Journal of Advanced Scientific Research

Available online through http://www.sciensage.info/jasr

ISSN
0976-9595
Research Article

STUDIES ON THE ISOTHERMS, KINETICS AND THERMODYNAMICS OF ADSORPTION OF CRYSTAL VIOLET ON LOW COST MATERIALS

Abdo Taher, Mohd Mohsin, Mazahar Farooqui, Maqdoom Farooqui*
Post Graduate and Research Center, Maulana Azad College, Aurangabad.
**Corresponding author: mazahar_64@rediffmail.com*

ABSTRACT

The low cost adsorbent namely Cassia Siamea (CS), Albizia Labbeck (AL), Nerium Indicum (NI), Durauta Erecta (DE), and Potato Husk (PH) have been tested for the effectiveness in declourisation of wastewater containing a crystal violet dye (CV) by an adsorption technique. The various parameters such as contact time, dye concentration, temperature, adsorbent dosage, pH and ionic strength were applied for the study. The equilibrium was attained within 50 min, the adsorption of the dye on solution was studied in the pH range 2-7, the salt dosage was increased from 0.05 to 0.5 g. Adsorption was carried out at different temperature in the range of 293 to *333 K±0.5K* It was observed that the adsorption increase with increasing in time, solution pH and dosage (g). It was also observed that adsorption decreases with increase in CV concentration and the addition of salt. The kinetic data were then fitted using both Pseudo –first order model and second order model, Langmuir and Freundlich models were often used to describe equilibrium adsorption isotherms and the thermodynamic parameters, change in enthalpy (ΔH) (*KJ/mol*) and change in entropy (ΔS) (*J/mol*) which related to the Gibbs free energy (ΔG).

Keywords: Crystal violet dye, Adsorption, Isotherms, Kinetic and thermodynamic, Low cost materials.

1. INTRODUCTION

The dye has been found to be amitotic poisoning agent which was carcinogenic, nonbiodegradable, and can persist in a variety of environments [1]. Crysal violet (CV) (Fig. 1) is a tri-phenylmethane dye used extensively as a biological stain, and in various commercial textile operations.

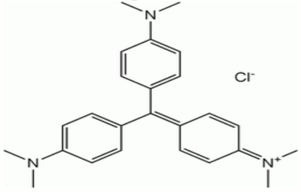

Fig. 1 Chemical structure of Crystal Violet

It is also known as hexamethyl pararosaniline chloride, a basic dye with molecular formula $C_{25}H_{30}N_3Cl$ [2]. CV, basic cationic dye imparts violet color in aqueous solution. It is toxic to mammalian cells and also a mutagen, mitotic poison and a proven potent carcinogen. It is responsible for moderate eye irritation, causing painful sensitization to light. Inhalation of CV may cause irritation to the respiratory tracks, vomiting, diarrhea, pain, headache, and dizziness. Long term exposure may cause damage to the mucous membrane and gastrointestinal tract [3], CV may cause human carcinogenesis and mutagenesis [4, 5]. Researchers had proved several low-cost materials such as low cost clay [6], sand [7], palygorskite and sepiolite [8], magnetic charcoal [9], etc. as adsorbents.

2. MATERIAL AND METHODS

The adsorbents were prepared from different types such as Cassia Siamea (CS) and Albizia Labbeck (AL) were trees's apicarps. The leaves of Nerium Indicum (NI) and Durauta Erecta (DE) plants were selected. And from Vegetable, Potato Husk (PH) was used. All the above adsorbents were divided into two portions, one was considered as untreated adsorbent and the second portion was treated with chemicals. For untreated powders, all adsorbents were collected, cleaned by water before drying to remove any dust and grinded to fine particles, wash with distilled water, filtered and then dried in shadow. The homogeneous powder was obtained by passing through mesh of desired particles size (micron) and used for the adsorption study. And the preparation of adsorbents with treatment: All adsorbents were collected, cleaned by water before drying to remove any dust and grinded to fine particles, wash with distilled water, filtered and then dried in shadow. Every adsorbent was treated with diluted hydrochloric acid and stirred for half an hour vigorously using mechanical stirrer at room temperature then filtered and washed with distilled water repeatedly to remove acid, then treated it with diluted sodium hydroxide solution, also, in the same manner and washed with distilled water repeatedly to remove base, finally with formaldehyde. After chemical treatment the residue was dried and powdered by electric grinder. The homogeneous powder was obtained by passing through mesh of desired particles size (micron) and used for the adsorption study. All solutions were prepared in double distilled water. For each experiment, 50 ml of CV solution (50 ppm), it was continuously stirred with 0.2 g of powder at 333±0.5K and initial concentration of CV was 50 ppm. The temperature is kept constant using a thermostat Dinesh, samples were withdrawn at appropriate time intervals, filtered and the absorbance of supernant liquid was determined at λ_{max}= 550 nm by using UV-visible spectrophotometer (Elico- SL 159). The effect of contact time, pH, temperature, etc., was studied likewise.

3. RESULTS AND DISCUSSION

3.1. Effect of contact time

The effect of contact time on the amount of dye adsorbed was investigated at various time intervals, and the remaining parameters were kept constants, samples were taken and the percentages were determined (Figures 1-5). The results of the kinetic studies were presented in Table 1. The kinetic data were then fitted using both Pseudo –first order model and second order model.

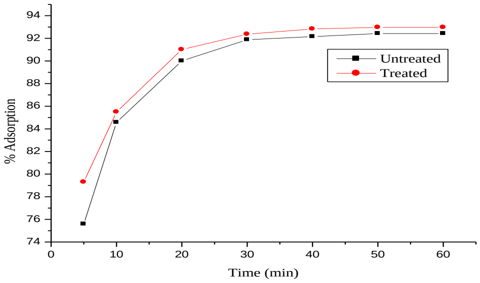

Fig. 1: Effect of contact time on adsorption of CV with CS

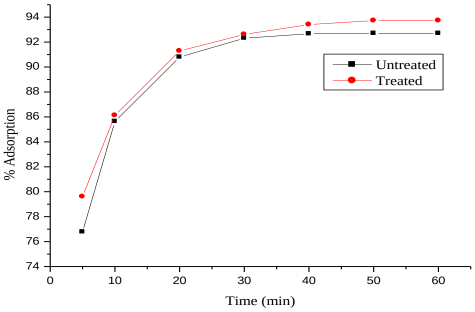

Fig. 2: Effect of contact time on adsorption of CV with AL

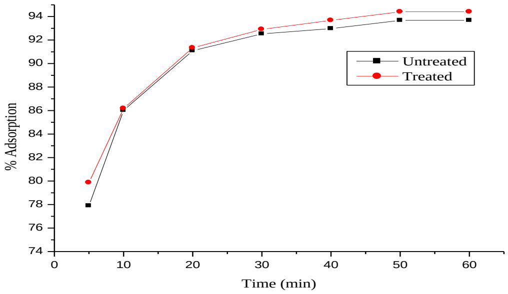

Fig. 3: Effect of contact time on adsorption of CV with DE

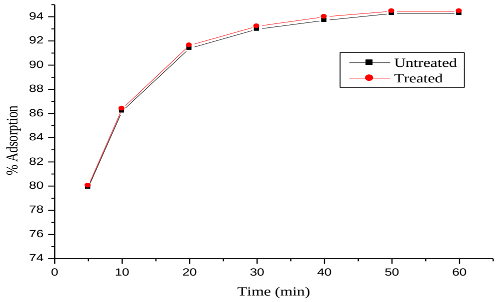

Fig. 4: Effect of contact time on adsorption of CV with NI

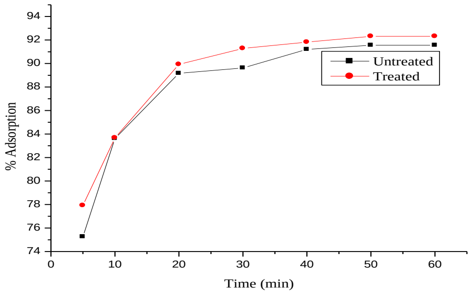

Fig. 5: Effect of contact time on adsorption of CV with PH

In Pseudo–first order kinetic model was given by Lagergren equations

$$\frac{q_e}{dt} = k_1 (q_e - q_t)\text{.......}1$$

The integrated form of this can be written as

$$\log q_e - q_t = \log q_e \frac{K_1}{2.303} t\text{.........}2$$

Where q_e and q_t represent the amount of dye adsorbed (mg/g) at at equilibrium time and at time t (min) respectively. k_1 represents the first order rate constant (min^{-1}). Based on experimental results, linear graphs were plotted between $\log$ q_e-$q_t$versus t, to calculate k_1, $q_e$and R^2.

In Second order adsorption kinetics; there are two possibilities that the rate may be proportion to the product of two equal concentrations or to the product of two different ones. The equation can be written as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t\text{.........}3$$

The graph was plotted $\frac{t}{q_t}$ versus t, to calculate k_2, q_e and R^2.

Where k_2 (mgg^{-1} min^{-1}) is adsorption rate constant for second-order adsorption rate.

Table 1. Isotherms, Thermodynamic and Kinetic parameters values of CV

Parameters		CS		AL		DE		NI		PH	
		Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated
Langmuir constants	Q^0(Mg/g)	50786	4917	14847	1563	142533	5322	2011	2197	108343	4574
	b × 10^{-5}(L/g)	80.332	919.08	294.72	3352.7	34.103	1010	2840	2743	32.046	879.2
	R_L	0.9614	0.6851	0.8716	0.3736	0.9832	0.664	0.41	0.422	0.9842	0.694
Freundlich Constant	K_f (mg/g(L/g))$^{1/n}$	63.087	67.205	65.65	74.73	72.109	76.32	77	80.56	54.266	61.21
	n	1.3767	1.3636	1.3468	1.4316	1.3734	1.351	1.32	1.322	1.3215	1.356
Thermodynamic parameters	ΔH(KJ/mol)	-4.170	-3.210	-3.298	-2.787	-1.888	-1.330	-1.735	-0.245	-3.309	-2.741
	ΔS(J/mol)	-6.81	-10.81	-10.34	-13.07	-16.03	-18.99	-17.21	-22.55	-8.85	-11.606
Pseudo –first order	K_1(Min^{-1})	0.121	0.131	0.175	0.105	0.089	0.085	0.091	0.097	0.1	0.098
	q_e(mg/g)	13.63	13.58	23.19	11.23	9.769	9.812	10.27	10.9	11.95	10.72
	R^2	0.987	0.998	0.978	0.995	0.969	0.991	0.995	0.997	0.954	0.988
Second order	K_2(g/mg min)	0.02	0.023	0.022	0.021	0.02	0.019	0.02	0.02	0.019	0.02
	q_e (mg/g)	50.71	42.71	44.9	46.61	50.32	51.91	50.08	49.81	53.34	49.55
	R^2	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999

In first order the values of R^2 for untreated powders were CS (0.987), AL (0.978), DE (0.967), NI (0.995) and PH (0.954), while for second order were CS (0.999), AL (0.999), DE (0.999), NI (0.999) and PH (0.999). And for treated powders, in first order were CS (0.998), AL (0.995), DE (0.991), NI (0.997) and PH (0.988), while for second order were CS (0.999), AL (0.999), DE (0.999), NI (0.999) and PH (0.999). By comparing of the calculated values of R^2 with experimental values, it is confirmed that the adsorption kinetics was pseudo second order. This observation is in agreement with many other studies of kinetics of adsorption of dyes [10-14].

3.2. Effect of adsorbent dose

The effect of amount of the adsorbents was necessary in order to observe the minimum possible amount, which shows maximum adsorption. It was studied by using different amount of adsorbents like 0.1, 0.2, 04, 0.8 and 1.0 g for the initial concentration i.e. 50 ppm at 303±0.5K pH 7 and contact time 50 min. The percentage of the dye adsorbed was increased with increasing in the amount of adsorbents (Figures 6-10).

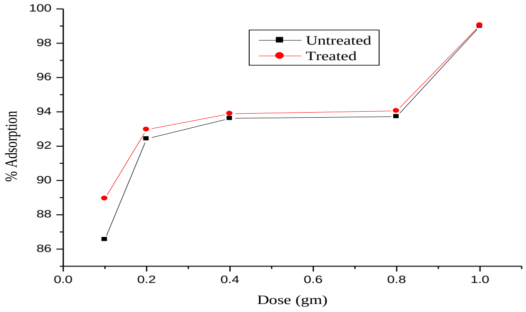

Fig. 6: Effect of adsorbent dose on adsorption of CV with CS

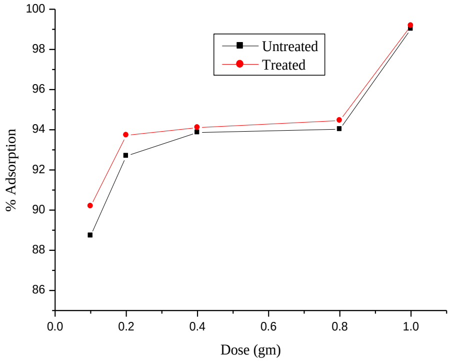

Fig. 7: Effect of adsorbent dose on adsorption of CV with AL

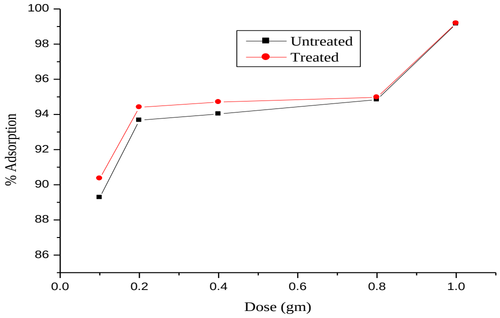

Fig. 8: Effect of adsorbent dose on adsorption of CV with DE

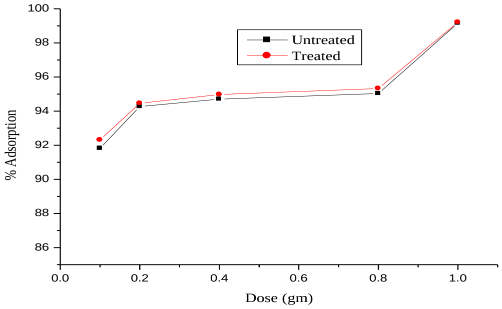

Fig. 9: Effect of adsorbent dose on adsorption of CV with NI

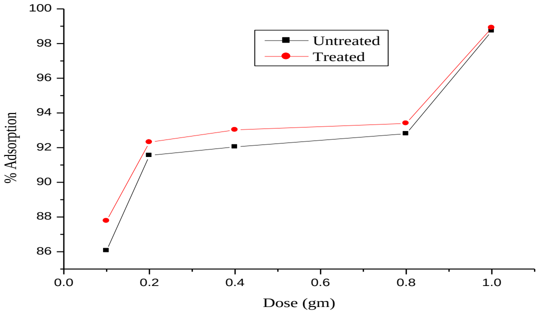

Fig. 10: Effect of adsorbent dose on adsorption of CV with pH

Langmuir and Freundlich models were often used to describe equilibrium adsorption isotherms. Langmuir model was calculated by the following expression:

$$\frac{C_e}{Q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \text{……….4}$$

Where Q_e is the amount adsorbed at equilibrium (mg/g) Q^0 and b are Langmuir constants related to capacity (mg/g) and energy of adsorption (l/g) respectively. The values of Q^0 and b are calculated from the slope and intercept by plotting the graph between Ce/Q_e and Ce.

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter R_L which is defined as

$$R_L = \frac{1}{1+bC_0} \text{……….5}$$

There were four probabilities for the value of R_L: (i) for favorable adsorption, $0 < R_L < 1$, (ii) for unfavorable adsorption, $R_L > 1$, (iii) for linear adsorption, $R_L = 1$, and (iv) for irreversible adsorption, $R_L = 0$ [15].

The obtained values of separation factor were for untreated powders were CS (0.961), AL (0.871), DE (0.983), NI (0.41) and pH(0.984), and for treated powders were CS (0.685), AL (0.373), DE (0.664), NI (0.422) and pH(0.694) (Table 1), clearly indicating the favorability of the adsorption process for all adsorbents.

The Freundlich adsorption isotherm is one of the most widely used empirical equation, the equation can be written in the linear form as:

$$\ln \frac{x}{m} = \ln k_f + \frac{1}{n} \ln c_e \text{……….6}$$

A plot of $\ln \frac{x}{m}$ against $\ln c_e$ gives a straight line with an intercept on the ordinate axis. The values of *n* and k_f can be obtained from the slope and the intercept of the linear plot. The Freundlich isotherm constant (K_F), which is adsorption capacity and 1/n is the adsorption intensity, were the n values for untreated powders CS (1.38), AL (1.35), DE (1.37), NI (1.32) and pH(1.32),while for treated powders were CS (1.36), AL (1.43), DE (1.35), NI (1.322) and pH(1.36) (Table 1). These agree with previous workers, the exponent 1/n was usually less than 1.0 because sites with the highest binding energies were utilized first, followed by weaker sites, and so on [16]. The mathematical calculations of n values between 1 and10 represent the best adsorption [17].

3.3. Effect of initial concentration

The adsorption experiments were performed in the concentration range (10–50 mg/l) at pH 7, adsorbent dose 0.2 g and temperature 303 ±0.5 K, the initial dye concentration was plotted against related CV removal percentage, The percentage removal of CV was high at low CV initial concentration and low at high initial CV concentrations. The maximum percentage removal of CV was for untreated powders CS (98.9), AL (99.0), DE (99.1), NI (99.1) and PH(98.7), while for treated powders was CS (99.2), AL (99.3), DE (99.4), NI (99.4) and PH(98.8) (Figures 11-15). The mass of the given adsorbent can absorb only a fixed amount of dye. Similar results have been reported in literatures and also when the amount of adsorbent is constant it means that the number of adsorption sites is constant, so by increasing the amount of MB, the percent removal should decrease due to the limitation of the adsorption sites [18-22].

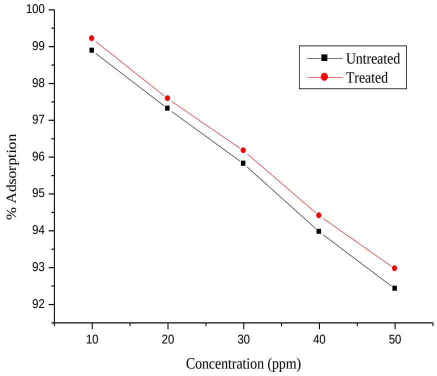

Fig. 11: Effect of initial concentration on adsorption of CV with CS

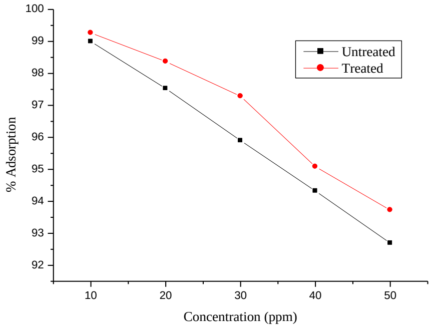

Fig. 12: Effect of initial concentration on adsorption of CV with AL

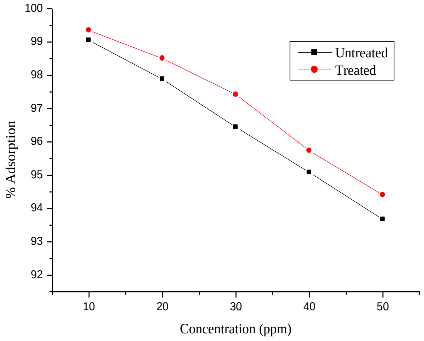

Fig. 13: Effect of initial concentration on adsorption of CV with DE

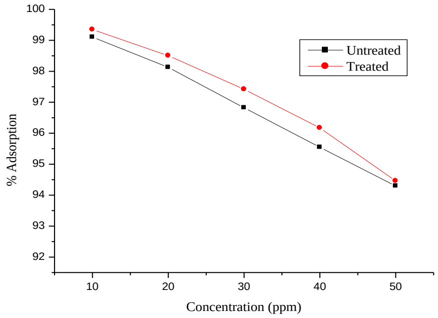

Fig. 14: Effect of initial concentration on adsorption of CV with NI

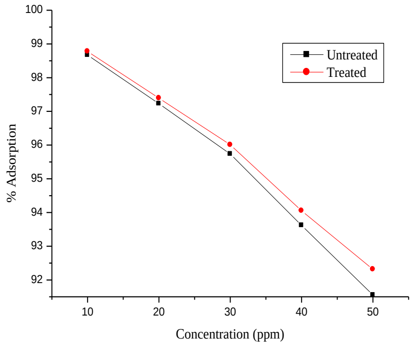

Fig. 15: Effect of initial concentration on adsorption of CV with pH

3.4. Effect of temperature

The effect of adsorption rate was carried out at different temperatures, with rising temperature from 293 to 333 *K*±0.5 within 50 min for 50 ppm CV solution; it was observed that adsorption decreases with increase to high temperature (Figures 16-20). The data were used to calculate the thermodynamic parameters, change in enthalpy (ΔH) (*KJ/mol*) and change in entropy (ΔS) (*J/mol*) which related to the Gibbs free energy (ΔG), by using the following equations,

$$\Delta G \;=\; -RTLnk_d \text{..........}7$$

After integration and rearrangements the above equation gives

$$lnK_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \text{...........}8$$

Where T is the absolute temperature in Kelvin (*K*), R is the gas constant (8.314J/ (*Kmol*)) and K_d is distribution coefficient for the adsorption (cm^3/ g). The values of ΔH and ΔS were determined from the slopes and intercepts of the plots $log\ K_d$ versus *1/T*.

The maximum Δ*G* values were for untreated powders CS (-21.4), AL (-22.9), DE (-23.3), NI (-24.5) and pH (-20.7), while for treated powders were CS (-21.5), AL (-24.1), DE (-24.5), NI (-24.6) and pH (-21.8) (Table 2). And the values of Δ*H* were for untreated powders CS (-4.2), AL (-3.3), DE (-

1.9), NI (-1.7) and pH (-3.3), while for treated powders were CS (-3.2), AL (-2.8), DE (-1.3), NI (-0.3) and pH (-2.7) (Table 1). The negative values of ΔG indicates that the adsorption of CV on all adsorbents were thermodynamically feasible and spontaneous at room temperature. The ΔG values obtained were in the physical adsorption. The negative values of ΔH confirmed that the adsorption was exothermic in nature. The negative ΔS values suggested that there was no significant changes occurred in the internal structure of the adsorbent. Moreover, the values of ΔH were less than 40 KJ/mol, which indicated the physical adsorption [23, 24]. All these indicating that the process is slightly exothermic in nature. This is probably due to tendency of dye molecules to escape from the solid phase to bulk phase with an increase in temperature of the solution, the same trend is observed for all adsorbents [25].

Table* 2.*Free Energies (KJ/mol) of MB solution at different Temperature

Temp (K)	CS		AL		DE		NI		pH	
	Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated
293	-20.2	-20.73	-20.7	-21.4	-21.71	-22.88	-22.07	-22.6	-19.42	-20.36
303	-20.8	-21.47	-21.13	-22.49	-22.41	-23.5	-23.29	-23.58	-19.82	-20.67
313	-21.4	-21.47	-22.88	-24.07	-23.33	-24.44	-24.49	-24.63	-20.7	-21.75
323	-20.11	-21.06	-20.67	-21.89	-22.22	-23.2	-22.6	-23.37	-19.53	-20.48
333	-18.3	-19.25	-19.11	-20.11	-20.73	-22.26	-21.4	-22.49	-17.76	-18.95

Amount of adsorbent = 0.2g; Conc. of adsorbate = 50 ppm
Time = 60 min; Amount of Adsorbate = 50 ml; pH = 7

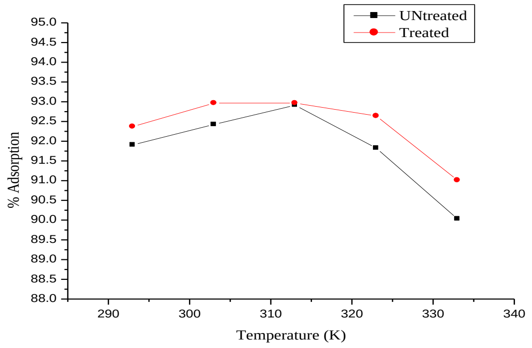

Fig. 16: Effect of Temperature on adsorption of CV with CS

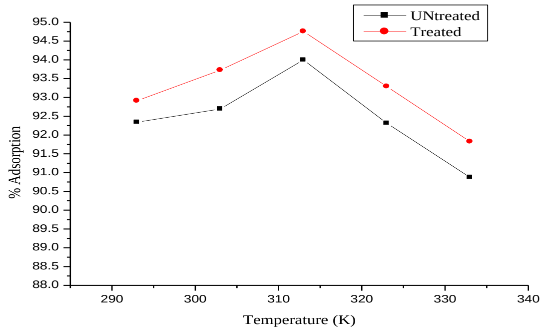

Fig. 17: Effect of Temperature on adsorption of CV with AL

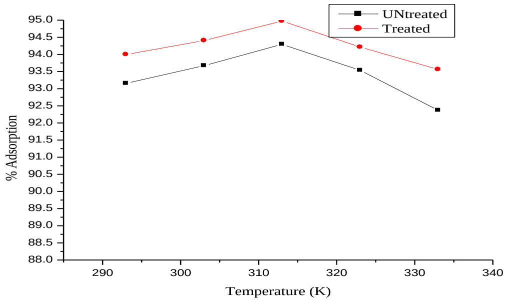

Fig. 18: Effect of Temperature on adsorption of CV with DE

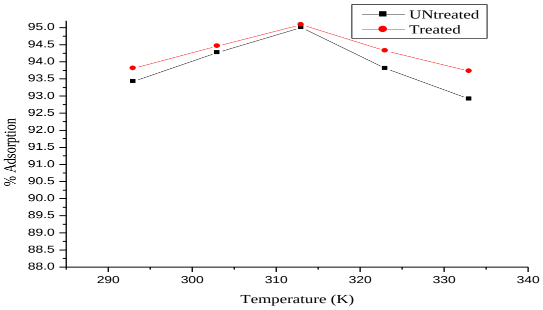

Fig. 19: Effect of Temperature on adsorption of CV with NI

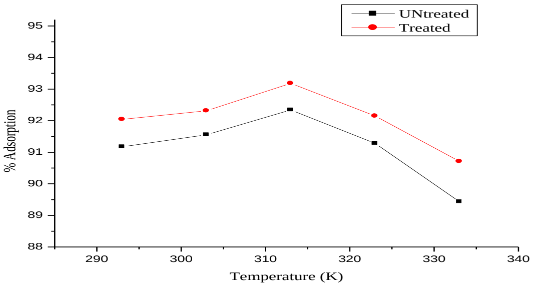

Fig. 20: Effect of Temperature on adsorption of CV with pH

3.5. Effect of Solution pH

The pH can influence the adsorption of CV. The experiments were carried out at different pH (2, 3, 4, 5, 6 and 7). The maximum percentage removal of CV was for untreated powders CS (92.4), AL (92.7), DE (93.7), NI (94.3) and pH (92.3),while for treated powders was CS (93.0), AL (93.7), DE (94.4), NI (94.5) and pH (92.3) (Figures 21-25). These were in accordance with previous researches [26, 27]. It is clear that the adsorption process was highly dependent on the pH of the solution, the low adsorption in acidic range was due to the fact that surface becomes positivity charged, thus making [H^+] ions compete effectively with dye cations causing decrease in adsorption [28-30].

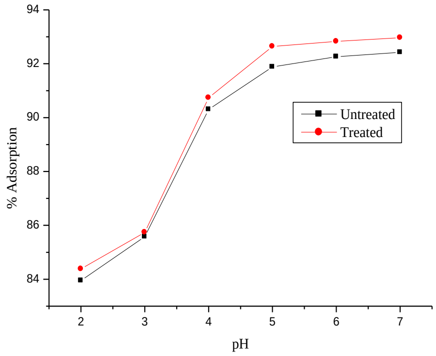

Fig. 21: Effect of Solution pH on adsorption of CV with CS

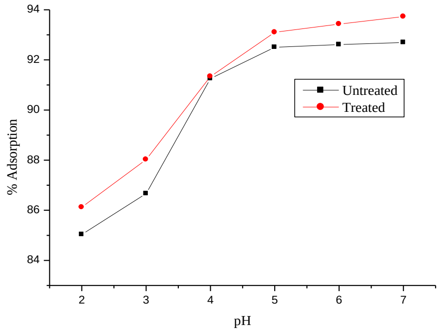

Fig. 22: Effect of Solution pH on adsorption of CV with AL

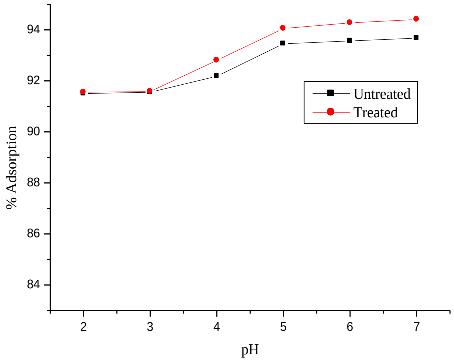

Fig. 23: Effect of Solution pH on adsorption of CV with DE

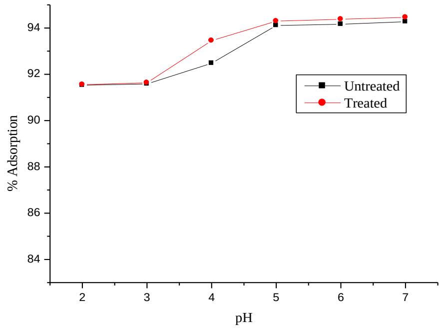

Fig. 24: Effect of Solution pH on adsorption of CV with NI

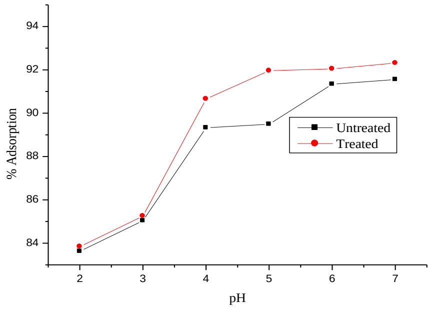

Fig. 25: Effect of Solution pH on adsorption of CV with pH

3.6. Effect of added salt (NaCl)

Sodium chloride is currently used in textile dyeing processes as it promotes the adsorption of the dyes by the textile fibers. Experiments had been carried out using different amount of salt, ranging (0.05-0.5 g). It was observed that when the amount of salt was increasing, the CV removal was decreased, the maximum percentage removal of CV was for untreated powders CS (92.4), AL (92.7), DE (93.7), NI (94.3) and pH(92.3), while for treated powders was CS (93.0), AL (93.7), DE (94.4), NI (94.5) and pH (92.3) (Figures 26-30). As seen, the adsorption capacity of the adsorbent depended on the ionic strength of the solution, when the ionic strength was increased; the electrical double layer surrounding the adsorbent surface was compressed and correspondingly resulted in a decrease in CV adsorption on to all adsorbents [31-33].

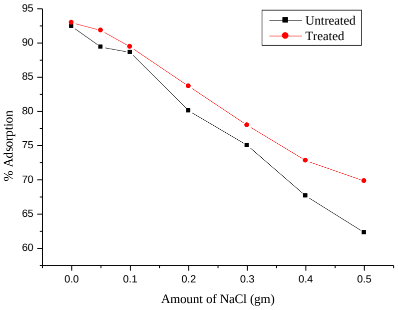

Fig. 26: Effect of amount of NaCl on adsorption of CV with CS

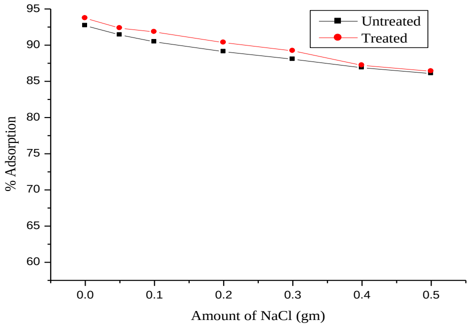

Fig. 27: Effect of amount of NaCl on adsorption of CV with AL

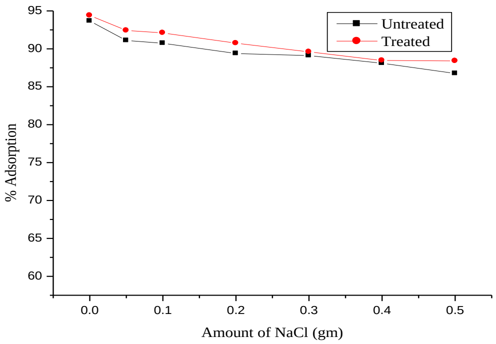

Fig. 28: Effect of amount of NaCl on adsorption of CV with DE

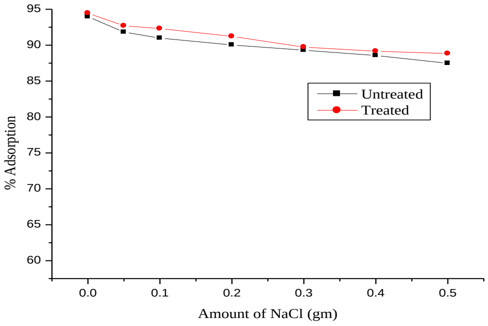

Fig. 29: Effect of amount of NaCl on adsorption of CV with NI

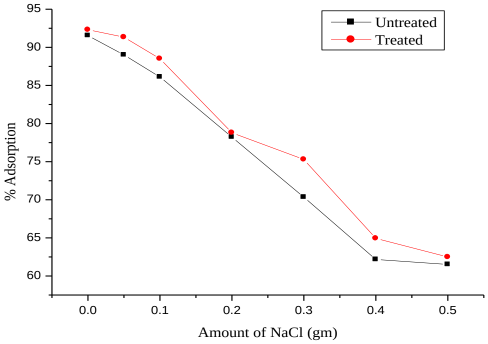

Fig. 30: Effect of amount of NaCl on adsorption of CV with pH

4. CONCLUSION

Based on results, the adsorption on the different adsorbents namely Cassia Siamea (CS), Albizia Labbeck (AL), Nerium Indicum (NI), Durauta Erecta (DE), and Potato Husk (PH) , were an effective for the removal of CV from aqueous solutions, the operational parameters such as contact time, dose, initial concentration, temperature, pH, and amount of salt, were studied. The highest percentage removal was at pH= 7, the percentage uptake of dyes is concentration dependent, decreasing with an increase in dye concentration. The kinetics of the CV removal fits well with the pseudo-second-order rate kinetic model, so the kinetic studies showed that the adsorption followed a pseudo-second-order kinetic model. The R_L values have been calculated using the Langmuir constant b and C_0; the values were between 0 and 1 which suggested favorable adsorption. The n values were greater than 1, which showed that were efficient adsorbent for CV dye. The thermodynamic investigation showed that ΔG and ΔH were negative at different temperatures for all the adsorbents, indicating that the adsorption is spontaneous and exothermic in nature.

Thus it was proved that adsorbent materials CS, AL, DE, NI and PH (untreated and treated) can be very effectively employed for the removal of dyestuff CV. The main advantages, these materials were available freely, locally, and abundantly, easy to prepare in large scale and have been proven to be much more efficient than the conventional expensive adsorbents. Therefore a conclusion can be drawn that CS, AL, DE, NI and PH can be used as good low-cost adsorbents for removal of CV from wastewater.

5. REFERENCES

1. Asma Saeed, Mehwish Sharif, Muhammad Iqbal. *J Haz Mat*, 2010; **175:** 564-572.
2. Sharma Mona, Anubha Kaushik, Kaushik CP. *Int Biodeterioration & Biodegradation,* 2011; **65:** 513-521.
3. Kunwar Singh P, Shikha Gupta, Arun Singh K, Sarita Sinha. *J Haz Mat*, 2011; **186:** 1462-1473.
4. Lin An, Jian Deng, Liang Zhou, Hui Li, Fei Chen, Hui Wang, Yating Liu. *J Haz Mat*, 2010; **175:** 883-888.
5. Littlefield, Blackwell B N, Hewitt C C, Gaylor D W. *Fundam Appl Toxicol,* 1985; **5:** 902-912.
6. Rytwo G, Ruiz-Hitzky E. *J Thermal Anal Calorimetry*, 2003; **71:** 751-759.
7. Rosario De Lisi, Giuseppe Lazzara, Stefania Milioto, Nicola Muratore. *Chemosphere*, 2007; **29:** 1703-1712.
8. Shariatmadari H, Mermut AR, Benke MB. *Clays and Clay Minerals*, 1999; **47(1):** 44-53.
9. Ivo S, Konstanca N, Mirka S. *J Chem Tech Biotechnol*, 1997; **69:** 1-4.
10. Senthilkumaar S, Kalaamani P, Subburaam CV. *J Haz Mat B*, 2006; **136:** 800-808.
11. Yousef H, Shahnaz Q, Ashley G, Sarmadia A and Reyad S. *J Haz Mat*, 2010; **175:** 1110-1112.

12. Malarvizhi R, Sulochana N. *World Appl Sci J (Special Issue For Env),* 2009; **5:** 114-120.
13. Kumar KV. *J Haz Mat*, 2007; **142:** 564 -567.
14. Shengfang Li. *Bioresource Technol,* 2010; **101:** 2197-2202.
15. Mittal A, Mittal J, Malviya A, Kaur D, Gupta VK. *J Coll Interf Sci,* 2010; **343:** 463-473.
16. Monash P, Pugazhenthi G. *Adsorption,* 2009; **15:** 390-405.
17. Madha VS, Manicka V K, Vasanthakumar R, Rasappan K, Mohanraj R and Pattabhi S. *E-J Chem*, 2009; 6**(4):** 1109-1116.
18. Reddy AY, Arivazhagan M and Sivashanmugham P. *Ind J Inv Prot*, 2007; **27(6):** 516-526.
19. Bilal A, Metin K, Metin D, Hakki AM, Fazilet T. *Asian J Chem,* 2010; **22(2):** 1394-1402.
20. Patel H, Vashi R T. *E-J chem*, 2010; **7(3):** 975-984.
21. Ahmad R. *J Haz Mat*, 2009; **171:** 767-773.
22. Nandi BK, Goswami A, Purkait MK. *Appl Clay Sci,* 2009; **42:** 583-590.
23. El Boujaady H, El Rhilassi A, Bennani-Ziatni M, El Hamri R, Taitai A, Lacout J L. *Desalination*, 2011; **275:** 10 -16.
24. Eren E, Afsin B. *Dyes and Pigments,* 2008; **76:** 220-225.
25. Mahesh S, Vijay Kumar G, Pushpa Agrawal. *J Env Biolog*, 2010; **31:** 277-280.
26. Monash P, Ram Niwas and Pugazhenthi G. *Clean Tech Env Policy*.
27. Ghosh D, Medhi C R, Solanki H and Purkait M K. *J Env Prot Sci,* 2008; **2:** 25 - 35.
28. Verma VK, Mishra AK. Indian *J Chem Tech* 2008; **15:** 140-145.
29. Dinesh M, Kunwar, Singh P, Singh G, Kumar K. *Ind Eng Chem Res,* 2002; **41:** 3688-3695.
30. Jayswal A, Chudasama U. *Ind J Chem Technol*, 2006; **13:** 539-543.
31. Gulay B, Begum A, Yakup AM. *Chem Eng J,* 2009; **152:** 339-346.
32. Madha VS, Manicka VK, Vasanthakumar R, Rasappan K, Mohanraj R, Pattabhi S. *E-J chem*, 2009; **6(4):** 1109-1116.
33. Eren E, Afsin B. *Dyes and Pigments,* 2007; **73:** 162-167.