumchloride),a monovalent cationic basic dye with molecular formula C25H30N3Cl and molecular weight of 407.98, λ_{max}=590 nm, classified as C.I. 42555,wasprocured from Sigma Aldrich Private Limited, Mumbai, India. All chemicals used were of analytical-grade reagents. The adsorption experiments were carried out at room temperature (25±28 °C), 300, 400 and 500C. Figure 1 shows the molecular structure of CV.

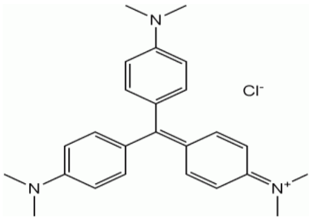

Fig. 1 Molecular structure of CV

B. Preparation of adsorbent

The PMS used in this study was procured from a local industry. It was dried in an oven at 60^0C for 24 h. The dried spent material was ground to fine powder and sieved through ASTM 80 mesh to obtain particle size of ≤ 177 µm, and stored in plastic bottles for further use. No other chemical or physical treatments were done prior to adsorption process.

C. Surface characterization

The surface morphology of PMS was visualized by a Scanning Electronic Microscope (Carl Zeiss Scanning Electron Microscope EvoLS15, Germany). The functional groups present in the adsorbent were identified by FTIR. Infrared spectra of the PMS before adsorption and after the CV-loaded samples adsorption were obtained using an ATR-FTIR spectrometer (Perkin Elmer Spectrum two).Point of zero charge (pHz) was determined to ascertain the surface charge of PMS.

D. Adsorption Experiment

Adsorption of CV from aqueous solution by PMS was investigated by batch method. The effects of various parameters affecting adsorption such as initial dye concentration, pH, temperature and adsorbent dosage were studied. Batch adsorption experiments were carried out by adding a fixed amount 50 mg of adsorbent into 250 mL Erlenmeyer flasks containing 50 mL of initial dye concentration (25-200mg/L). The flasks were agitated (Kemi Orbital Shaker, India) at 150 rpm at 28±30°Cfor 180 min, until equilibrium was reached. Later centrifuged the samples for 10 minutes. The supernatant liquid containing un-adsorbed dye solution was removed using micropipette and the absorbance of the colored solution was measured by a double beam UV/Vis spectrophotometer (Systronics 166) at 590 nm. The amount of CV adsorbed at equilibrium, qe (mg/g) was calculated using following equation 1.

$$q_e = (C_0 - C_e)\frac{V}{W} \ldots\ldots(1)$$

Where, C_0 and C_e are concentrations (mg/L) of CV at initial and at equilibrium respectively, V is solution volume (L) and W is adsorbent weight (g). For kinetic studies, the same procedure was followed, but the aqueous samples monitored at pre-set time intervals. The concentrations of CV were similarly measured. The amount of CV adsorbed at any time, qt (mg/g), was calculated using equation 2.

$$q_t = (C_0 - C_t)\frac{V}{W} \ldots\ldots(2)$$

Where C_t (mg/L) is the concentration of CV measured at time t, initial concentrations of 25, 50 and 100 mg/L of the dye and adsorption time of 15 min (2 min intervals) were used. For determining optimum amount of adsorbent per unit mass of adsorbate, 50 mL of dye solution with PMS (50mg) till equilibrium was attained. To find out the influence of pH on dye adsorption, 50mg of PMS along with 50mL of dye solution of concentration 100mg/L were agitated using orbital shaker. The experiment was done with pH values of 2-12. The pH was adjusted with 0.1N dil HCl and/or 0.1N NaOH solution. Solution pH was determined by pH meter (Systronics 802, India). Agitation was continued for 180 min and at 140-150 min equilibrium was reached with constant agitation speed of 150 rpm. Agitation speed of 150rpm for 180min was fixed for all studies. At equilibrium, the dye concentration was measured using double beam UV/Vis spectrophotometer at 590nm. The extent of removal of dye was determined by following equation 3.

$$\text{Dye removal efficiency }\% = \frac{(C_0 - C_e)}{C_o} \times 100 \ldots\ldots(3)$$

Modeling studies

A. Adsorption isotherms

Adsorption isotherm models provide information about interaction mechanisms, surface properties and affinities of adsorbent. The most accepted models for single solute system with two parameters are Langmuir and Freundlich [16].The models were used to test the equilibrium adsorption at ambient temperature.

The non-linear forms of isotherm models studied are shown below.

$$\text{langmuir isotherm} \ : {}^{1}/_{x/m} = {}^{1}/_{\theta^{\circ}bc} + {}^{1}/_{\theta^{\circ}} \ \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

$$\text{Freundlich isotherm} : \log {}^{x}/_{m} = {}^{1}/_{n} \ \log C + \log kf \ldots\ldots\ldots\ldots(5)$$

Where, qe is the amount of dye at equilibrium in unit mass of adsorbent (mg/g), Ce is concentration of dye solution at equilibrium (mg/L), θ◦ and b are the Langmuir coefficient related to adsorption capacity (mg/g) and adsorption energy (L/mg), respectively. K_f and n are the Freundlich coefficient related to adsorption capacity [(mg/g) / (mg/L) 1/n] and adsorption intensity of adsorbent, respectively. In our present study on PMS with CV both Langmuir and Freundlich model fits to the data. Langmuir isotherm best fits to the experimental results and shows good correlation.

B. Adsorption kinetics

The controlling of the adsorption process was done by fitting experimental data with pseudo-first-order and pseudo-second-order. The models were fitted according to linear least – square method. The controlling mechanism of the adsorption process was found by fitting the experimental data with the respective kinetic equations.

C. Thermodynamic parameters

Energy and entropy enable to understand the feasibility of mechanism. In the present study, thermodynamic parameters, including standard free energy (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were estimated by using rate law and also kinetic data to find out the extent and enthalpy of the adsorption process.

III. RESULTS AND DISCUSSION

Surface Characterization

A. Scanning electron microscope

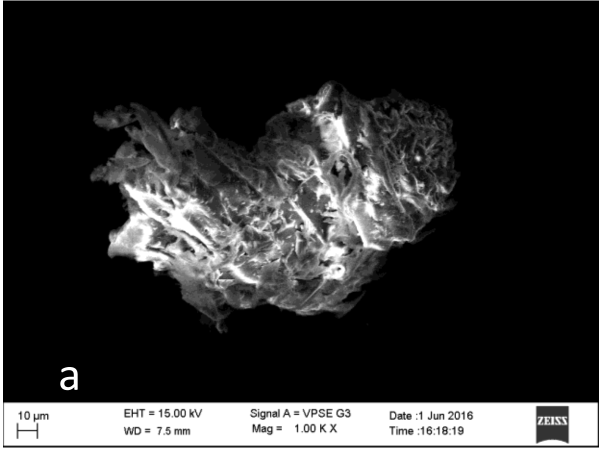

Fig. 2a SEM image of PMS before adsorption

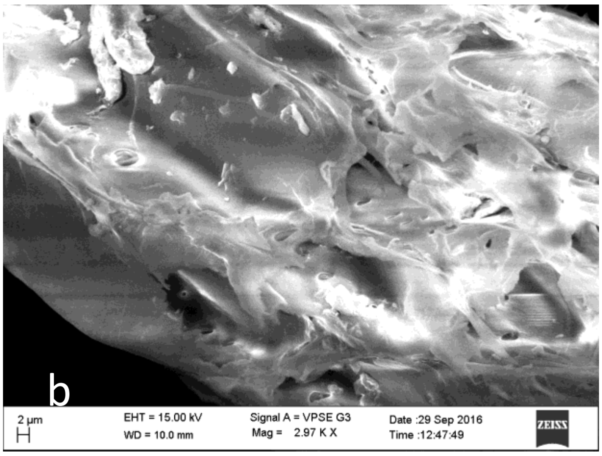

Fig. 2b SEM image of PMS with CV after adsorption

B. Point of zero charge

To determine pH_z, 0.1M KCl was prepared, and its initial pH was adjusted to 2.0 - 12.0 using 0.1N NaOH and/or 0.1N HCl. An amount of 50 mg of PMS was added to each 250 ml conical flask containing 50 ml of 0.1 M KCl with preset pH. After 24 h, the final solution pH was measured. Graphs were plotted between pH_{final} and $pH_{initial}$ [16] shown in Figure 3.

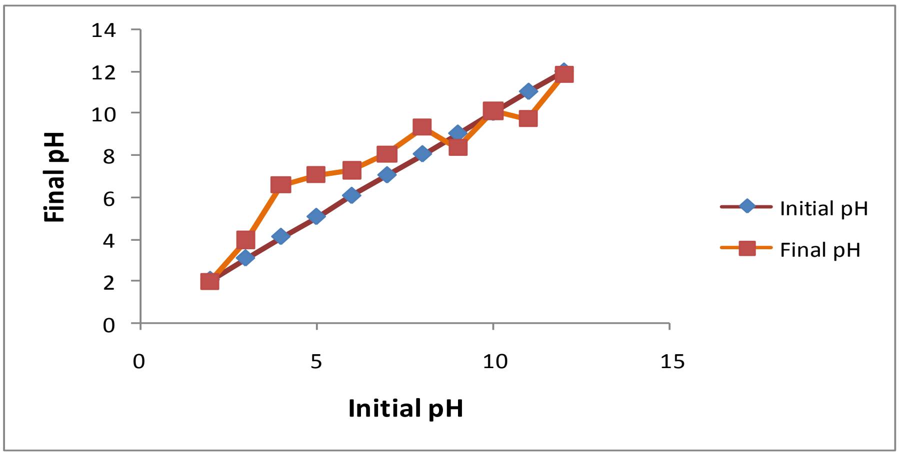

Fig. 3 Point of Zero charge of PMS

C. FTIR characterization of CV adsorbed on to PMS

The FTIR spectroscopy analyzes the interaction between PMS and CV shown in figure 4. The FTIR Spectra of PMS recorded shows the vibrational frequency of the functional groups in the adsorbent. The broad band lies 3354.98cm^{-1} is hydroxyl groups, bands at 2151.03 cm^{-1} are due to the stretching vibrations of C-H bonds in alkanes, 1594.95cm^{-1} is C=C stretching vibrations. The band at 1365.87 cm^{-1}and 1035.75 cm^{-1}indicates C-H bending vibrations of alkanes, 674-646 cm^{-1} is due to c=c bending vibrations of cis-alkene.

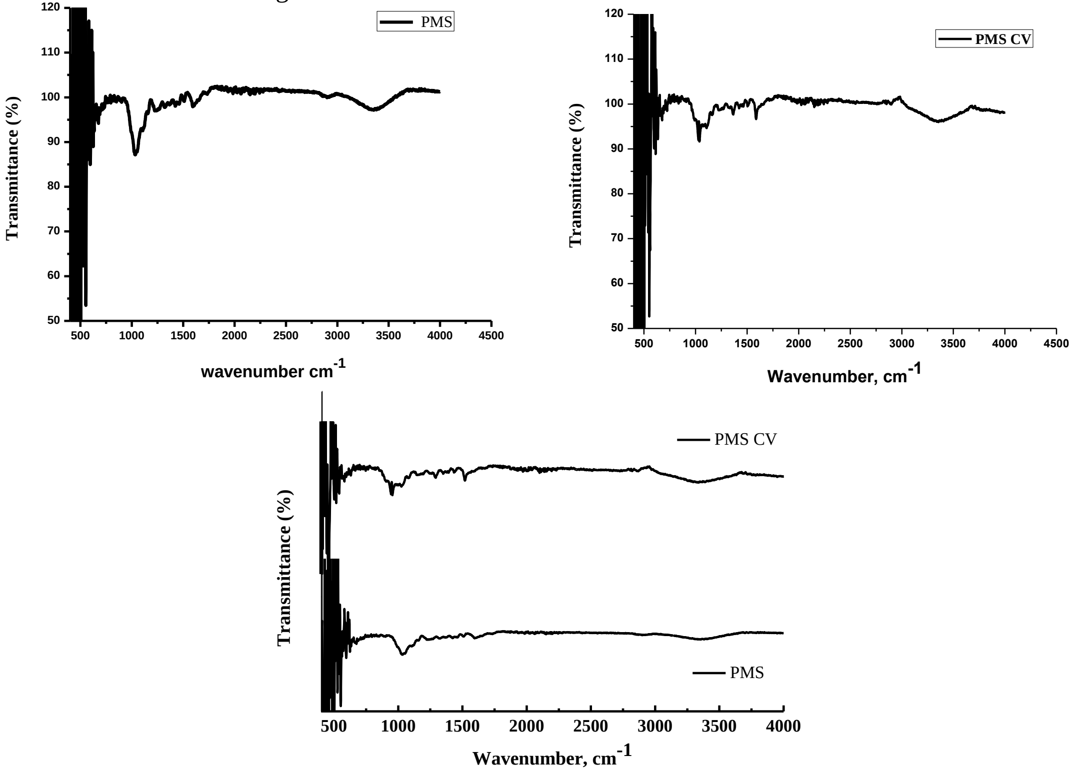

Fig. 4 FTIR spectra of PMS before adsorption and PMS - CV after adsorption

Adsorption of CV

A. Effect of initial dye concentration

As seen in Figure 5, the dye uptake increased from 22 to 82 mg/g of PMS with the increase in dye concentration from 25 to 200mg/L. This indicates that there is an increase on the driving force of the concentration gradient due to the increase in the initial dye concentration. Adsorption was rapid initially due to the dye getting adsorbed onto exterior surface. Later, the dye molecules, probably entered into pores (interior surface), which is relatively a slow process. The adsorption of CV was more with higher concentration and remained almost constant after equilibrium time.

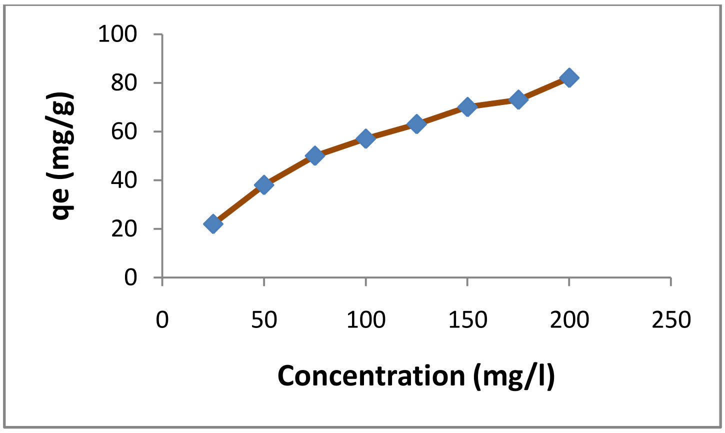

Fig. 5 Effect of initial dye concentration on adsorption of CV

B. Influence of adsorbent dosage

The influence of adsorption of the dye onto PMS increased with the enhancement in the adsorbent dosage from 0.010 to 0.100g. This may be due to the binding of almost all dye molecules on the adsorbent surface and establishing equilibrium of dye molecules and the adsorbent. Hence dye sorption increased with sorbent dosage and remained at equilibrium after certain sorbent dosage as shown in Figure 6.

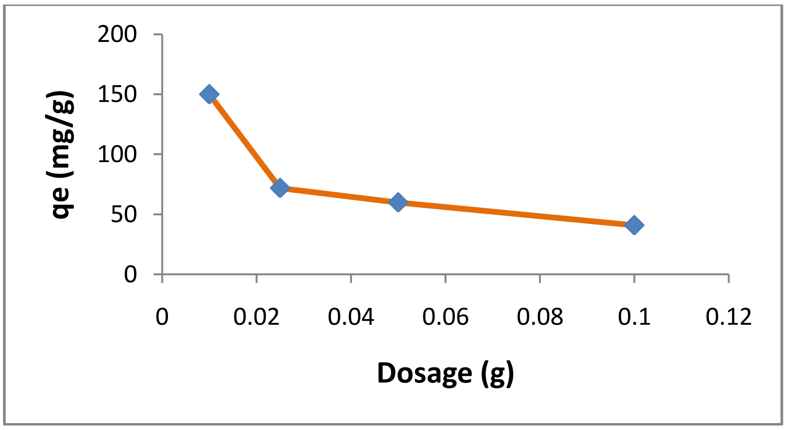

Fig. 6 Effect of adsorbent dosage on adsorption of CV

C. Effect of Temperature

Temperature is an influencing factor in the adsorption process and it was studied at 30°C, 40° C and 50°C and the results are shown in Figure 7. It can be observed that with the increase in temperature, the adsorption capacity increases marginally, which indicates that the process is exothermic in nature. The increase in adsorption with temperature is may be due to the increase in the mobility of the dye molecule with increase in their kinetic energy and the enhanced rate of intra-particle diffusion of adsorbate with the rise in temperature. The slight increase in removal of dye due to increasing temperature may be due to higher interaction between adsorbate and adsorbent.

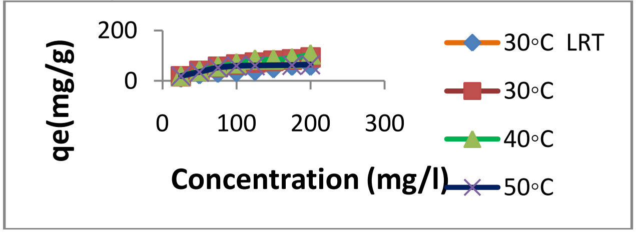

Fig. 7 Effect of Temperature on adsorption of CV

D. Effect of pH

The pH is one of the most important parameters in the adsorption process. It controls the adsorption capacity by influencing adsorbent surface properties and ionic forms of dye. The adsorption capacity of PMS slightly increased with increase in solution pH and maximum adsorption capacity of CV was under acidic condition. In acidic pH an excess of H^+ ions compete with cations of the dye for adsorption sites. When the surface charge density gets lowered with increased solution pH, the repulsion between the positively charged dye and the surface of the adsorbent gets lowered. This results in increased adsorption as depicted in Figure 8.

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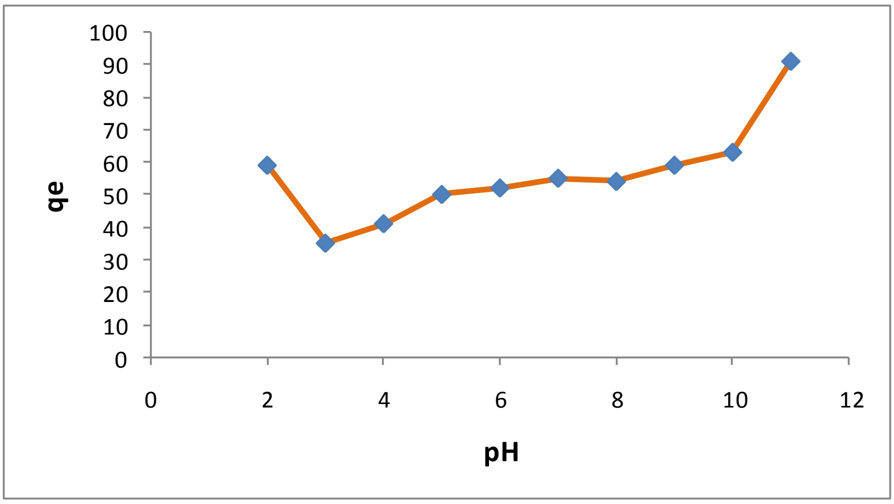

Fig. 8 Effect of pH on adsorption at 100mg/L concentration of CV

E. Adsorption isotherms

The Langmuir adsorption isotherm exhibits monolayer phenomena of adsorption on CV-PMS system. Langmuir constants θ◦ and b related as adsorption capacity and adsorption energy. Langmuir parameters are listed in Table 1. The experimental data shows a straight line to the model CV-PMS adsorption indicates a good correlation coefficient (R2) indicating best applicability of Langmuir adsorption isotherms.

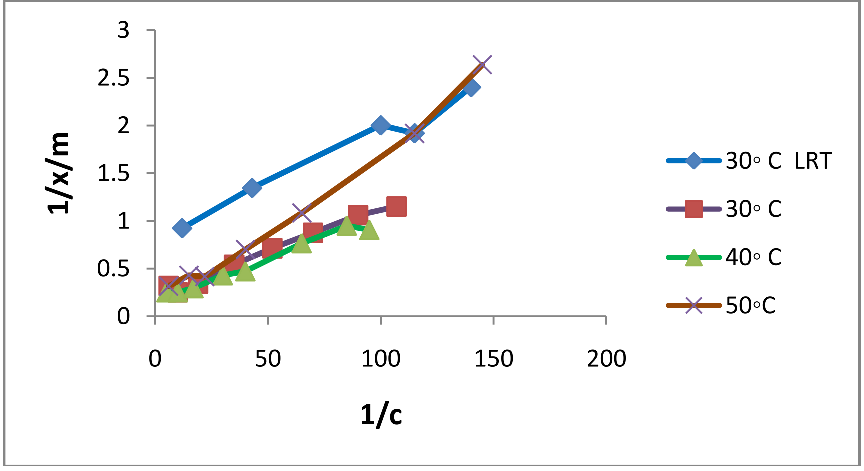

Fig. 9 Langmuir adsorption Isotherm for CV adsorption on PMS

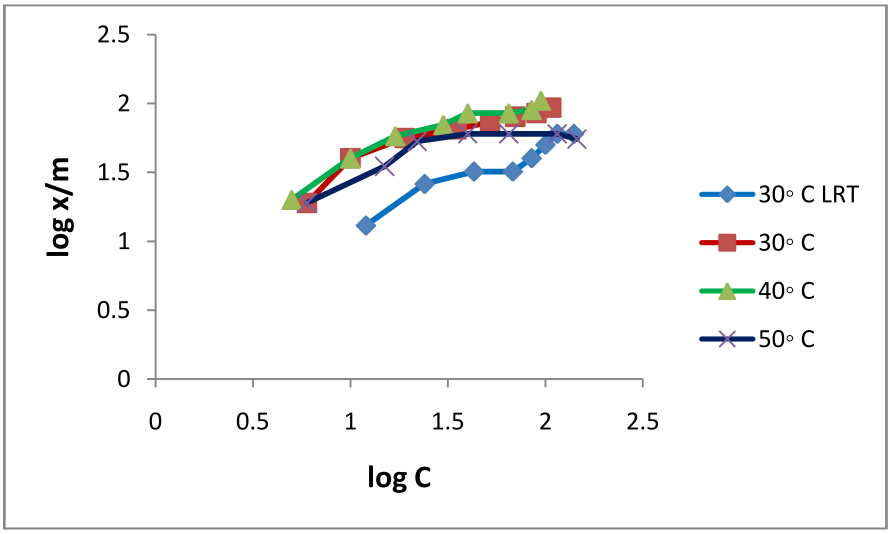

Fig. 10 Freundlich adsorption Isotherm for CV adsorption on PMS

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Table 1. Langmuir & Freundlich Isotherm constants for CV adsorption on to Pterocarpus Marsupium spent

	Langmuir constants			Freundlich constants		
Temp (◦C)	θ◦(mg/g)	b(l/mg)	R2	Kf(mg/g) (mg/l)1/n	n	R2
Room Temp	0.8953	0.010	0.9368	0.6856	0.4993	0.8582
30	0.1825	0.009	0.9907	1.2946	0.3311	0.9822
40	0.1608	0.008	0.9756	1.2761	0.3727	0.9273
50	0.0570	0.017	0.9893	1.4545	0.1590	0.4685

F. Adsorption kinetics

The rate constants for the adsorption of CV on PMS were obtained using the pseudo-first order and pseudo-second order kinetic models.

G. Pseudo-first order kinetic model

When the adsorption is preceded by diffusion through a boundary, the kinetics in most cases follows the pseudo-first order rate equation. The differential rate equation is as follows

$$dqt/dt = k1\ (qe - q\ t) \qquad (6)$$

Where, qt and qe are the amounts of dye adsorbed at time t (mg/g) and at equilibrium (mg/g), respectively and k1 is the pseudo-first order rate constant (min−1). Integration of the above equation expressed as equation 7 [17,18,19,].

$$\log\ (qe - q\ t) = \log qe - (k1/2.303)\ t \qquad (7)$$

The values of k1 and qe were calculated from the slopes and intercepts of the linear plots of log (qe − q t) verses t. Therefore, it was concluded that the adsorption of CV onto PMS is not followed the pseudo-first order kinetic model.

H. Pseudo-second order kinetic model

The pseudo-second order kinetic model [20,16] is presented in equation 8:

$$t/qt = 1/k2\ qe2 + t/\ qe \qquad (8)$$

Where, qt and qe are the amount of dye adsorbed at time t (mg/g) and at equilibrium (mg/g), respectively and k2 is the pseudo-second order rate constant (g/mg min).The values of k2 and qe were calculated from intercepts and slopes of the linear plots of t/qt vs. t respectively and presented in Table 2. Table 2 shows that the calculated qe values are very close to that of experimentally obtained qe and the values of correlation coefficients (R2) are closer to unity confirms that adsorption of CV onto PMS follows pseudo-second order kinetics.

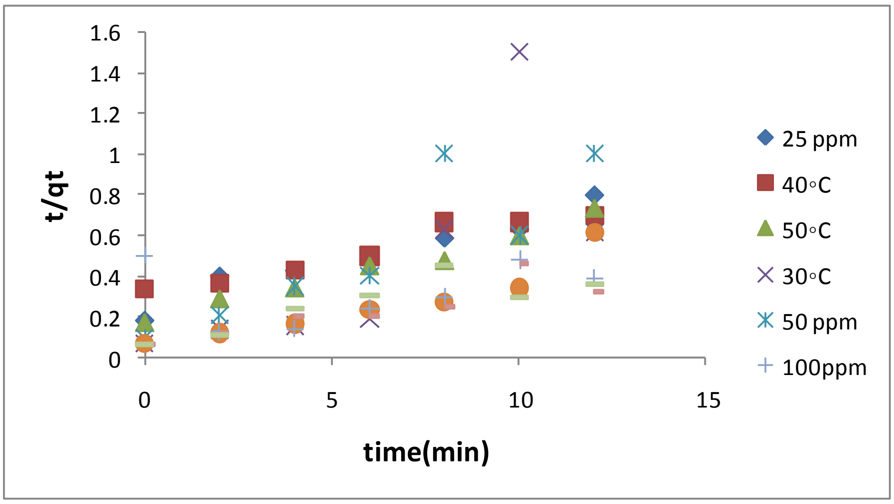

Fig. 11 Pseudo-Second order kinetic model of PMS on CV

Table 2. Pseudo second order kinetic constants for CV adsorption on to PMS

concentration (mg/L)	Temp (◦C)	qe (exp) (mg/g)	k2 (g/mg min)	qe (cal) (mg/g)	R^2
25	30	13.0	0.0385	0.2109	0.9449
	40		0.0368	0.2240	0.9195
	50		0.0437	0.0877	0.9661
50	30	31.0	0.0980	- 0.3483	0.4890
	40		0.0755	- 0.0860	0.6979

	50		0.0427	- 0.0941	0.8462
100	30	40.0	0.0342	- 0.0298	0.8429
	40		0.8100	0.0338	0.9069
	50		0.0221	0.0965	0.5249

I. Effect of Adsorption thermodynamics

The Activation energy (Ea) for the reaction using Arrhenius equations by the method of least squares [21,22] a relationship between the rate constant k and temperature T,

$$\mathrm{k} = \mathrm{A.e}^{-\mathrm{Ea}}/_{\mathrm{RT}} \ldots \ldots . \ldots \ldots \ldots \ldots \ldots \;..(9)$$

It follows in form as:

$$\log \mathrm{k} = -\frac{\mathrm{Ea}}{2.303\,\mathrm{RT}} + \log \mathrm{A} \ldots \quad \ldots \ldots \ldots \ldots .(10)$$

$$\mathrm{K_c} = \frac{\mathrm{C_{ac}}}{\mathrm{C_e}} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (11)$$

$$\Delta\mathrm{G}^\circ = -\mathrm{RT} \ln \mathrm{K_c} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (12)$$

$$\ln \mathrm{K_c} = {}^{\Delta\mathrm{S}^\circ}/_{\mathrm{R}} - {}^{\Delta\mathrm{H}^\circ}/_{\mathrm{RT}} \ldots \ldots \ldots \ldots \ldots ..(13)$$

Where, Kc is the thermodynamic equilibrium constant, Cac and Ce are the initial and equilibrium concentration(mg/L) of dye in solution, ΔH°, ΔG° and ΔS° can be determined from the slope and the intercept of the linear plot of lnKc vs. 1/T [16].

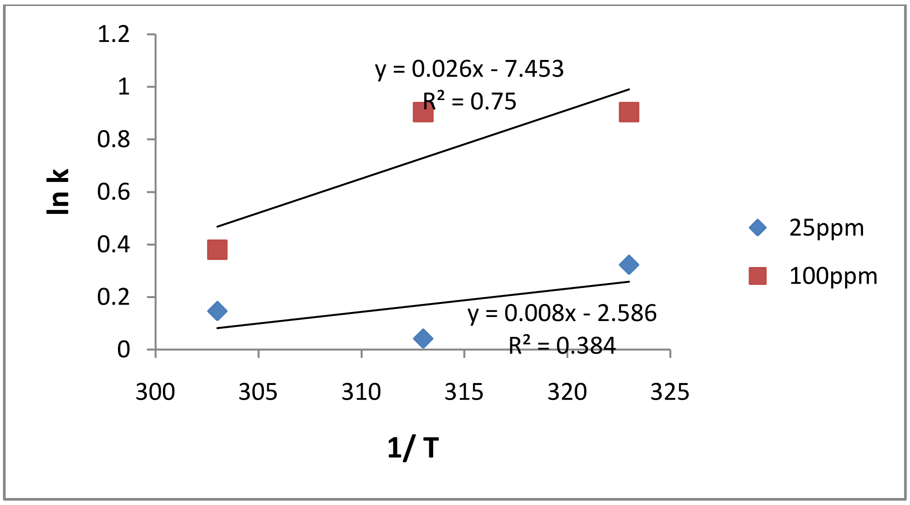

Fig. 12: plot of Van’t Hoff equation for adsorption Crystal violet on PMS

Table 3. Thermodynamic parameters for CV adsorption onto PMS Spent

concentration (mg/L)	Temperature(K)	ΔH◦ (KJ /mol)	ΔS ◦(KJ/mol K)	ΔG (KJ/mol)
25	303 K	-219.76	-245.31	310.07
	313 K	-228.19	-247.60	323.29
	323 K	-236.47	-242.50	326.72
100	303 K	-139.76	-235.86	298.44
	313 K	-148.08	-230.03	300.62
	323 K	-156.39	-230.34	310.62

The Gibbs free energy, entropy and enthalpy changes of adsorption were calculated by Van’t Hoff and Gibbs-Helmholtz equations. As seen in Table-3,the negative ΔH° value suggests the exothermic nature of adsorption while the low magnitude and very similar values of enthalpy irrespective of changes in initial dye concentration also clearly indicate that the adsorption is physical i.e., involving weak interactions. The ΔG° is positive for all studied temperatures indicating that the adsorption of CV onto PMS follows a Non-spontaneous at higher temperatures. The decrease in ΔG° with increase in temperature indicates increase in adsorption at higher temperatures. The Negative value of ΔS° suggests good affinity of CV towards the adsorbent and increased randomness at the solid solution surface.

IV. CONCLUSIONS

The major conclusions of this study are:

- PMS has been developed as efficient, environmental-friendly and cost-effective biosorbent for the remediation of dye Crystal violet.
- Operational parameters such as; initial dye concentration, adsorbent dose, temperature and pH, influenced the adsorption efficiency of PMS.
- The experiments and analyses of the results for adsorption isotherms and kinetic studies confirmed the complexity involved in the dye adsorption mechanism.
- Thermodynamic study demonstrated the spontaneous and endothermic nature of biosorption process. It also confirmed that the adsorption is physical in nature.
- An alternative to burning of walnut shell generated abundantly would reduce carbon foot print has been explored.
- The authors envisage that the concept demonstrated will help overcoming resource depletion through utilization of agro-based spent which has neither feed or fertilizer value.
- PMS is appropriate ready-to-use matrix in field of adsorption science.

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REFERENCES

[1] A.K. Verma, R.R. Dash and P. Bhunia,"A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters," Journal of environmental management, 93(1),154-168,2012.

[2] E. Fernando, T. Keshavarz and G. Kyazze,"Simultaneous co-metabolic decolourisation of azo dye mixtures and bio-electricity generation under thermophillic (50 C) and saline conditions by an adapted anaerobic mixed culture in microbial fuel cells,"Bioresource technology, 127, 1-8, 2013.

[3] J.L. Wang and L.J. Xu,"Advanced oxidation processes for wastewater treatment: formation of hydroxyl radical and application," Critical Reviews in Environmental Science and Technology, 42(3), 251-325, 2012.

[4] S. Dawood and T.K. Sen,"Removal of anionic dye Congo red from aqueous solution by raw pine and acid-treated pine cone powder as adsorbent: equilibrium, thermodynamic, kinetics, mechanism and process design," Water research, 46(6), 1933-1946, 2012.

[5] S. Wang, Y.Y. Zhai, Q. Gao, W.J. Luo, H. Xia and C.G. Zhou,"Highly efficient removal of acid red 18 from aqueous solution by magnetically retrievable chitosan/carbon nanotube: batch study, isotherms, kinetics, and thermodynamics. Journal of Chemical & Engineering Data, 59(1), 39-51, 2013.

[6] F. Fu and Q. Wang,"Removal of heavy metal ions from wastewaters: a review. Journal of environmental management," 92(3), 407-418, 2011.

[7] T. Ainane, A. Abourriche, M. Kabbaj, M. Elkouali, A. Bennamara, M. Charrouf and M. Talbi,"Journal of Chemical and Pharmaceutical Research," 6(4), 599-606, 2014.

[8] M. Fomina and G.M. Gadd,"Biosorption: current perspectives on concept, definition and application," Bioresource technology, 160, 3-14, 2014.

[9] S. Chowdhury, and P.D. Saha,"Biosorption of methylene blue from aqueous solutions by a waste biomaterial: hen feathers," Applied water science, 2(3), 209-219, 2012.

[10] S. Wang, Y.Y. Zhai, Q. Gao, W.J. Luo, H. Xia and C.G. Zhou,"Highly efficient removal of acid red 18 from aqueous solution by magnetically retrievable chitosan/carbon nanotube: batch study, isotherms, kinetics, and thermodynamics," Journal of Chemical & Engineering Data, 59(1), 39-51, 2013.

[11] B.K. Chakravarthy, S. Gupta, S.S. Gambhir and K.D. Gode,"Pancreatic beta-cell regeneration in rats by (-)-epicatechin," The Lancet, 318(8249), 759-760, 1981.

[12] S.S. Subramanian,"Epicatechin as an anti-diabetic drug," Indian drugs, 18, 259-261, 1981.

[13] R.J. Marles and N.R. Farnsworth,"Antidiabetic plants and their active constituents," Phytomedicine, 2(2), 137-189, 1995.

[14] M. Manickam, M.Ramanathan, M.A. Farboodniay Jahromi, J.P.N. Chansouria and A.B. Ray,"Antihyperglycemic activity of phenolics from Pterocarpus marsupium," Journal of natural products, 60(6), 609-610, 1997.

[15] V.K. Gupta, A. Mittal, D. Jhare and J. Mittal,"Batch and bulk removal of hazardous colouring agent Rose Bengal by adsorption techniques using bottom ash as adsorbent," RSC advances, 2(22), 8381-8389, 2012.

[16] R. Ahmad and R. Kumar,"Adsorption studies of hazardous malachite green onto treated ginger waste," Journal of environmental management, 91(4), 1032-1038, 2010.

[17] N.K. Amin,"Removal of direct blue-106 dye from aqueous solution using new activated carbons developed from pomegranate peel: adsorption equilibrium and kinetics," Journal of hazardous materials, 165(1), 52-62, 2009.

[18] D. Suteu and D. Bilba,"Equilibrium and kinetic study of reactive dye Brilliant Red HE-3B adsorption by activated charcoal," Acta Chim. Slov, 52(1), 73-79, 2005.

[19] F. Mogaddasi, M.M. Heravi, M.R. Bozorgmehr, P. Ardalan and T. Ardalan,"Kinetic and thermodynamic study on the removal of methyl orange from aqueous solution by adsorption onto camel thorn plant," Asian Journal of Chemistry, 22(7), 5093,2010.

[20] Y.S. Ho and G. McKay,"Pseudo-second order model for sorption processes," Process biochemistry, 34(5), 451-465, 1999.

[21] P.S. Low, J.L. Bada and G.N. Somero,"Temperature adaptation of enzymes: roles of the free energy, the enthalpy, and the entropy of activation," Proceedings of the National Academy of Sciences, 70(2), 430-432, 1973.

[22] G. Feller and C. Gerday, "Psychrophilic enzymes: molecular basis of cold adaptation," Cellular and Molecular Life Sciences, 53(10), 830-841, 1997.