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Novel Eco-Friendly Adsorbents for the Removal of Victoria Blue Dye

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ABSTRACT

Adsorption kinetics of removal of Victoria Blue (VB) on Commercial Activated Carbon CAC and Bentonite (clay) have been studied comparatively. This study investigated the potential use of bentonite (natural clay) as alternative adsorbent for the removal of Victoria blue (VB) from wastewater by batch adsorption technique at room temperature. The effect of adsorbent dosage, initial dye concentration, pH and contact time were experimentally studied to evaluate the adsorption capacity, kinetics and equilibrium. The dye uptake process obeyed the pseudo-first order kinetics the monolayer formation is confirmed by using Langmuir adsorption isotherm. Intra-particle diffusion studies showed that the adsorption mechanism was controlled by the diffusion process. These results indicate that bentonite could be employed as low-cost adsorbent for the alternatives for the removal of cationic dye from industrial wastewater.

Keywords: Victoria blue dye, CAC, Bentonite, Adsorption Isotherms, Kinetics of Adsorption, Batch technique, Intra-particle Diffusion.

INTRODUCTION

Large quantities of colored effluents are discharged into receiving waters each year. It is estimated that 10–15% w/w of this capacity is discharged in effluents. From environmental point of view, the discharge of dyes into natural water bodies represents a serious problem because of their persistence and non-biodegradable characteristics [1]. Highly colored effluents containing dyes can affect aquatic life present in natural water bodies by decreasing sunlight penetration and/or even leading to direct poisoning of living organisms [2–5]. In order to avoid these problems, effluents containing dyes must be treated for their removal before disposal. For this task some processes can be employed like: (i) photochemical degradation, which is not an efficient process due to the high stability of most dyes in front of light and (ii) chemical or anaerobic digestion, which are not suitable for dyes elimination because their intrinsic resistance [6].

The application of the adsorption technique has assumed remarkable importance in the treatment of contaminated waters and effluents, especially if the adsorbent employed presents low cost and does not require any treatment before its utilization [7-9]. Therefore, the development of suitable adsorption techniques for the removal of dyes from aqueous medium becomes an interesting approach. Many adsorbents based on low cost agricultural by-products had been used for dye adsorption from wastewater, which included banana pith [10], lemon peel [11], wheat straw [12], sawdust [13], powdered waste sludge [14], wheat shells [15], wheat bran [16] and hen feathers [17].

Recently, several solid materials have been recently used for the adsorption of basic dyes [18-31]. In this scenario, Bentonite is natural clay, can be considered suitable adsorbents for the retention of chemical substances, since they are cheap and can be used without any previous treatment. Besides, bentonite present excellent chemical and thermal resistance, high efficiency and are easily found in the market [32].

The present work describes to investigate the efficiency of bentonite as an adsorbent for removal of Victoria blue and the obtained results were compared with CAC. The effects of various operating parameters on adsorption such as initial concentration, pH, dosage and contact time were monitored and optimal experimental conditions were determined. Different adsorption isotherms and kinetic models were used to find out most suitable models describing our experimental findings. The data thus obtained may be helpful to environmental engineers for designing and establishing a continuous treatment plant for water and wastewater.

EXPERIMENTAL SECTION

The natural clay bentonite was supplied by S.D. Fine chemical Ltd, India. CAC was procured from E.Merck, India. Victoria blue (VB) is a basic dye obtained from BDH was used as received. All the other chemicals used in this study were analytical grade and supplied by BDH (India). Double distilled was employed for preparing all the solutions and reagents. A stock solution of VB (1000 mgl^{-1}) was prepared and suitably diluted to the required initial concentrations. Adsorption experiments were carried out at room temperature (30±1°C) under batch mode [33]. The absorbance are measured using Elico UV-visible spectrophotometer (Model: SL207) for O.D at 599 nm (λ_{max}) value of dyes and the percentage removal of dye and amount adsorbed (in mg/g) were calculated using the equations.

The concentrations of the VB solutions before and after adsorption were estimated by measuring OD at 599 nm (λ_{max}) with the help of Systronics spectrophotometer (Model: SL207) and then interpolated into the standard curves. The initial pH of the dye solution was adjusted to the required value by adding either 1 N HCl or 1 N NaOH solution. The values of percentage removal and the amount of VB adsorbed were calculated using the following relationships:

$$\textbf{Percentage removal} = [\ (C_i - C_f) / C_i\ ] \times 100 \qquad \text{-------------- (1)}$$

$$\textbf{Amount adsorbed } (q_e) = (C_i - C_f) / m \qquad \text{-------------- (2)}$$

Where C_i is the initial concentration in ppm, C_f is the final concentration in ppm and m is mass of adsorbent in g L^{-1}. Control experiments were also carried out. The average values of duplicate runs were reported and analysed (Error: ±1 - 2% for percentage removal and ±0.005 - 0.01 mg g^{-1} for amount adsorbed).

RESULTS AND DISCUSSION

The adsorption experiments were carried out at different experimental conditions and the results obtained are discussed below.

Effect of initial concentration

The studies on the removal of Victoria Blue dye on CAC and bentonite were carried out at different initial concentration of dye from 10 to 100 ppm and 3to30and for contact time 30 min. The data obtained are tabulated in Table 1. The extend of the percentage removal of the dye decreases exponentially with the increase in the initial concentration of dye. This may be due to the reduction in the immediate solute adsorbent surface compared to the relative larger number of required site for the high concentration of dye. At the optimum initial concentration of dye of 30 ppm for CAC, 15 ppm for bentonite for the percentage removal of dye was found to be maximum (Figure 1).

This indicates a decrease in adsorption, which is attributed due to the lack of available active sites required for the high initial concentration of VB. Similar results have been reported in literature on the extent of removal of dyes [34], [35] and [36], Metal ions [37] and Eriochrome Black-T Carboxylic acid [38].

Adsorption isotherm

The study of adsorption isotherm has been of important and significant in the waste water treatment by adsorption technique, as they provide an approximate estimation of the adsorption capacity of the adsorbent. The equilibrium data for the removal of dye on CAC and bentonite at 30 ±1°C were used in the Langmuir and Freundlich isotherms.

Freundlich isotherm: $q_e = K+C_e^{1/m}$ **--------------- (3)**
Langmuir isotherm: $(C_e/q_e) = (C_e/Q_o) + (1+Q_o b)$ **--------------- (4)**

The data obtained from the adsorption experiments were fitted into Langmuir and Freundlich isotherms respectively by plotting log q_e and log(x/m) against C_e and C_e/q_e. They are found to be linear(for the evidence the figures 2 and 3), indicating the applicability of theses adsorption isotherms for removal of dye by these adsorbents are the monolayer formation .The monolayer adsorption capacities of the adsorbents (based on Q_o values) are found to be the order bentonite << CAC. Further , the important characteristics of the Langmuir isotherms can be described by a separation factor R_L. The values of separation factor R_L, indicates the shape of the isotherm and nature of the adsorption process as given below,

R_L values	Nature of the adsorption process
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$O < R_L > 1$	Favourable
$R_L = 0$	Irreversible

In the present study, the values computed are found to be (fraction) in the range of 0-1, indicating that the adsorption process is favorable for the low cost adsorbents. The details data were given in table -2

Effect of contact time

Inorder to study the kinetics and dynamics of adsorption of VB, adsorption experiments were carried out at different contact time (5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 min.,) at constant optimum initial concentration of dye 30ppm for CAC and 15ppm for bentonite. Relevant experimental data are given in Table 1.

The percentage removal of VB increases with increase in contact time and reaches a maximum value. The contact time at which the maximum percentage removal of VB occurs is fixed as the contact time(Figure 4) .The removal of VB by adsorption on bentonite and CAC was found to be rapid at the initial period of contact time and then become slow and stagnant with increase in contact time: The following kinetic equations were employed to study the kinetics and dynamics of adsorption of dye under the condition of first order kinetics (Figures 5 & 6).

Natarajan and Khelaf equation : $K= (2.303/t) \log (C_o/C_t)$ ------ (5)
Bhattacharya & Venkobachar equation : $\mathrm{Ln}\ [1-(C_o/C_t)/(C_o/C_e)= -Kt$ ------ (6)
Lagergren equation : $\mathrm{Log}\ (q_e-q_t) =\log q_e -(k/2.303t)$ ------ (7)

C_o - initial concentration, C_t - Concentration at time T,T – time, K- first order rate constant for adsorption of dyes (in min^{-1}),q_e-amount adsorbed per unit mass of adsorbent (mg g^{-1})at equilibrium, q_t – amount adsorbed per unit mass of adsorbent at any given time ‘t’(mg g^{-1}), C_e-concentration at equilibrium time.

Intra-particle diffusion study

Besides adsorption at the outer surface of the adsorbent there is also a possibility of intra-particle diffusion of dye molecule from the bulk of the outer surface into the pores of the materials of the adsorbent. For adsorption of dye using various adsorbents, the intra-particle diffusion has been reported. This possibility was exposed by plotting the amount of dye adsorbed against time, for the dye with respect to the bentonite. These result in a linear relationship indicating the existence of intra-particle diffusion forces (Figure 7 & 8).

Table 1. Effect of various experimental parameters on the extent of removal of Victoria Blue (VB) dye by adsorption technique

Variation	Initial conc (ppm)	Contact time (min.)	Dose of AC (g/L)	Initial pH	Particle size (µ)
Initial concentration					
CAC	10 - 100	30	2	2 – 11	90
Bentonite	3 - 30	30	4	2 - 11	90
Contact time					
CAC	30	30	2	2 – 11	90
Bentonite	15	5 - 50	4	2 - 11	90
Dose of AC					
CAC	30	30	2	2- 11	90
Bentonite	15	30	2 – 10	2 - 11	90
Initial PH					
CAC	30	30	2	2- 11	90
Bentonite	15	30	4	2- 11	90
Particle size					
CAC	30	30	2	2 – 11	90
Bentonite	15	30	4	2 - 11	90

Effect of dose of adsorbent

The amount of VB adsorbed by bentonite was found to increase with increase dose of adsorbent. It is due to the increased availability of active adsorption sites. This may also be due to the increase in effective surface area resulting from the conglomeration of the adsorbent (Figure 9).

Effect of initial pH:

The effect of initial pH on the amount adsorbed was studied by varying the initial pH of the dye solution. The increase of pH increases the amount of dye adsorbed which is depend upon the nature of surface functional group of the adsorbent and the nature of the dye. The percentage removal of graph is given in the figure 9. The results are found to be in harmony with the available literature reports for the adsorption of basic dyes.

Table 2. Result and correlation analysis of the adsorption isotherm for the removal of Victoria Blue dye by CAC and bentonite

S. No	Parameters	Adsorbent	
		CAC	Bentonite
1	**Freundlich isotherm**		
	Slope(1/n)	1.464	1.837
	Intercept (log k)	0.907	0.274
	Correlation coefficient(r)	0.966	0.936
2	**Langmuir isotherm**		
	Slope($1/Q_o$)	0.030	0.186
	Intercept ($1/Q_ob$))	0.159	0.729
	Correlation coefficient(r)	0.758	0.597
	Q_o (mg/g)	33.638	5.367
	b (g/L)	0.187	0.255
	R_L	0.237	0.023

Table 3. Kinetics and dynamics of adsorption of VB on bentonite and CAC

S. No	**Parameters**	**Adsorbent**	
		CAC	**Bentonite**
1	**Natarajan and Khalaf equation**		
	Correlation Coefficient(r)	0.960	0.987
	10^2 K(min^{-1})	0.022	0.010
2	**Lagergren equation**		
	Correlation coefficient(r)	0.983	0.994
	10^2 K(min^{-1})	0.013	0.030
3.	**Bhattacharya and Venkobachar equation**		
	Correlation coefficient(r)	0.969	0.998
	10^2 K(min^{-1})	0.029	0.028
4	**Intra-particle diffusion model**		
	K_P	0.129	0.417
	Correlation coefficient(r)	0.955	0.974
	Intercept	13.652	0.441
5	**Log(Time) Vs (% Removal)**		
	Slope	0.016	0.357
	Correlation coefficient(r)	0.909	0.969
	Intercept	1.956	1.024

Figure 1: Effect of Initial Concentration

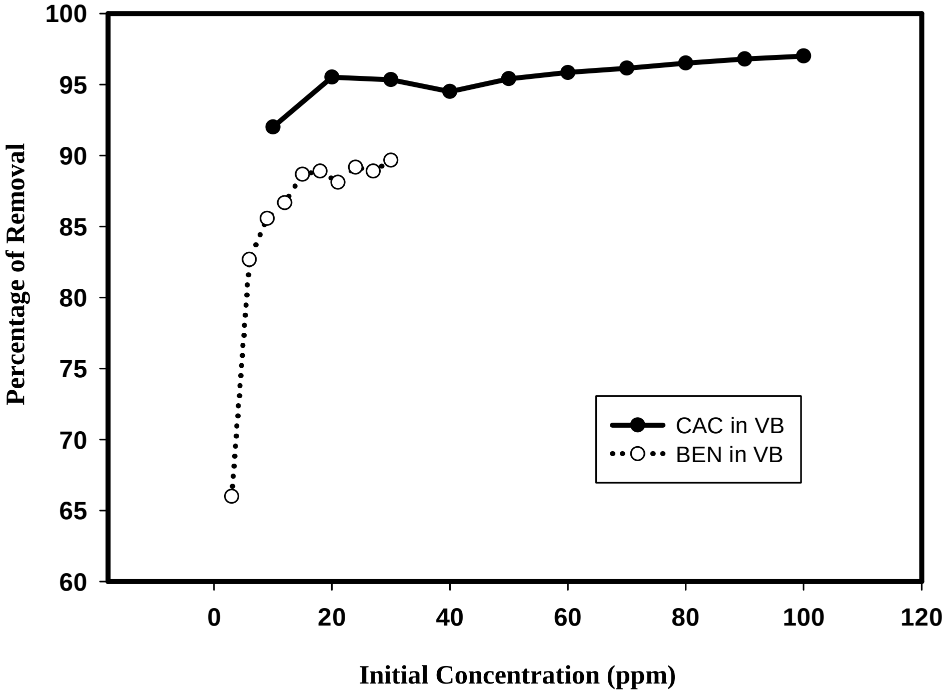


Figure 2: Effect of Concentration Variation: Langmuir adsorption Isotherm

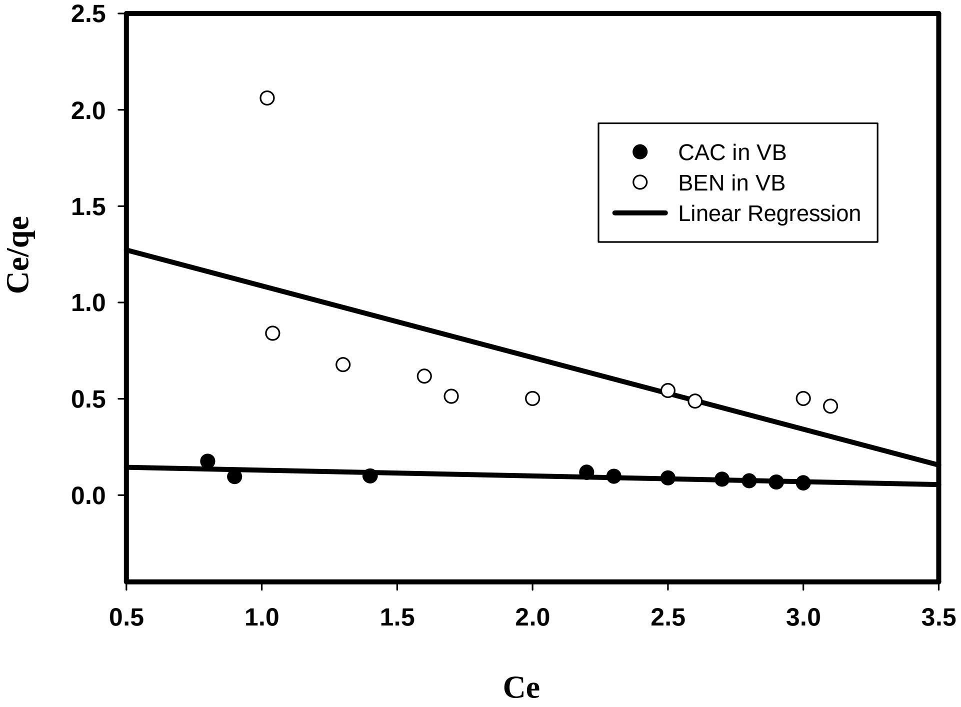


Figure 3: Effect of Concentration Variation: Freundlich adsorption Isotherm

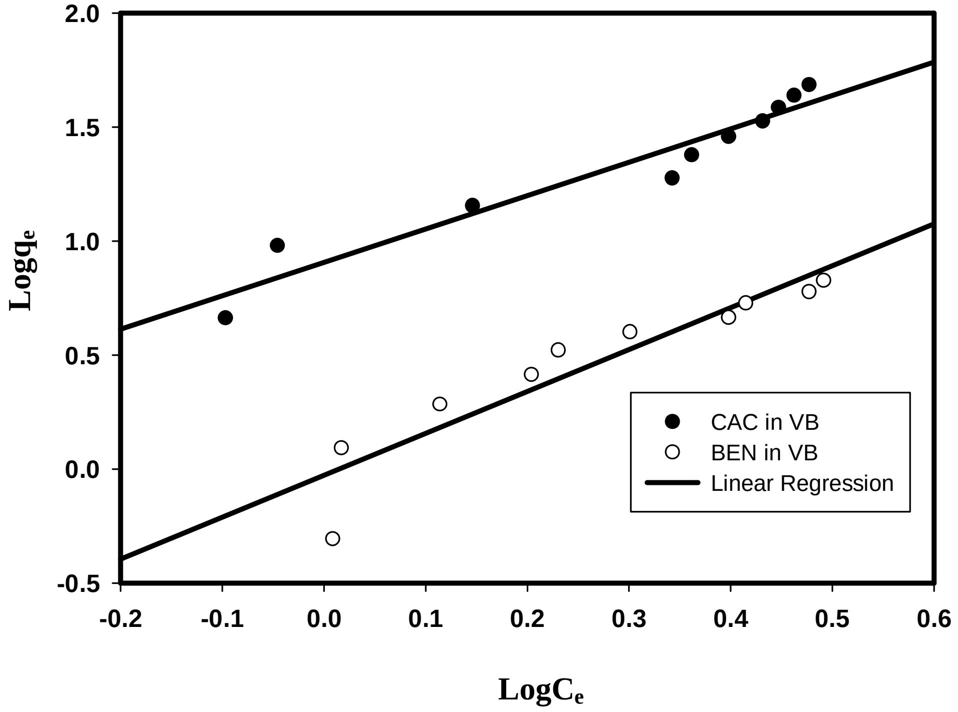


Figure 4: Effect of Contact Time on the percentage removal of dye

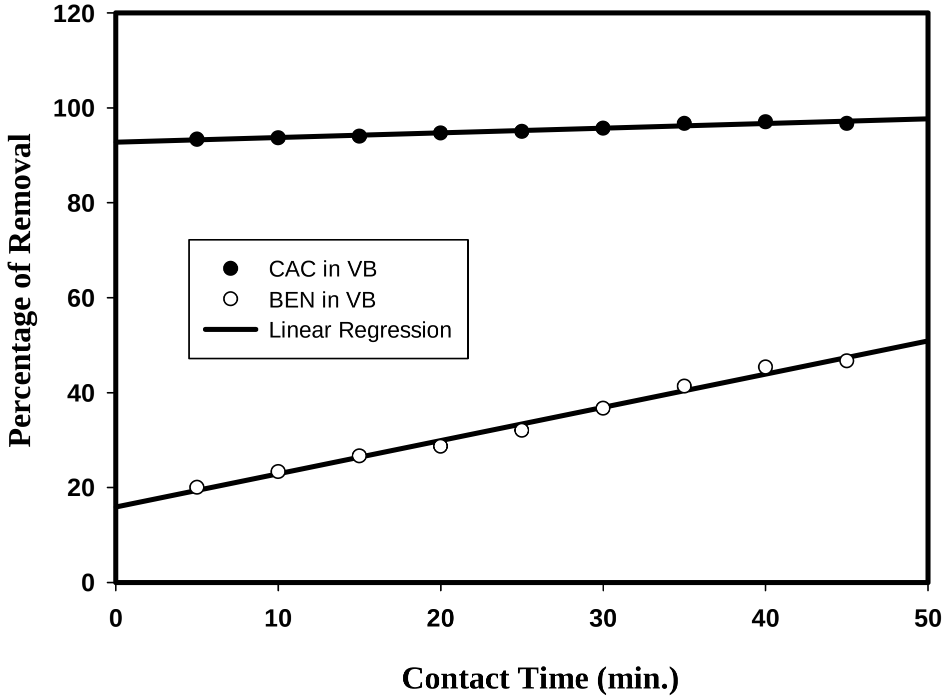


Figure 5: Effect of Contact Time Variation: Natarajn and Khalaf equation

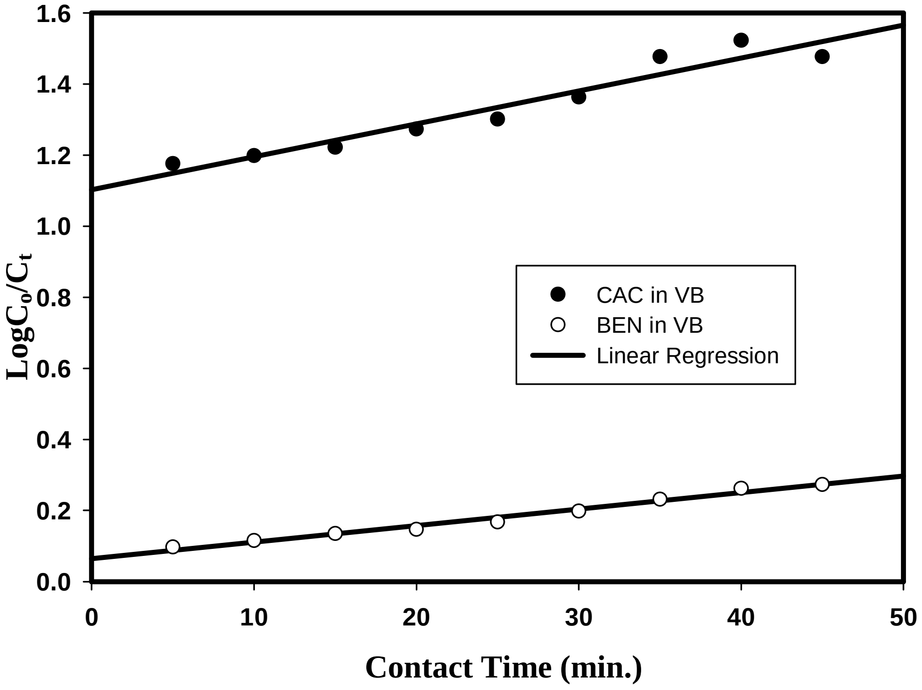
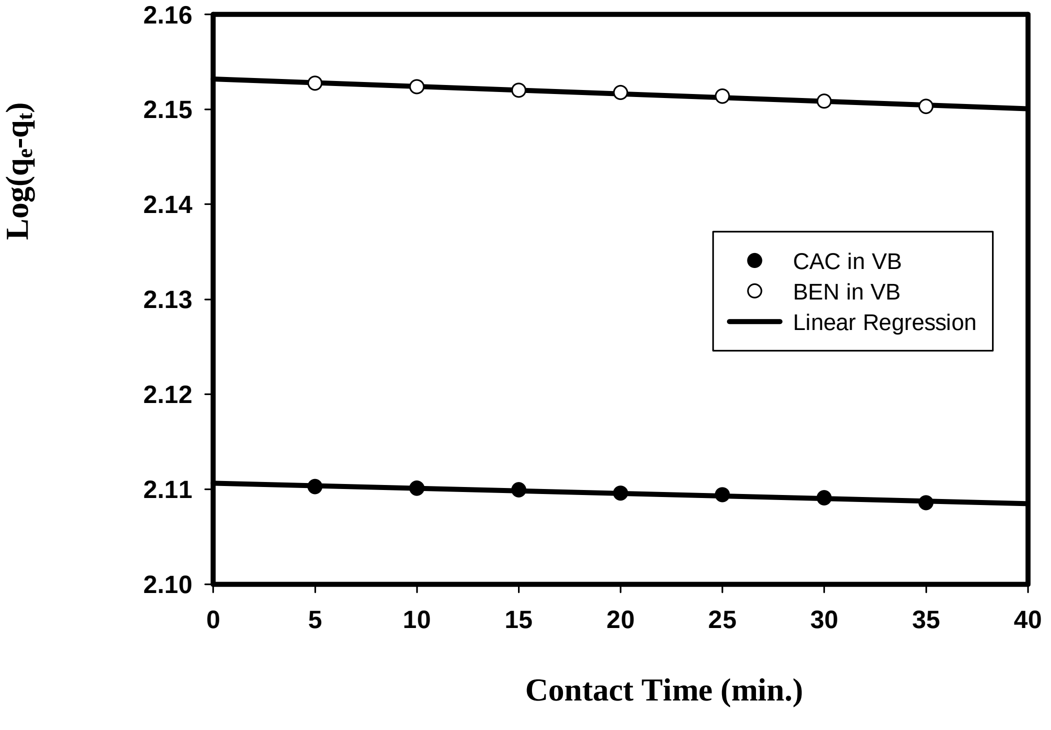


Figure 6: Effect of Contact Time Variation:

Lagergren equation



q_t

Figure 7: Effect of Contact Time Variation: Intra-Particle Diffusion model

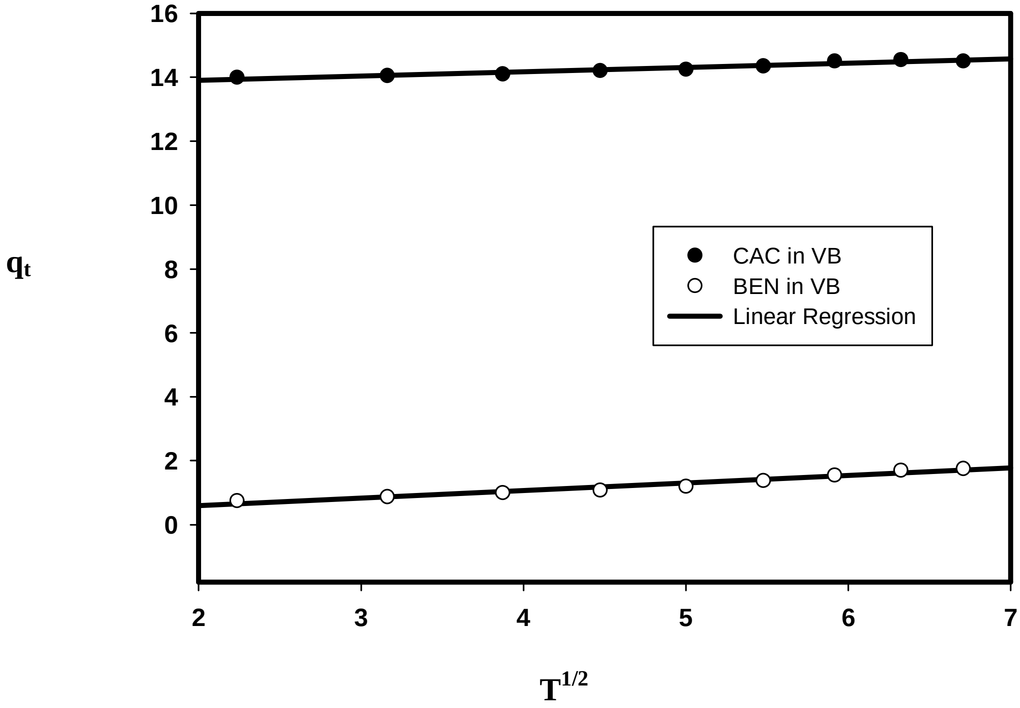


Figure 8: Effect of Contact Time Variation: Log (Time) vs Log (Percentage of Removal

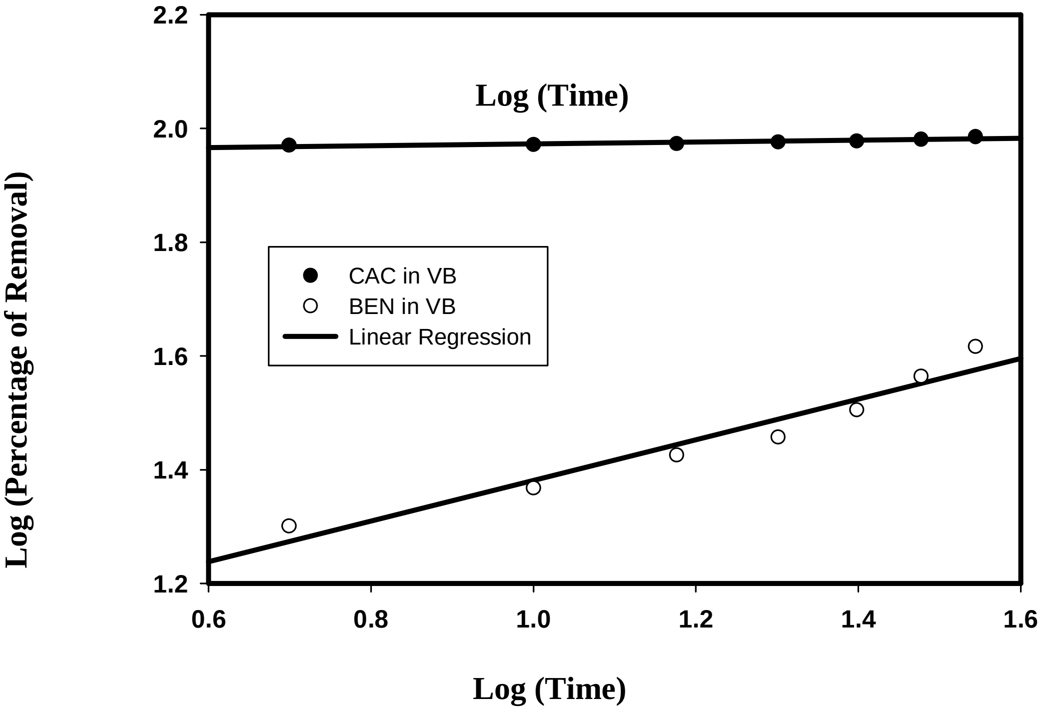
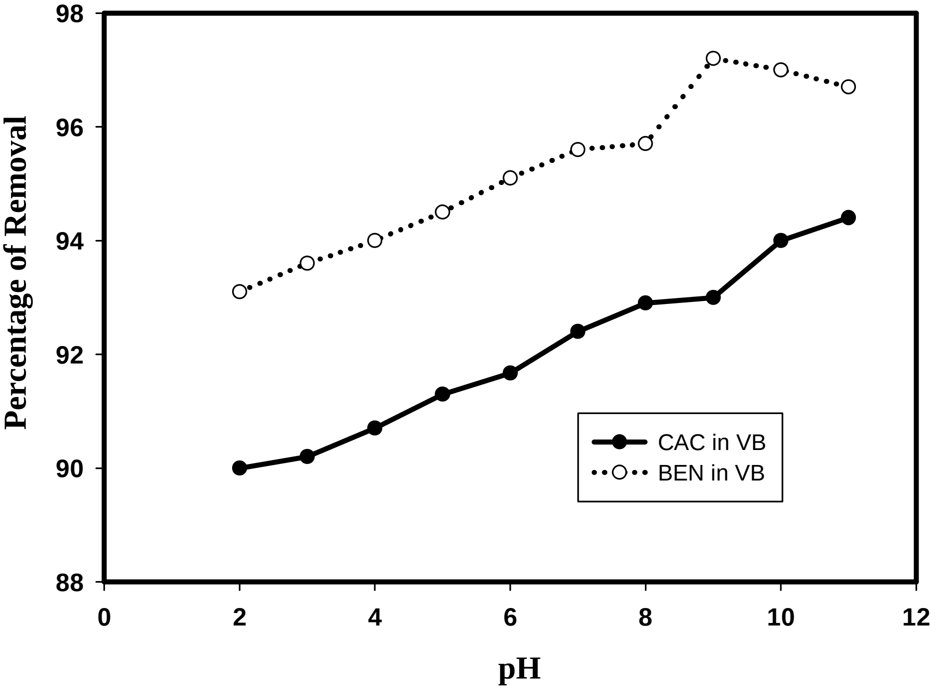


Figure 9: Effect of pH Variation



CONCLUSION

The removal of dye VB by adsorption process on bentonite as an adsorbent was found to decrease with increase in initial concentration of dye, increase in contact time, and increase in dose of adsorbent and decrease in P^H. The present study concludes that bentonite can be used as a better adsorbent for the effective removal of dyes from water and waste water.

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