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Thermodynamic, Kinetic and Isotherm Studies for the Removal of Methyl Red Dye from Aqueous Solution by using *Vigna radiata* L. Pericarp - Activated Carbon

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ABSTRACT

Textile industries discharge wastewater containing various dyes including Methyl red dye. These dyes are very harmful for human health, animals and plants. Therefore, the attempt is made for studies of adsorption on removal of Methyl Red dye by using *Vigna radiata* L. pericarp - activated carbon carried out under various experimental methods and optimization conditions. Adsorption data presented to Freundlich, Langmuir and Tempkin adsorption isotherms. Thermodynamic parameters like as ΔG^o, ΔH^o and ΔS^o are calculated; it showed adsorption was spontaneous and endothermic process. Based on kinetic study, pseudo-second order kinetic more fit than the pseudo-first order kinetic. The adsorbent used to study and characterized by SEM study before and after adsorption of dye solution.

***Key words*:** Thermodynamic, Isotherm, Kinetic, Methyl Red dye, SEM

Owing to prompt progress of industries, an eclectic of wastes is created in diligences is eventually liquidated water resources, there by moving an excellence of aesthetic water [1-2]. It is a severe anxiety for emerging nations. Amongst various wastes created from the industries, particularly, dyes, colour substances are the utmost dischargeable contaminants [3]. The dyes are crucial for some reasons such as penetration, reducing light penetration, affecting drinking water quality, causing allergies and skin irritation, cancer, damaging central nervous system, genetic mutations etc. Hence, reducing and eliminating the dyes pollutants are significantly essential [4].

Nowadays, some methods have been proposed for dye removal purposes like as adsorption [5], Coagulation, flocculation, degradation and membrane process. Among these methods, adsorption has gained more attention, because simplicity of handling and cost-effectiveness [6-7]. Consequently, copious predecessors obligate remained charity with accomplishment grounding of activated carbons plus, Rice husk [8], Bagasse [9], Maize cob carbon [10], Magnetic Fe_3O_4 core-shell NPs [11], ZVI nanoparticles [12], Microgel based on nano-cellulose/poly vinyl amine [13], Malachite / clay nanocomposite [14], Polyaniline / carboxymethyl cellulose / Tio_2 nanocomposites [15], Modified mango seed [16], Cashew nutshells [17], Modified saw dust [18], Treated saw dust [19], Fly ash [20] and Tobacco stem ash [21]. Based on the above literature review, the carbonized *Vigna radiata* L. pericarp - activated carbon (VRPAC) is economical and low-cost material obtained from the local area and found to have great potential to adsorb Methyl Red Dye (MRD) from aqueous solutions; hence it was used in this study.

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MATERIALS AND METHODS

The Methyl Red dye (E-Merck) aqueous solution used as adsorbate and *Vigna radiata* L. pericarp - activated carbon used as adsorbent. Entirely the chemicals recycled for this learning are commercially obtainable Analar grade (E-Merck and SD-fine, India).

Activated carbon prepared from *Vigna radiata* L. pericarp and this raw material obtained from indigenous retailer. The material cleaned with boiling purified liquid eradicates down-to-earth matter, bowdlerized slight smithereens desiccated up. The activated carbon remained arranged commencing the overhead materials imbued Conc. H_2SO_4. For impregent, proportion of 0.5:1 of acid volume

and weight of the material hired. Afterwards, the overdone material washed numerous times in purified H_2O until the pH of washing befits impartial. Then the material was desiccated and carbonized at 350^0C using deaden kiln. Lastly, it was milled and sieved the obtained activated carbon used for further studies.

A standard aqueous solution of the adsorbate comprising 1000 *mg/L* of dye solution ready by liquefying known amount of Methyl Red Dye (MRD) in twice as purified H_2O. Doubly purified H_2O was used throughout experiments. The adsorption experiments were approved out batch equilibrium method. 100 *mg* adsorbent taken in iodine flask and added 100 *ml* of known concentration of MRD solution and mixture was frantic with diverse time interludes in temperature regulator water-bath shaker (Techno). The solutions centrifuged at consistent interludes and remaining concentration of MRD solution present in filtrate at each stage was determined using Spectrophotometer (Systronics 169 model) at 465 *nm*. The experiments were repeated at diverse temperatures viz., 303, 313 and 323 *K* for confiscation of MRD solution.

RESULTS AND DISCUSSION

Effect of adsorbent dosage, pH and agitation time

Experiments were through expending from 50 *mg* to 300 *mg* of adsorbents, 100 *ml* of 20 *mg/L* of Methyl Red dye solution and agitation of different time interludes. The grades indicated that optimal dose is fixed as 100 mg owing to the mass of dye uptake was added; optimal pH was fixed as 4 due to maximum exclusion of MRD solution. All experiments piloted at optimal agitation time of 70 *min* [22-23].

Effect of initial concentration and temperature

Equilibrium time was independent of initial MRD concentration (C_o). The results shown in (Table 1) revealed that, the amount of MRD adsorbed (q_e) increases with the proportion elimination decreases while increasing the initial concentration of MRD, owing to relatively higher dynamic force for mass transfer. At higher concentrations of colour solution, dye removal decreased, perhaps owed to condensed obtainability of lively sites on the seeming of VRPAC as such as mass transfer oppositions amongst aqueous solution and solid phase [24]. The percentage of MRD removal increases from 30°C to 50°C, the adsorption process considered as endothermic nature. It was shown that, fleeing propensity of MRD from solid phase to bulk phase, due to electrostatic contact between lively sites of adsorbent and adsorbate species.

Table 1 Equilibrium parameters and removal of MRD

Initial conc. of MRD (C_o), mg/L	Equilibrium Conc. of MRD (C_e), mg/L			Quantity of MRD adsorbed at equilibrium (q_e), mg/g			MRD removal (%) by VRPNS		
	30ºC	40ºC	50ºC	30ºC	40ºC	50ºC	30ºC	40ºC	50ºC
20	6.7568	4.8649	3.2432	13.2432	15.1351	16.7568	66.22	75.68	83.78
40	16.0811	11.7568	9.4595	23.9189	28.2432	30.5405	59.80	70.61	76.35
60	26.2162	20.8108	17.9730	33.7838	39.1892	42.0270	56.31	65.32	70.05
80	38.3784	32.4324	27.9730	41.6216	47.5676	52.0270	52.03	59.46	65.03
100	52.8378	47.8378	42.7027	47.1622	52.1622	57.2973	47.16	52.16	57.30

Adsorption isotherms

The adsorption statistics generally defined cum modelled by using isotherms of adsorption. It refers to quantity of dye adsorbed per unit weight of the adsorbent to equilibrium concentration of bulk phase. It specifies that the adsorbent pore size was nearly equivalent to molecule size of adsorbate.

Rearranged Langmuir model [25] and Freundlich equation [26] are studied. The principles of monolayer adsorption capacity (Q_o) decreases with temperature, signifying that adsorption is favoured lower temperature. It can be credited to the point that dyes prolix into adsorbent at slower rate with temperature increases. The adsorption energy (b_L) values recommend the affinities of binding sites with dyes are favourable. The values of adsorption ability (k_f) raised with temperature 30^oC to 50°C. It revealed that adsorption is favoured at high temperature. The adsorption intensity (n) prices slightly changes when temperature increases. The values of n for this system were found to be 2. The values of all n are > 1, indicating favourable adsorption [27].

Tempkin isotherm plot was chosen to estimate adsorption potential of adsorbent aimed at adsorbate. Due to adsorbate and adsorbent contacts, the warmth of adsorption of molecules in layer falls linearly with exposure. During, the MRD adsorption, shown that the minimum binding energy and minimum heat of adsorption based on values of equilibrium binding constant and heat of adsorption. The adsorption equilibrium data was offered in (Table 2, Fig 1-3).

Table 2. Results for adsorption isotherm models

Temp. (°C)	Langmuir Isotherm			Freundlich Isotherm			Tempkin Isotherm		
	Correlation coefficient	Constants		Correlation coefficient	Constants		Correlation coefficient	Constants	
	r^2	Q_o (mg/g)	b_L (L/mg)	r^2	k_f	n	r^2	b_T (kJ mol^{-1})	a_T (L/mg)
30	0.997	78.125	0.029	0.996	4.084	1.584	0.993	0.026	0.537
40	0.999	72.993	0.054	0.987	6.798	1.812	0.998	0.026	0.308
50	0.997	73.529	0.081	0.994	9.811	2.042	0.994	0.027	0.108

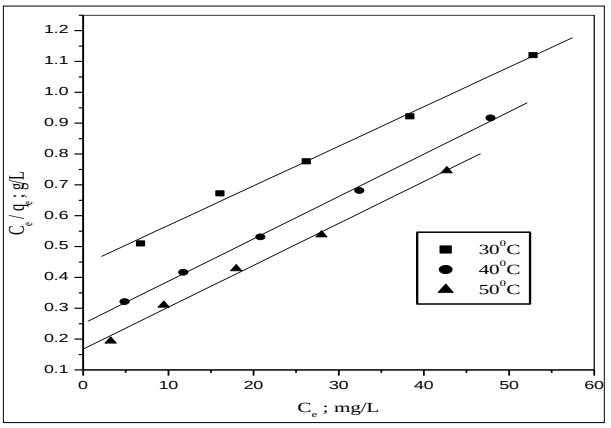

Fig 1 Langmuir isotherm for the adsorption of MRD on VRPAC

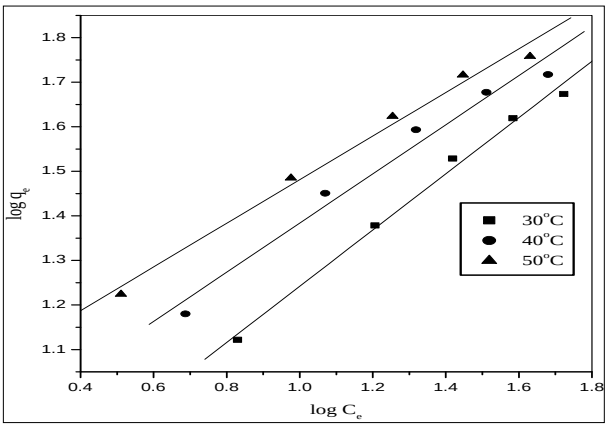

Fig 2 Freundlich isotherm for the adsorption of MRD on VRPAC

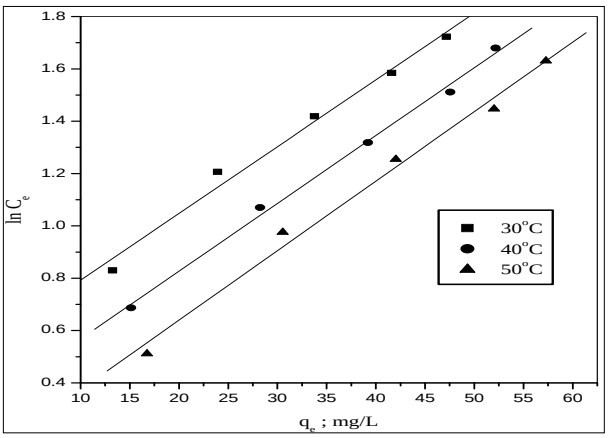

Fig 3 Tempkin isotherm for the adsorption of MRD on VRPAC

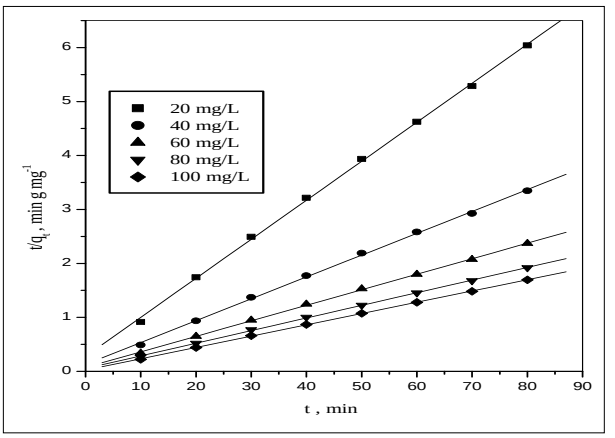

Fig 4 Pseudo-second order kinetic

Thermodynamic parameters

The equilibrium constants, ΔH°, ΔG° and ΔS° changes were shown in (Table 3). The temperature increases with rise in K_o, shown the endothermic nature of adsorption. The results showed the standard ΔG° values increase with increasing initial concentration of Methyl Red Dye (MRD). The standard ΔG° values negative, shows the adsorption is spontaneous. The ΔH° observed in the range 16 from 49 *kJ mol*$^{-1}$for adsorption of MRD on *Vigna radiata* L. pericarp - activated carbon (VRPAC).

Table 3 Thermodynamic parameters

C_o		K_o			ΔG°(kJ mol^{-1})		ΔH°	ΔS°
(mg/L)	30°C	40°C	50°C	30°C	40°C	50°C	(kJ mol^{-1})	(J K^{-1} mol^{-1})
20	1.96	3.11	5.17	-1.70	-2.95	-4.41	39.40	135.52
40	1.49	2.40	3.23	-1.00	-2.28	-3.15	31.59	107.75
60	1.29	1.88	2.34	-0.64	-1.65	-2.28	24.30	82.47
80	1.08	1.47	1.86	-0.20	-1.00	-1.67	21.96	73.25
100	0.89	1.09	1.34	0.29	-0.23	-0.79	16.57	53.71

The positive values of ΔH° suggested that adsorption process is endothermic nature. The ΔS° values adsorption process is positive, range from 54 to 136 *J* K^{-1} mol^{-1} adsorption of MRD from aqueous solution. This observation suggested that more degree of arbitrariness at solid-solution interface by adsorption of MRD on *Vigna radiata* L. pericarp - activated carbon (VRPAC).

Adsorption kinetics

Adsorption data are used to study the Lagergren pseudo-first order and pseudo- second order adsorption kinetic. Its outcomes offered in (Table 4, Fig 4).

Table 4 Adsorption kinetic models

C_o (mg/L)	q_e(exp) (mg/g)	Pseudo-first order kinetic model				Pseudo-second order kinetic model			
		q_e(cal) (mg/g)	k_1 (min^{-1})	r^2	P	q_e(cal) (mg/g)	k_2 (g mg^{-1} min^{-1})	r^2	P
20	13.243	3.951	0.042	0.988	70.16	13.831	0.019	0.999	4.25
40	23.919	4.857	0.032	0.994	79.69	24.691	0.013	0.999	3.13
60	33.784	7.171	0.042	0.965	78,77	34.843	0.011	0.999	3.04
80	41.622	8.279	0.046	0.964	80.11	42.735	0.011	0.999	2.61
100	47.162	4.787	0.042	0.953	89.84	47.847	0.018	0.999	1.43

The correlation coefficients (r^2) of pseudo-second order kinetic plots are recognized to be 0.999. Based on the values of correlation coefficients and less percentage of deviation, shown that the pseudo-second order kinetic fit better than the first order kinetic [28].

Fourier transform - Infrared spectroscopic (FT-IR) studies

FT-IR spectra of VRPAC are taken before and after adsorption of MRD. The VRPAC spectrum at 3424 cm^{-1} indicated the presence of –OH groups of activated carbon. The aromatic –CH stretching observed at 2922 cm^{-1}. A peak at 2851 cm^{-1} indicated the presence of –CO stretching group of aldehydes. The region at 1601 cm^{-1} indicated the N-H bending of primary amines and -C-C stretching of aromatic groups. The region at 1384 cm^{-1} indicated –CH stretching of alkanes group. The presence of these active groups are shown that that there is a good participation of adsorption of MRD on VRPAC.

Scanning electron microscope studies

The SEM photographs of VRPAC before and after adsorption are shown in the (Fig 5-6). It is visibly specified the existence of permeable structure of adsorbent and rough surface of the adsorbent which increases the surface area accessible for adsorption. After adsorption of MRD, SEM photograph evidently shown that the surface of VRPAC are covered by MRD. It has clearly indicated that adsorbent structure is altered upon the adsorption of MRD [29-30].

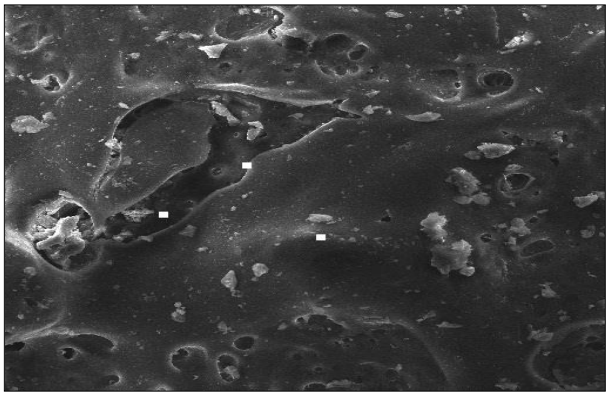

Fig 5 SEM study for before adsorption

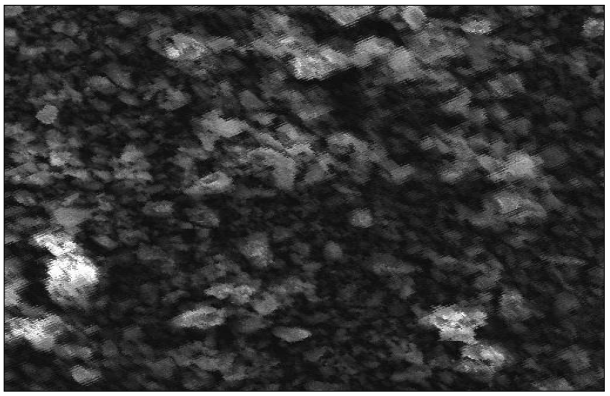

Fig 6 SEM study for after adsorption

CONCLUSION

Vigna radiata L. pericarp - activated carbon (VRPAC) is locally available, environmental friendly and low-cost material. This is a possible adsorbent for the confiscation of Methyl red dye from aqueous solution. The optimum pH of the solution is 4, adsorbent dosage is 100 *mg* and optimum contact time is 70 *min* used for confiscation of Methyl Red Dye (MRD). The Freundlich, Langmuir and Tempkin adsorption isotherm described the adsorption behaviour of MRD on *Vigna radiata* L. pericarp - activated carbon (VRPAC). The pseudo-second order kinetic more suitable than the pseudo-first order kinetic. The percentage of removal of MRD raised with enhances the temperature from 30 to 50°C. The adsorption of MRD is characterized with SEM studies.

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