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Adsorption Characteristics of Activated Palmyra Male Inflorescence for the Reclamation of Coloured Effluents Containing Malachite Green Oxalate

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Abstract : *Adsorption characteristics of activated palmyra male inflorescence for the removal of malachite green oxalate, basic dye from aqueous solutions, have been Investigated. The effect of temperature, and pH on the removal of Malachite green oxalate was investigated. The study of the thermodynamic properties revealed the process of removal of dye is exothermic and spontaneous.*

Keywords: *Adsorption, Chemically Activated, Malachite Green Oxalate, Palmyra, Thermodynamic study*

1. Introduction

In recent years various adsorbents were developed for the treatment of water and coloured wastewater treatment through adsorption. Commercially activated carbon proven to be very successful as an effective adsorbent for the adsorption process. However, the commercial activated carbon is costly and there is a need for alternate low cost adsorbents materials for the adsorption purpose. The development of naturally available low-cost adsorbents for the waste coloured streams treatment is essential especially for the developing countries like India [1,2]. Palmyra male inflorescence is one of such material which is abundantly available in coastal region and capable of removing contaminants from waste water streams. However, there are very few studies that explore the usability of Palmyra male inflorescence as an adsorbent in the literature [1]. In this work, the adsorption characteristics of activated Palmyra male inflorescence for the reclamation of coloured effluents containing malachite green oxalate have been invested through adsorption isotherm studies.

2. Experimental Procedure

2.1 Materials

The Palmyra male inflorescences have been collected from vaduvakuppam village in Puducherry, India. They have been washed with distill water and dried in oven. The carbonization is carried in a muffle furnace under airtight condition at 750 ^{o}C for one hour. The three samples were prepared by activating with 0.1N solution of KOH, H_3PO_4 and $ZnCl_2$ respectively.

The malachite green oxalate (CAS No. 2437-29-8, mass fraction purity 0.988) was purchased from Loba Chemie, India and used without further purification. The dye solution was prepared by dissolving accurately weighed amounts of malachite green oxalate in distilled water. The concentration of dye in the sample solution was analyzed using spectrophotometer at 617 nm. The UV response curves and calibration graphs used for the experiments are shown in Fig.1 [4].

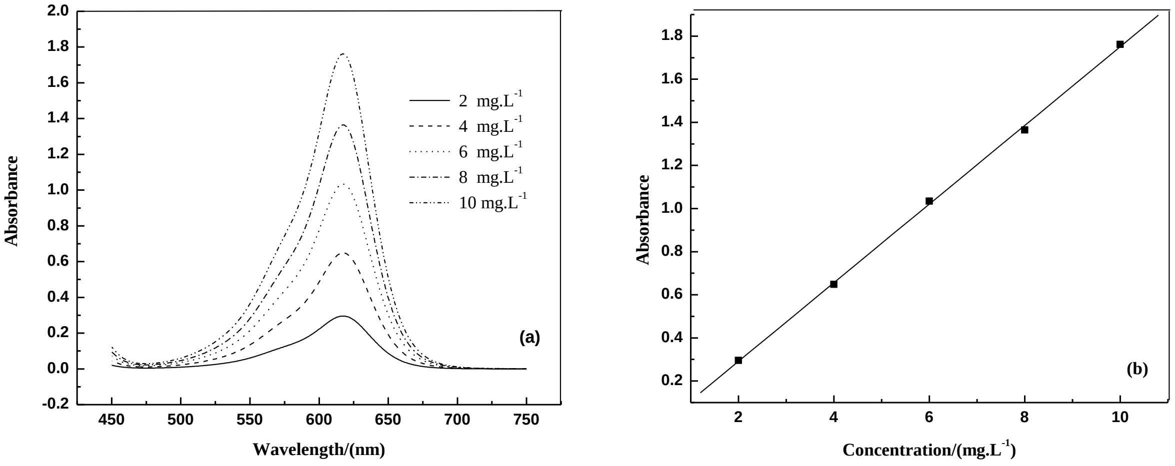

Fig. 1. (a) Absorbance vs. wavelength for malachite green oxalate. (b) Absorbance vs. concentration for malachite green oxalate.

2.2 Batch test

Adsorption studies were performed in 250 mL stoppered conical flasks by shaking a selected weight of Palmyra chemical activated carbon ranging from 0.1g to0.6 g mixed with 50ml of 500 ppm concentrated solution for three days in a temperature controlled water bath. The temperature was controlled at desired temperature with a precision ±0.1 K. After adsorption equilibrium has been achieved, the final concentration of solute in the solution at equilibrium me was measured. The experimental results for the batch adsorption of malachite green oxalate dye from aqueous solutions on different activated Palmyra samples at T = (303, 313 and 323) K and atmospheric pressure are reported in Table1.

2.3 Isotherm models

Freundlich correlated the quantity q to c as

$$q = K_F C^n \qquad (1)$$

where K and n are the model constants that can be estimated from experimental isotherm data. The adsorption isotherm is correlated by Langmuir has the following form as

$$q = \frac{q_m K_L C}{1 + K_L C} \qquad (2)$$

where q_m and K_L are the model constants.

The Redlich-Peterson(P-R) isotherm is given as

$$q = \frac{K_R C}{1 + a_R C^{\beta}} \tag{3}$$

where K_R , a_R and β are model constants.

The Temkin isotherm is given as

$$q = \frac{RT}{B}(K_T C) \tag{4}$$

where K_T and B are model constants.

The Toth isotherm is given as

$$q = \frac{q_{Th}\, C}{(\frac{1}{K_{Th}} + C^{Th})^{\frac{1}{Th}}} \tag{5}$$

where Th , K_{Th} and q_{Th} are model constants.

3. Thermodynamic treatment of adsorption data

The thermodynamic parameters namely Gibbs energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were calculated with the help of Langmuir model parameters. The equations used in calculating thermodynamic parameters are

$$\Delta G = RT \ln(K_L) \tag{6}$$

$$\Delta H = -R\left(\frac{T_1 T_2}{T_2 - T_1}\right)\ln\left(\frac{K_{L_2}}{K_{L_1}}\right) \tag{7}$$

$$\Delta S = \frac{\Delta G - \Delta H}{T} \tag{8}$$

where K_L, K_{L_1}, K_{L_2} are Langmuir parameters at T, T_1 and T_2 temperatures respectively.

4. Results and discussion

The FTIR results for the Palmyra male inflorescence carbon are presented in the Fig. 2. The effect of pH on adsorption was studied by varying the pH from 2 to 12. The effect of pH on various samples was represented in Figure3. The adsorption isotherms of malachite green oxalate from aqueous solution on Palmyra male inflorescence carbon are shown in Table 1. The adsorption capacity of palmyra carbon increases with temperature. The isotherms models discussed in section 2.3 were evaluated with the experimental results. The model parameters were reported in Table 2, 3 and 4. Figures 4, 5 and 6 represents the Langmuir fit. The values of ΔG, ΔH and ΔS of the adsorption process of the malachite green oxalate are shown in Table 3. The negative value of ΔG indicates that the adsorption process is spontaneous [4]. The decrease in the values of ΔG with increase in temperature indicates that the adsorption process is favoured at higher temperature. The ΔS change is related to randomness of the system. The positive values for entropy change ΔS indicate that the basic dye molecules more randomic condition [3,4] in the adsorbed state containing same molecules in solution. The negative values of ΔH indicate an exothermic process as it is common in several adsorption processes [4].

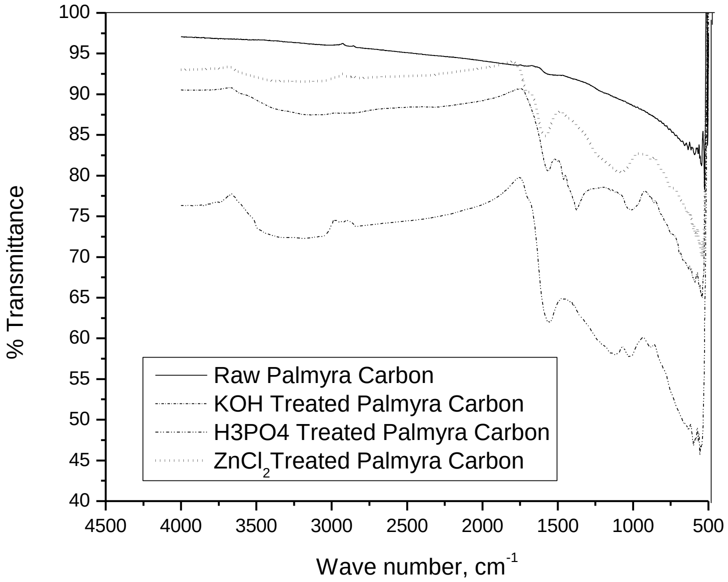

Fig. 2 FTIR spectroscopy of palmyra male influrorescence carbon

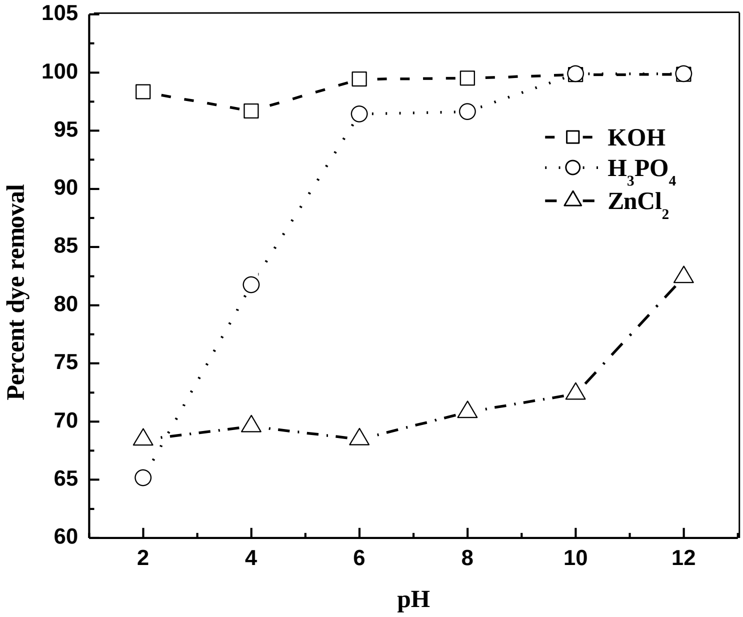

Fig. 3. Effect of pH on the removal of malachite green oxalate by Palmyra male inflorescence carbon at a dosage of 2 g and volume of 5×10-4 m3 at T = 303K

Table 1 Equilibrium isotherm data for malachite green oxalate- Palmyra male inflorescence activated carbon system

Activated chemical	T=303 K		T=313K		T=323K	
	C/mg/l	q/mg/g	C/mg/l	q/mg/g	C/mg/g	q /mg/g
KOH	98.0	201.0	87.22	206.39	77.63	211.19
	21.97	119.51	19.99	120.01	18.19	120.45
	6.62	82.23	5.03	82.45	3.82	82.7
	3.67	62.04	3.01	62.13	2.47	62.19
	2.18	49.78	1.7	49.83	1.4	49.86
	1.11	41.57	1.1	41.56	1.1	41.58
H_3PO_4	189.2	155.4	172.17	163.91	149.79	175.11
	85.0	103.75	77.35	105.66	67.29	108.18
	50.24	74.96	45.72	75.71	39.78	76.70
	35.25	58.09	32.08	58.49	27.91	59.01
	29.76	47.02	27.08	47.29	23.56	47.64
	25.4	39.55	23.11	39.74	20.11	39.99
$ZnCl_2$	368.0	66	364.32	67.84	362.5	68.75
	268.28	57.93	265.6	58.60	260.29	59.93
	204.23	49.3	198.10	50.32	192.16	51.31
	162.65	42.17	157.77	42.78	153.04	43.37
	135.22	36.48	131.16	36.88	127.23	37.28
	115.27	32.06	111.81	32.35	108.46	32.63

Table 2. Isotherm parameters for malachite green oxalate- KOH treated Palmyra carbon

Freundlich	$K_F\ (mg \cdot g^{-1})(mg \cdot L^{-1})^{-1/n}$		n	R^2
303 K	39.65		2.78	0.99
313 K	41.65		2.76	0.99
323 K	44.26		2.76	0.98
Langmuir	$K_L\ (L \cdot mg^{-1})$		$q_m\ (mg \cdot g^{-1})$	
303 K	0.103		217.39	0.99
313 K	0.118		222.22	0.98
323 K	0.135		226.24	0.98
Redlich Peterson	$K_R\ (L \cdot mg^{-1})$	β	a_R	
303 K	322.58	0.66	7.46	0.99
313 K	338.98	0.66	7.462	0.99
323 K	357.14	0.65	7.4625	0.99
Toth	q_{Th}	Th	$K_{Th}\ (mg \cdot L^{-1})$	
303 K	1.01	0.90	133.03	0.97
313 K	1.01	0.89	135.03	0.97
323 K	1.01	0.88	136.47	0.97
Tempkin	$K_T\ (L \cdot mg^{-1})$		B	
303 K	1.881		35.75	0.96
313 K	2.08		36.95	0.96
323 K	2.34		37.79	0.96

Table 3. Isotherm parameters for malachite green oxalate- H_3PO_4 treated Palmyra carbon

Freundlich	$K_F\ (mg \cdot g^{-1})(mg \cdot L^{-1})^{-1/n}$		n	R^2
303 K	5.07		1.50	0.98
313 K	5.02		1.45	0.98
323 K	5.06		1.39	0.98
Langmuir	$K_L\ (L \cdot mg^{-1})$		$q_m (mg \cdot g^{-1})$	
303 K	.007		270.27	0.99
313 K	0.0069		303.03	0.99
323 K	0.007		344.82	0.98
Redlich Peterson	$K_R\ (L \cdot mg^{-1})$	β	a_R	
303 K	3.29	0.58	0.136	0.97
313 K	3.42	0.56	0.136	0.97
323 K	3.70	0.55	0.136	0.97
Toth	q_{Th}	Th	$K_{Th}\ (mg \cdot L^{-1})$	
303 K	2.009	0.465	24.46	0.95
313 K	2.009	0.444	26.04	0.95
323 K	2.009	0.417	28.93	0.95
Tempkin	$K_T\ (L \cdot mg^{-1})$		B	
303 K	0.11		45.51	0.95
313 K	0.12		47.18	0.94
323 K	0.13		49.71	0.93

Table 4. Isotherm parameters for malachite green oxalate- $ZnCl_2$ treated Palmyra carbon

Freundlich	$K_F\ (mg \cdot g^{-1})(mg \cdot L^{-1})^{-1/n}$		n	R^2
303 K	1.68		1.59	0.99
313 K	1.75		1.60	0.99
323 K	1.86		1.61	0.98
Langmuir	$K_L\ (L \cdot mg^{-1})$		$q_m (mg \cdot g^{-1})$	
303 K	0.00298		128.21	0.99
313 K	0.00305		130.21	0.99
323 K	0.00325		129.03	0.99
Redlich Peterson	$K_R\ (L \cdot mg^{-1})$	β	a_R	
303 K	0.849	0.547	0.137	0.97
313 K	0.819	0.547	0.137	0.97
323 K	0.906	0.546	0.137	0.97
Toth	q_{Th}	Th	$K_{Th}\ (mg \cdot L^{-1})$	
303 K	2.009	0.458	6.84	0.97
313 K	2.009	0.469	7.45	0.97
323 K	2.009	0.464	7.45	0.97
Tempkin	$K_T\ (L \cdot mg^{-1})$		B	
303 K	0.028		28	0.99
313 K	0.029		28.28	0.99
323 K	0.030		28.56	0.99

Table 5. Thermodynamic parameters for the adsorption of Malachite green oxalate dye on Palmyra male inflorescence activated carbon

Activated chemical	T/K	ΔG/J/mol	ΔS/ J/molK	ΔH/J/mol
KOH	303	-29092	58.61	-11323.5
	313	-30405	60.94	
	323	-31738	63.17	
H_3PO_4	303	-22315	69.61	-1210.57
	313	-23013	71.92	
	323	-23787	74.47	
$ZnCl_2$	303	-20162	48.80	-5367.75
	313	-20889	49.56	
	323	-21727	50.62	

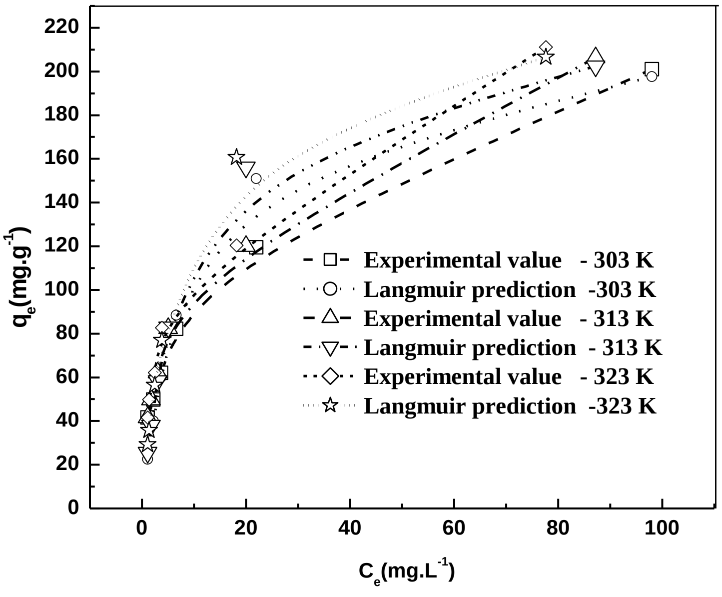

Fig. 4. Experimental and Langmuir model prediction for the adsorption of malachite green oxalate onto Palmyra carbon treated with KOH.

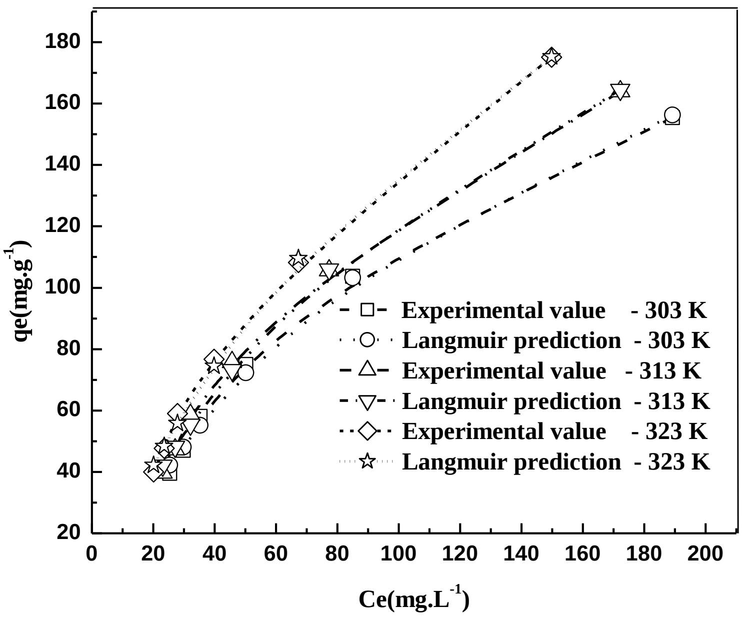

Fig. 5. Experimental and Langmuir model prediction for the adsorption of malachite green oxalate onto Palmyra carbon treated with H_3PO_4.

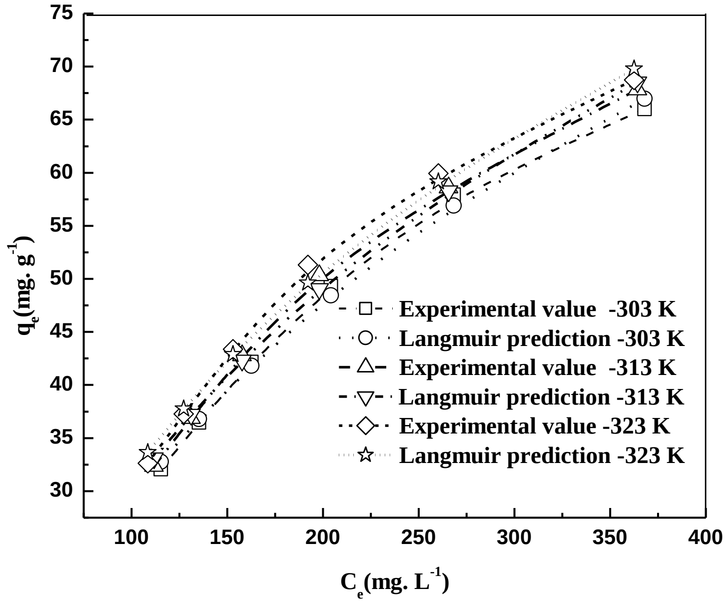

Fig. 6. Experimental and Langmuir model prediction for the adsorption of malachite green oxalate onto Palmyra carbon treated with $ZnCl_2$.

5. Conclusions

The equilibrium adsorption of malachite green oxalate from aqueous solution on Palmyra activated carbon at T = (303, 313 and 323) K and atmospheric condition was determined. Isotherms were successfully modeled with various isotherm models. Thermodynamic parameters were evaluated for the adsorbate-adsorbent system.

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