THERMODYNAMICS AND ISOTHERMS ANALYSES ON THE REMOVAL OF METHYLENE BLUE DYE USING ACTIVATED NANO-POROUS CARBON

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ABSTRACT - This analytical paper aimed to evaluate the removal of Methylene Blue dyes from aqueous solution by using plant material from Cassia Auriculata. Batch adsorption studies were carried out by observing the effect of experimental parameters such as pH, contact time, initial concentration of the adsorbate, adsorbent dosage and temperature. Adsorption kinetic data were tested using pseudo-second-order, Elovich model and intra particle diffusion models. The present experimental data were found to follow the Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Hurkins-Jura, Halsey, Radlich-Peterson, Jovanovich and BET isotherm models. Thermodynamic parameters such as Gibbs free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were investigated. The study confirmed that removal of Methylene Blue dye using activated Cassia Auriculata is found to be favourable and hence it could be used as an adsorbent for the treatment of effluents from various dye industries.

KEYWORDS: Adsorption, Activated Cassia Auriculata Nano Carbon (ACANC), Methylene Blue dye, Kinetic models, Isotherm models and Thermodynamic Studies.

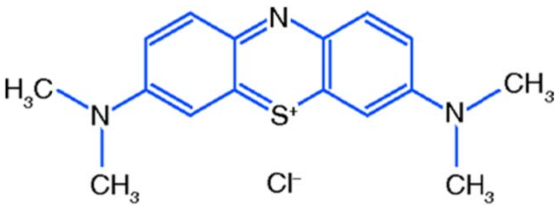
1. INTRODUCTION:

Nowadays the removal of dyes from wastewaters of various industries like textiles, plastics, paper, leather and food etc., are causing serious environmental problems. This waste water containsa non - biodegradable inorganic and organic material, surfactants, pesticides and some organic compounds.These types of wastewaters are difficult to treat.Several research reports proved that even small quantities of dyes are highly toxic which causes acute disorders to both aquatic organisms and non-aquatic organism. Methylene Blue (MB) is one of the most important cationic dyes used as a coloring agent in paper, cottons and wools, but the same time if it is present in water to produce various dangerous effects on human beings and animals. Further, it causes serious diseases such as heart rate increasing, nausea, vomiting, diarrhea and even cancer.In present day many treatment methods have been used to remove the dyes from wastewater namely electrochemical coagulation, reverse osmosis, nano filtration, adsorption using activated materials etc., Among these methods, adsorption is one of the best treatment method because of highly effective, low operating cost and economical method for the removal of both inorganic and organic pollutants from wastewaters. In this study has used Cassia Auriculata activated carbon. The carbon was prepared from through carbonization and activation process using concentrated sulphuric acid. The prepared activated carbon has high surface area, high adsorptive capacity and easily available. In the present work, the removal of Methylene Blue Dye from aqueous solutions using the above adsorbent with the following parameters viz the effects of initial dye concentration, contact time, pH and adsorbent dose on Methylene Blue adsorption have been studied and adsorption isotherm, kinetics are also established, calculated and discussed.

2. MATERIALS AND METHODS:

2.1 *PREPARATION OF ADSORBATE*:

The adsorbate was prepared by dissolving 1g of dye in 1L of distilled water to give concentration of 1000 mg/L. The serial dilutions say 25, 50, 75, 100 and 125 mg/L were made by diluting the dye stock solution in accurate proportions. The chemical structure of the Methylene Blue dye is shown in figure.



Structure of Methylene Blue

2.2 *PREPARATION OF ADSORBENT*:

The adsorbent (Cassia Auriculata) were collected from various regions of Tiruvarur District in Tamil Nadu, India. Further it was air –dried in sunlight and carbonized with concentrated sulphuric acid in the weight ratio of 1:1(w/v). The carbonized materials were powdered and activated in a muffle furnace kept at 800°C for a period of 60 minutes. The resulting carbon named as Activated Nano Carbon, finally it was stored in a vacuum desiccator.

3. RESULTS AND DISCUSSION:

3.1 *EFFECT OF CONTACT TIME*:

The effect of contact time on the amount of dye adsorbed was investigated at 1000 mg/L concentration of the dye (Fig. 1). It was observed that the percentage removal of dye increases rapidly with an increase in contact time initially, and thereafter, beyond a contact time of about 50 min, no noticeable change in the percentage removal was observed the percentage removals after 50 min were 93%. Therefore, the study found that the optimum contact time is considered to be 50 min. This is also the equilibrium time of the batch adsorption experiments, since beyond a contact time of 50 min, adsorption is not changed. The rapid removal of dye was observed at the beginning of the contact time due to the percentage of large number of binding sites available for adsorption.

3.2*EFFECT OF ADSORBENT DOSE:*

The adsorption of the Methylene Blue dye on Cassia Auriculata was studied by varying the adsorbent dose (25 – 125 mg/50ml) for 50 mg/L of dye concentration. The percentage of adsorption increased with increased in the adsorbent dose, which was attributed to increased carbon surface area and the availability of more adsorption sites**.** Hence, all studies were carried out with 0.025g of adsorbent/50 ml of the varying adsorbate solutions. 25,50,75,100 and 125 mg/L. The results obtained from this study were shown in Fig.2. The amount of Methylene Blue dye adsorbed per gram reduced with increased in the dosage of Cassia Auriculata. This revealed that the direct and equilibrium capacities of Methylene Blue dye were functions of the activated Cassia Auriculata dosage.

3.3 *EFFECT OF pH*:

The effect of pH on the adsorption of Methylene Blue dye onto ACANC was examined in the pH range of 2 to 10. Different pH solutions were prepared by adding 0.1 M HCl and 0.1 M NaOH solutions drop wise to achieve pH values. The Fig.3 revealed that the efficiency of Methylene Blue dye removal increased with increasing pH from 5 to 7 after that the marginal increase was observed. In the study observed that the highest Methylene Blue dye removal was achieved at pH range from 5 to 7.The results suggested that the removal efficiency of ACANC were found to decrease both at lower and higher than pH 9.5.

3.4ADSORPTION ISOTHERMS:

It is an important to determine the most appropriate correlation for equilibrium adsorption isotherm, to optimize the design of a sorption system. The Langmuir, Freundlich, Temkin, Dubinnin-Radushkevich, Hurkins-Jura, Halsay, Radlich-Peterson, Jovanovic and BET isotherm models were used to analyses the adsorption equilibrium. Experimental isotherm data were obtained at an adsorption time of 45 min at different temperatures.

3.4.1 *FREUNDLICH ADSORPTION ISOTHERM*

The Freundlich adsorption isotherm is based on the equilibrium adsorption on heterogeneous surfaces. This isotherm was derived from the assumption that the adsorption sites are distributed exponentially with respect to heat of adsorption. The adsorption isotherm is expressed by the following equation.

$$q_e = K_F C_e^{1/nF} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

This can be linearized as

$$\ln q_e = \ln K_F + 1/nF \ln C_e \ldots\ldots\ldots\ldots (2)$$

Where q_e is the amount of Methylene Blue dye adsorbed (mg/g), C_e is the equilibrium concentration of dye in solution (ppm). K_F(L/g) and 1/nF are the Freundlich constants related to adsorption capacity and sorption intensity, respectively.

The Freundlich constants K_F and $1/n_F$ were calculated from the slope and intercept of the $\ln q_e$Vs$\ln C_e$ plot, as shown in Fig.4, and the model parameters are shown in table 2. The magnitude of K_F showed that adsorbent had a high capacity for Methylene Blue dye adsorption from the aqueous solutions studied. The Freundlich exponent, n_F, should have values in the range of 1 and 10 (i.e., $1/n_F<1$) to be considered as favorable adsorption. A $1/n_F$ value of less than 1 indicated that Methylene Blue dye is favorably adsorbed by adsorbent. The Freundlich isotherm did not show a good fit to the experimental data as indicated by SSE and Chi-square statistics.

3.4.2 *LANGMUIR ADSORPTION ISOTHERM*

The theoretical Langmuir isotherm is used for adsorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. Therefore, the Langmuir isotherm model was chosen for estimation of the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface. The Langmuir non-linear equation is commonly expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad \ldots\ldots\ldots (3)$$

Where C_e is the equilibrium concentration of adsorbate in the solution (mg/L), q_e is the amount adsorbed at equilibrium (mg/g),q_m and b are Langmuir constants related to adsorption efficiency and energy of adsorption, respectively. The linear plots of $C_e/\ q_e$ vs. $C_e$as shown in Fig.5 suggest the applicability of the Langmuir isotherms. The values of q_m and b were calculated from slope and intercepts of the plots are given in Table 2. From the results, it is obvious that the value of adsorption efficiency q_m and adsorption energy b of the ACANC increases on increasing the temperature. The values can conclude that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with endothermic nature of adsorption. To confirm the favorability of the adsorption process, the separation factor (R_L) was determined and given in Table 3. The values were established to be between 0 and 1 and confirm that the ongoing adsorption process is favorable.

3.4.3 *TEMKINADSORPTIONISOTHERM*

The Temkin adsorption isotherm assumes that the heat of adsorption decreases linearly with the sorption coverage due to adsorbent-adsorbate interactions. The Temkin isotherm equation is given as:

$$q_e = \frac{RT}{bT} \ln(K_T C_e) \ \ldots\ldots\ldots\ldots\ldots (4)$$

This can be represented in the following linear form

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Where, K_T (L/g) is the Temkin isotherm constant, b_T (j/mol) is a constant related to heat of sorption, R is the ideal gas constant (8.314 J/mol K), and T is absolute temperature (k). A plot of q_e versus $\ln C_e$ enables the determination of isotherm constants K_T and b_T from the slope and intercept, as shown in Fig.6. The model parameters are listed in Table 2. The Temkin isotherm appears to provide a good fit to the Methylene Blue dye adsorption data.

The adsorption energy in the model, b_T, is positive for Methylene Blue dye adsorption from the aqueous solution, which indicates that the favorable adsorptions. The experimental equilibrium curve is close to that predicted by Temkin model. Consequently, the adsorption isotherm of Methylene Blue dye on ACANC can be described reasonably well by the Temkin isotherm.

3.4.4 *HURKINS-JURA ADSORPTION ISOTHERM*

The Hurkins-Jura adsorption isotherm can be expressed as:

$$q_e = \sqrt{\frac{A_H}{B_H + \log C_e}} \text{...................}(6)$$

This can rearranged as follows:

$$\frac{1}{qe^2} = \frac{B_H}{A_H} - \frac{1}{A_H}\log Ce \ldots\ldots\ldots (7)$$

Where, A_H (g^2/L) and B_H (mg^2/L) are two parameters characterizing the sorption equilibrium.

The isotherm equation accounts for multilayer adsorption and can be explained by the existence of a heterogeneous pore distribution. The Harkins-Jura isotherm parameters are obtained from the plots of $1/q_e^2$ versus log C_e enables the determination of model parameters A_H and B_H from the slope and intercept in Fig.7.

3.4.5 *HALSAY ADSORPTION ISOTHERM*

The Halsay adsorption isotherm can be given as

$$q_e = \exp\left(\frac{\ln K_{Ha} - \ln C_e}{n_{Ha}}\right) \text{.................}(8)$$

And, a linear form of the isotherm can be expressed as follows:

$$\ln q_e = \frac{\ln K_{Ha}}{n_{Ha}} - \frac{\ln C_e}{n_{Ha}} \text{................}(9)$$

Where, K_{Ha} (mg/L) and n_{Ha} are the Halsay isotherm constants.

A plot of lnqeVslnCe, shown in Fig.8, enables the determination of nHa and KHa from the slope and intercept. This equation is suitable for multilayer adsorption and the fitting of the experimental data to this equation attest to the heteroporous nature of adsorbent. Fig. 8 also shows that the experimental data and the model predictions based on the non-linear form of the Halsay models. The model parameters are listed in Table 2. This result also shows that the adsorption of Methylene Blue dye on ACANC was not based on significant multilayer adsorption. The Halsay model is also not suitable to describe the adsorption of Methylene Blue dye on ACANC, because this model also assumes a multilayer behavior for the adsorption of adsorbate onto adsorbent.

3.4.6 *RADLICH-PETERSON ADSORPTION ISOTHERM*

The Radlich-Peterson adsorption isotherm contains three parameters and incorporates the features of Langmuir and Freundlich isotherms into a single equation. The general isotherm equation can be described as follows

$$q_e = \frac{K_R C_e}{1 + a_R C_e^g} \text{.................}(10)$$

The linear form of the isotherm can be expressed as follows:

$$\ln\frac{C_e}{q_e} = g\ln C_e - \ln K_R \text{..............}(11)$$

Where, K_R (L/g) and a_R (L/mg) are the Radlich-Peterson isotherm constants and ‘g’ is the exponent between 0 and 1. There are two limiting cases: Langmuir form for g=1 and Henry’s law for g=0.

A plot of $\ln C_e/q_e$ versus $\ln C_e$ shown in Fig.9 enables the determination of isotherm constants g and K_R from the slope and intercept. The values of $K_{R,}$ presented in table 2, indicate that the adsorption capacity of the ACANC decreased with an increase temperature. Furthermore, the value of g lies between 0 and 1, indicating favorable adsorption.

3.4.7 *DUBININ-RADUSHKEVICH ADSORPTION ISOTHERM*

The Dubinin-Radushkevich adsorption isotherm is another isotherm equation. It is assumed that the characteristic of the sorption curve is related to the porosity of the adsorbent. The linear from of the isotherm can be expressed as follows

$$\ln q_e = \ln Q_D - B_D\left[RT\ln\left(1 + \frac{1}{C_e}\right)\right]^2 \text{..............}(12)$$

Where, Q_D is the maximum sorption capacity (mol/g), and B_D is the Dubinin-Radushkevich constant (mol^2/kJ^2). A plot of $\ln q_e$Vs$R_T\ln(1+1/C_e)$ shown in Fig.10 enables the determination of isotherm constants B_D and Q_D from the slope and intercept. The Q_D values obtained (table 2) from the graph shows the adequate tendency of ACANC adsorbent to adsorb Methylene Blue.

3.4.8 *JOVANOVIC ADSORPTION ISOTHERM*

The model of an adsorption surface considered by Jovanovic is essentially the same as that considered by Langmuir. The Jovanovic model leads to the following relationship:

$$q_e = q_{max}\left(1 - e^{K_J C_e}\right) \text{ ……….. (13)}$$

The linear form of the isotherm can be expressed as follows:

$$\ln q_e = \ln q_{max} - K_J C_e \text{ ………… (14)}$$

Where, K_J (L/g) is a parameter. Q_{max} (mg/g) is the maximum Methylene Blue dye uptake.

The q_{max} is obtained from a plot of $\ln q_e$ and C_e shown in Fig.11, Their related parameters are listed in table 2. By comparing the values of the error functions, it was found the Langmuir and Jovanovic models are best to fit the Methylene Blue dye adsorption on the ACANC. Both models show a high degree of correlation.This is clearly confirms the good fitness of Langmuir and Jovanovic with the experimental data for removal of Methylene Blue dye from the solution.

3.4.9 *THE BRUNAUER-EMMETT-TELLER (BET) ISOTHERM MODEL*

Brunauer-Emmett-Teller (BET) isotherm is a theoretical equation, most widely applied in the gas-solid equilibrium systems. It was developed to derive multilayer adsorption systems with relative concentration ranges from 10 to 50 mg/L corresponding to a monolayer coverage lying between 0.1439 and 0.0528. Its extinction model related to liquid-solid interface is exhibited as:

$$q_e = \frac{q_s C_{BET} C_e}{(C_s - C_e)[1 + (C_{BET} - 1)(C_e / C_s)]} \text{ ....(15)}$$

Where, C_{BET}, Cs, qs and qe are the BET adsorption isotherm relating to the energy of surface interaction (L/mg), adsorbate monolayer saturation concentration (mg/L), theoretical isotherm saturation capacity (mg/g) and equilibrium adsorption capacity (mg/g), respectively. As C_{BET} and C_{BET} (C_e/C_s) is much greater than 1,

In the linear form as used is represented as

$$\frac{C_e}{q(C_s - C_e)} = \frac{1}{q_s C_{BET}} + \left(\frac{C_{BET} - 1}{q_s C_{BET}}\right)\left(\frac{C_e}{C_s}\right) \text{ ....(16)}$$

In the BET isotherm model for slope and intercept of the C_e/q_e (C_s-C_e) VsC_e/C_s shown in Fig.12, plot were used to calculate C_{BET} and q_s the arrived C_{BET} and q_s values are listed in table 2, the BET model graph indicates the physical nature of adsorption of Methylene Blue dye onto ACANC.

3.5 KINETIC PARAMETERS:

The rate and mechanism of the adsorption process can be elucidated based on kinetic studies. Methylene Blue dye adsorption on solid surface may be explained by two distinct mechanisms: (1) an initial rapid binding of Methylene Blue dye molecules on the adsorbent surface; (2) relatively slow intra-particle diffusion. To analyze the adsorption kinetics of the Methylene Blue dye, the pseudo-first-order, the pseudo-second-order, and intra-particle diffusion models were applied. Each of these models and their linear modes of them equations presented in below.

KINETIC MODELS AND THEIR LINEAR FORMS

Model	Nonlinear Form	Linear Form	Number of Equation
Pseudo-first-order	$dq_t / d_t = k_1 (q_e - q_t)$	$\ln (q_e - q_t) = \ln q_e - k_1 t$	(17)
Pseudo-second-order	$dq_t / d_t = k_2 (q_e - q_t)^2$	$t/q_t = \frac{1}{k^2 q_e^2 + (1/q_e)t}$	(18)

Where, q_e and q_t refer to the amount of Methylene Blue dye adsorbed (mg/g) at equilibrium and at any time, t (min), respectively and k_1 (1/min), k_2 (g/mg.min) are the equilibrium rate constants of pseudo-first order and pseudo-second order models, respectively.

Pseudo-first order is a simple kinetic model, which was proposed by Lagergren during 1898 and is used for estimation of the surface adsorption reaction rate. The values of ln (q_e-q_t) were linearly correlated with t. The plot of ln (q_e-q_t) Vs t should give a linear relationship from which the values of k_1 were determined from the slope of the plot. In many cases, the first-order equation of Lagergren does not fit well with the entire range of contact time and is generally applicable over the initial stage of the adsorption processes.

In the pseudo-second order model, the slope and intercept of the t/qtVs t plot were used to calculate the second-order rate constant, k_2. The values of equilibrium rate constant (k_2) are presented in Table 5. According to Table 5, the values of R^2 (0.999) related to the pseudo-second order model revealed that Methylene Blue dye adsorption followed this model.

3.6 THE ELOVICH EQUATION:

The Elovich model equation is generally expressed as

The simple Elovich model is expressed in the form,

$$q_t = \alpha + \beta \ln t \text{ ………………..(19)}$$

Where α is the initial adsorption rate (mg g^{-1} min^{-1}) and β is the desorption constant (g/mg) during any one experiment. To simplify the Elovich equation.Chien and Clayton (1980) assumed αβt>>t and by applying boundary conditions q_t=0 and q_t at t=t Eq.(19) becomes:

$$Q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t \text{ ……(20)}$$

Methylene Blue dye adsorption fits with the Elovich model, a plot of $q_t$vs.ln(t) yields a linear relationship with a slope of (1/β) and an intercept of (1/β)ln(αβ). The Elovich model parameters α,β, and correlation coefficient (γ) are summarized in Table 5. The experimental data such as the initial adsorption rate (α) adsorption constant (β) and the correlation co-efficient (γ) calculated from this model indicates that the initial adsorption (α) increases with temperature similar to that of initial adsorption rate (h) in pseudo-second-order kinetics models. This may be due to increase the pore or active site on the adsorbent

3.7INTRA-PARTICLE DIFFUSION MODEL:

Kinetic data was further analyzed using the Intra-particle diffusion model based on the theory proposed by Weber and Morris. The amount of Methylene Blue dye adsorbed (q_t) at time‘t’ was plotted against the square root of time ($t^{1/2}$), according to eq.

$$q_t = K_{id} t^{1/2} + C \text{………………..(21)}$$

Where, K_{id} is the Intra-particle diffusion rate constant and c is the intercept related to the thickness of the boundary layer. According to above equation a plot of $q_t$vs $t^{1/2}$ gives a straight line from the origin says the adsorption mechanism follows the intra-particle diffusion process only. However, the data exhibit multi linear plots, says the process are governed by two or more steps, it is clear from that there are two separate zones: first linear portion (phase I) and second linear part (phase II). The first linear portion (Phase I) can be attributed to the immediate utilization of the most readily available adsorbing sites on the adsorbent surface, phase II may be attributed to very slow diffusion of the adsorbate from the surface site in to the inner pores. Thus initial portion of Methylene Blue dye adsorption by adsorbent may be governed by the initial intra-particle transport of Methylene Blue dye controlled by surface diffusion process and the later part controlled by pore diffusion. However, the intercept of the line fails to pass through the origin which may be due to the difference in the rate of mass transfer in the initial and final stages of adsorption. Further, such deviation of the straight lines from the origin reveals that the pore diffusion is not the sole rate-controlling.

3.8THERMODYNAMIC STUDIES:

Thermodynamic parameters related to the adsorption process, i.e., Gibb’s free energy change (ΔG^0, KJ mol^{-1}), enthalpy change (ΔH^0, KJ mol^{-1}) and entropy change (ΔS^0, J mol^{-1} K^{-1}) are determined by the following equations:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \text{ ……………(22)}$$

$$\Delta G^0 = -RT\ln(K_c) \text{ ……………..(23)}$$

Where, R is the universal gas constant (8.314 JK^{-1} mol^{-1}), T is the absolute temperature (Kelvin) and K represents the equilibrium adsorption constants of the isotherm fits (K_L, Langmuir equilibrium constant and K_f, Freundlich equilibrium constant, which must be converted to SI units, by using the molecular mass of the dye) obtained from the isotherm plots. ΔH^0 and ΔS^0 values can be calculated from the slope and intercept of the linear plot of ln(K) versus 1/T. Thermodynamic results are depicted in Table4. Enthalpy changes (ΔH^0) indicate that adsorption followed endothermic processes. Negative values of ΔG^0 indicate that the Methylene Blue dye adsorption by the adsorbent is spontaneous and favorable processes for all studied temperatures. The positive values of ΔS^0 confirm a high preference of Methylene Blue molecules for the carbon surface of adsorbent and also suggest the possibility of some structural changes or readjustments in the dye-carbon adsorption complex. Besides, it is consistent with the dehydration of dye molecule before its adsorption to carbon surface, and the releases water molecules to the bulk solution. The increase in the adsorption capacities of adsorbent at higher temperatures may be attributed to the enhanced mobility and penetration of dye molecules within the adsorbent porous structures by overcoming the activation energy barrier and enhancing the rate of intra-particle diffusion.

In order to support that physical adsorption is the predominant mechanism, the values of activation energy (Ea) and sticking probability (S^*) were calculated from the experimental data. They were calculated using modified Arrhenius type equation related to surface coverage (θ) as follows:

$$\theta = \left(1 - \frac{C_e}{C_i} \right) \ldots\ldots\ldots\ldots\ldots\ldots (24)$$

$$S* = (1-\theta)_e \frac{-E_a}{RT} \ldots\ldots\ldots\ldots\ldots (25)$$

The sticking probability, S^*, is a function of the adsorbate/adsorbent system under consideration but must satisfy the condition $0 < S^* < 1$ and is dependent on the temperature of the system. The values of E_a and S^* can be calculated from slope and intercept of the plot of ln(1-θ) versus 1/T respectively and are listed in table 4.

The result as shown in table 4 indicate that the probability of the Methylene Blue dye to stick on surface of biomass is very high as $S^* << 1$, these values confirm that, the sorption process is physisorption. The activation energy (E_a) value 40 KJ/mol confirms the physical nature of adsorption.

3.9 CONCLUSION:

On the basis of the above studies, the following can be concluded:

Characterization of Cassia Auriculata was carried out which revealed that the surface of the adsorbent was rough and suitable for adsorption. Cassia Auriculata has shown a potential to remove Methylene Blue dye from aqueous solution. Initial concentration of the Methylene Blue dye plays an important role in the removal process. Kinetics of the removal was studied and the values of rate constants were determined. The dye removal was found to be governed by film diffusion mechanism where external transport of the adsorbate over surface of the adsorbent is greater than internal transport which was confirmed by the intra-particle diffusion and the process of removal was found to follow second order kinetics. Thermodynamic parameters were calculated for the removal of Methylene Blue dye and their values indicated that the process of removal was spontaneous and endothermic. The equilibrium data's were found to best fitted in Langmuir and BET isotherm model. It can therefore be concluded that Cassia Auriculata offers promise as an economically viable alternative for sequestering of the Methylene Blue dye from the aqueous solution. The work can be extended for the removal of Methylene Blue dyes from effluents as well.

Table: 1. Equilibrium parameters for the adsorption of methylene blue dye onto acanc

M_0	**C_e (mg / L)**				**Q_e (mg / L)**				**Removal %**			
	30°C	**40°C**	**50°C**	**60°C**	**30°C**	**40°C**	**50°C**	**60°C**	**30°C**	**40°C**	**50°C**	**60°C**
25	1.5308	0.9185	0.6130	0.5817	46.939	48.163	48.774	48.837	93.877	96.326	97.548	97.673
50	3.3677	3.0629	2.7682	2.1438	93.265	93.870	94.464	95.712	93.265	93.874	94.464	95.712
75	7.3728	6.6754	5.8169	5.3895	135.25	136.65	138.37	139.22	90.170	91.100	92.244	92.814
100	10.7410	9.8227	9.3174	8.7398	178.52	180.35	181.37	182.52	89.259	90.177	90.683	91.260
125	15.919	15.367	15.028	14.136	218.16	219.26	219.94	221.73	87.264	87.706	87.977	88.691

Table: 2. Isotherm parameters for the adsorption of methylene blue dye onto acanc

Model	**Constant**	**Temperature (° C)**			
		30	**40**	**50**	**60**
Freundlich	**K_f(mg/g) (L/mg)$^{1/n}$**	38.282	50.584	60.429	64.248
	N	1.5576	1.8483	2.0949	2.1135
Langmuir	**Q_m(mg/g)**	347.14	295.25	273.85	269.18
	b (L/mg)	0.0999	0.1633	0.2251	0.2671
Temkin	**b_T (J/mol)**	71.122	59.693	52.713	53.053
	K_T (L/mg)	1.3093	2.5468	3.2691	3.5612
Hurkins-Jura	**A_H (g^2/L)**	-2502.3	-2987.1	-3409.4	-3533.4
	B_H (mg^2/L)	-1.1008	-1.0786	-1.0616	-1.0293
Halsay	**K_{Ha}(mg/L)**	292.19	1411.1	5390.0	6620.8
	n_{Ha}	1.5576	1.8483	2.0949	2.1135
Radlich-Peterson	**G**	0.3580	0.4590	0.5227	0.5269
	K_R (L/g)	0.0261	0.0198	0.0165	0.0156

Dubinin-Radushkevich	**q_s (mg/g)**	172.44	162.45	159.53	164.06
	$K_D \times 10^{-4}$ mol^2 kJ^{-2}	1.6397	1.6192	1.6097	1.6148
Jovanovic	**K_J (L/g)**	0.0970	0.0972	0.0959	0.0998
	q_{max} (mg/g)	55.529	59.574	63.328	65.388
BET	**C_{BET} (L/mg)**	14.515	26.055	39.976	47.047
	qs (mg/g)	0.0689	0.0384	0.0250	0.0213

Table: 3. Dimensionless seperation factor (r_l) for the adsorption of methylene blue dye onto acanc

(C_i)	**Temperature °C**			
	30°C	**40°C**	**50°C**	**60°C**
25	0.2860	0.1967	0.1509	0.1302
50	0.1668	0.1091	0.0816	0.0697
75	0.1178	0.0755	0.0559	0.0475
100	0.0910	0.0577	0.0425	0.0361
125	0.0742	0.0467	0.0343	0.0291

Table: 4. Thermodynamic parameter for the adsorption of methylene blue dye onto acanc

(C_0)	**ΔG^0**				**ΔH^0**	**ΔS^0**	**E_a**	**S^***
	30°C	**40°C**	**50°C**	**60°C**				
25	-6877.1	-8500.4	-9891.4	-10346.3	29.079	119.44	27.963	8×10^{-7}
50	-6620.5	-7102.8	-7618.2	-8598.1	12.824	63.864	12.123	6×10^{-4}
75	-5582.9	-6052.5	-6649.1	-7083.2	9.8805	51.014	9.0466	3×10^{-3}
100	-5334.2	-5769.5	-6110.6	-6494.6	6.2484	38.288	5.6418	1×10^{-2}
125	-4848.1	-5113.2	-5344.7	-5702.1	3.5949	27.821	3.1626	4×10^{-2}

Table: 5. The kinetic parameters for the adsorption of methylene blue dye onto acanc

C_0	**Temp °C**	**Pseudo second order**				**Elovich model**			**Intraparticle diffusion**		
		q_e	**k_2**	**γ**	**h**	**α**	**β**	**γ**	**K_{id}**	**γ**	C
25	**30**	49.383	0.0053	0.9877	12.81	3.8×10^3	0.2345	0.9874	0.0977	0.9962	1.7939
	40	49.507	0.0097	0.9869	23.68	5.6×10^6	0.3909	0.9894	0.0554	0.9889	1.8823
	50	49.636	0.0151	0.9897	37.26	6.4×10^{10}	0.5856	0.9934	0.0360	0.9908	1.9233
	60	49.652	0.0160	0.9908	39.46	2.9×10^{11}	0.6171	0.9904	0.0340	0.9898	1.9274
50	**30**	96.540	0.0036	0.9930	33.94	3.5×10^5	0.1636	0.9938	0.0692	0.9945	1.8407
	40	96.975	0.0040	0.9897	37.22	7.8×10^5	0.1712	0.9884	0.0654	0.9898	1.8514
	50	97.520	0.0044	0.9923	41.94	2.0×10^6	0.1796	0.9904	0.0617	0.9888	1.8630
	60	98.287	0.0048	0.9940	46.40	1.2×10^7	0.1982	0.9874	0.0550	0.9908	1.8794
75	**30**	138.40	0.0036	0.9880	69.37	3.0×10^8	0.1630	0.9884	0.0471	0.9948	1.8660
	40	140.48	0.0040	0.9871	78.01	8.7×10^7	0.1500	0.9945	0.0505	0.9888	1.8694
	50	142.77	0.0034	0.9863	69.74	6.9×10^6	0.1287	0.9930	0.0584	0.9908	1.8608
	60	142.61	0.0047	0.9865	96.32	1.7×10^8	0.1516	0.9946	0.0490	0.9888	1.8821
100	**30**	183.26	0.0036	0.9884	120.49	7.0×10^7	0.1112	0.9920	0.0521	0.9929	1.8606
	40	185.06	0.0034	0.9893	115.19	5.7×10^7	0.1091	0.9878	0.0527	0.9898	1.8629
	50	185.92	0.0036	0.9914	123.12	1.0×10^8	0.1118	0.9909	0.0511	0.9953	1.8687
	60	187.12	0.0035	0.9925	124.28	1.2×10^8	0.1118	0.9940	0.0507	0.9909	1.8721
125	**30**	223.19	0.0021	0.9912	107.08	1.3×10^8	0.0949	0.9887	0.0503	0.9911	1.8455
	40	224.45	0.0021	0.9933	106.40	1.1×10^8	0.0935	0.9947	0.0509	0.9898	1.8468
	50	224.80	0.0022	0.9880	113.03	3.6×10^8	0.0990	0.9934	0.0478	0.9908	1.8538
	60	226.83	0.0020	0.9940	106.46	1.1×10^8	0.0925	0.9904	0.0508	0.9940	1.8512

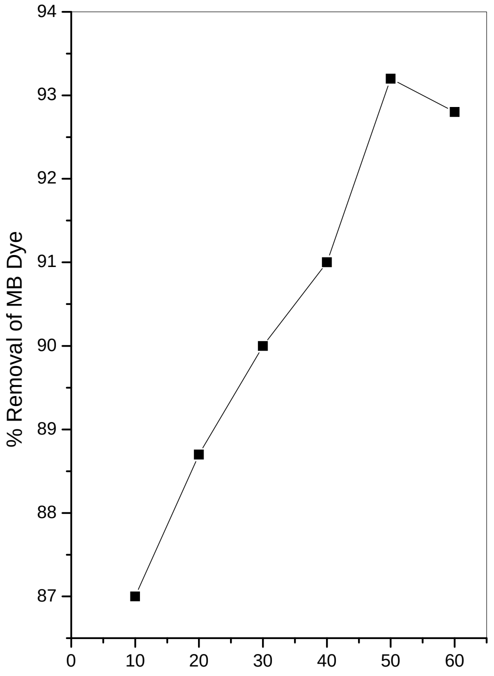


Fig.1- Effet of Contact Time in Min

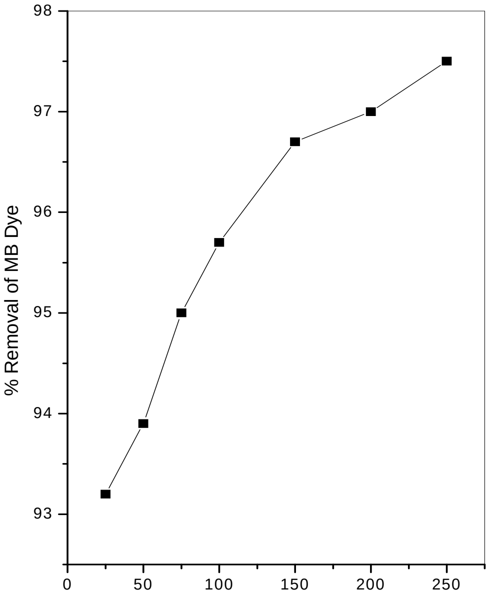


Fig.2-Adsorbent dose in mg

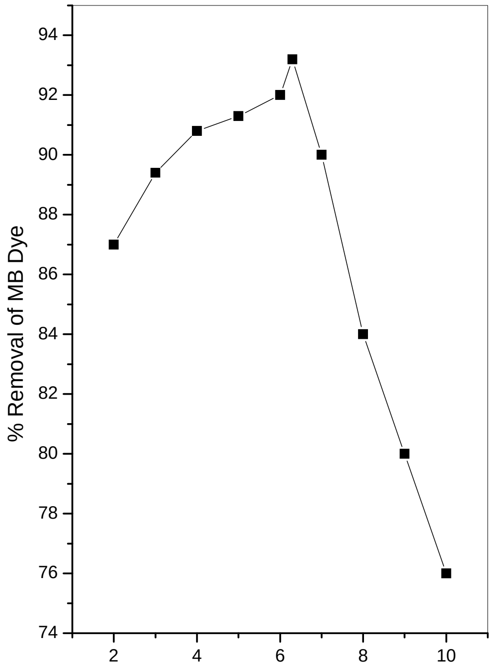


Fig.3- Effect of initial pH

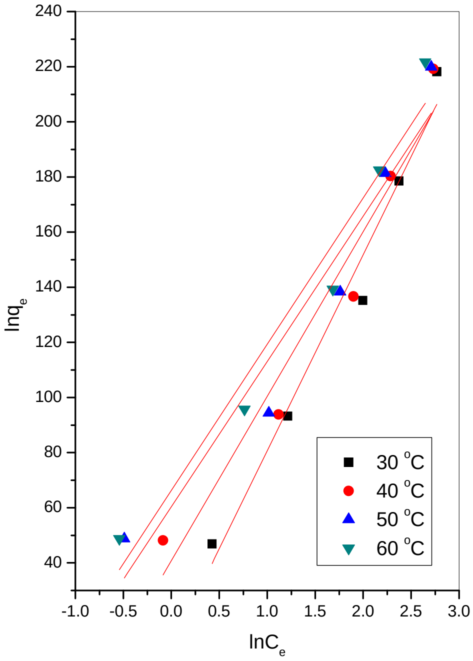


Fig.4- Freundlich adsorption isotherm

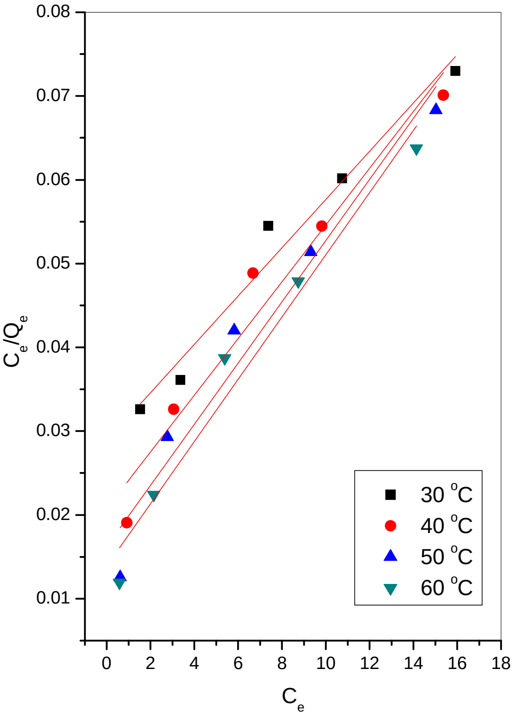


Fig.5- Langmuir adsorption isotherm

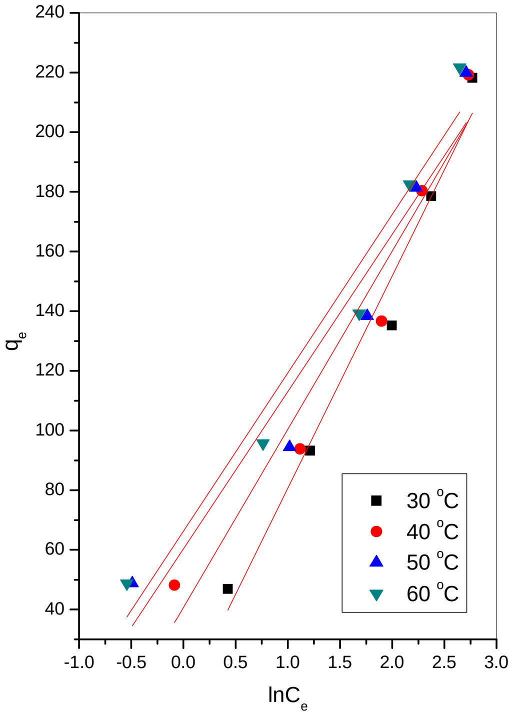


Fig.6 - Temkin adsorption isotherm

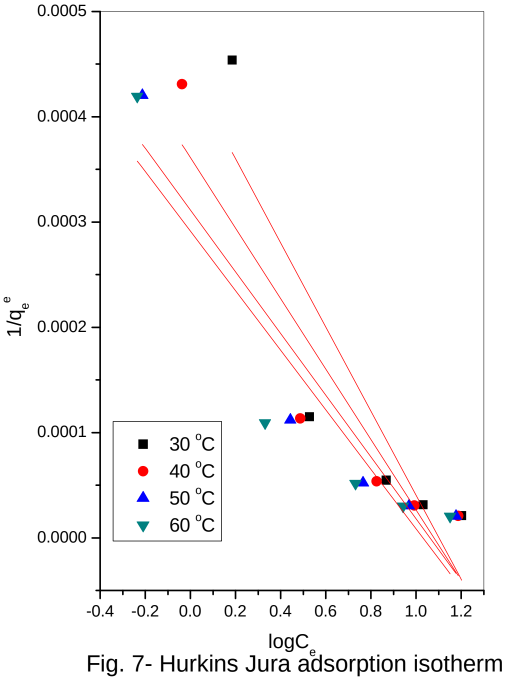


Fig. 7- Hurkins Jura adsorption isotherm

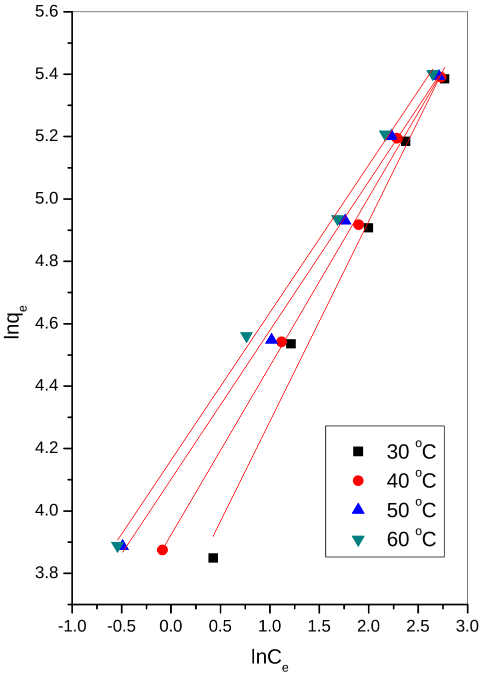


Fig.8- Halsay adsorption isotherm

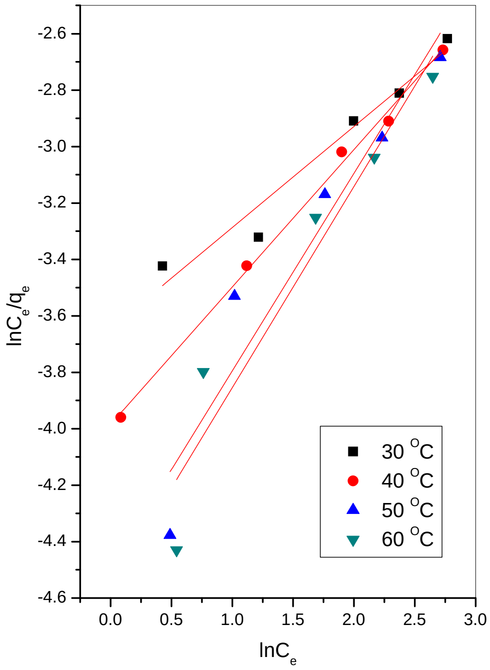


Fig.9 - Radlich - Peterson adsorption isotherm

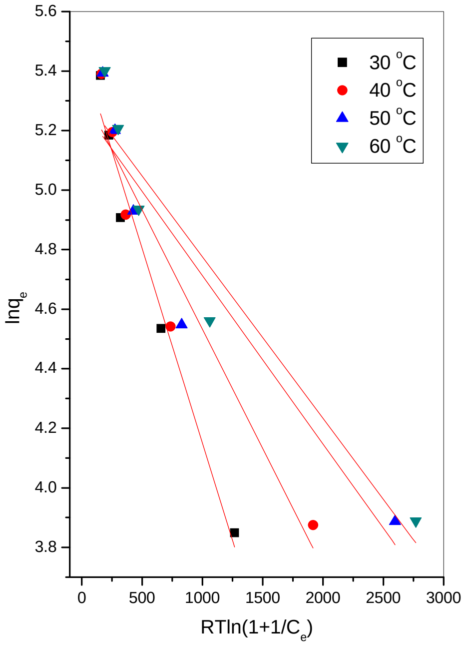


Fig.10- Dubinin-Radushkevich adsorption isotherm

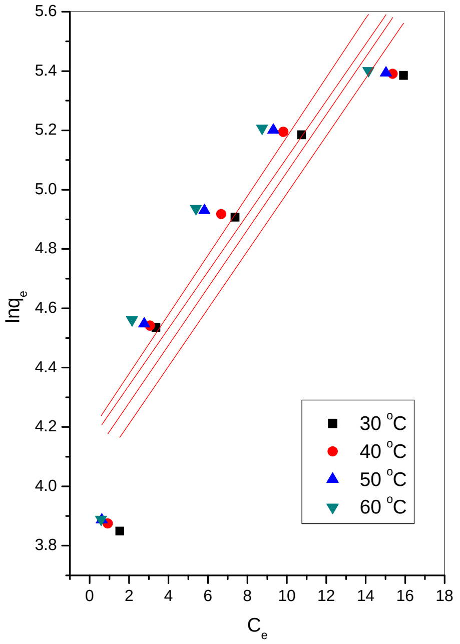


Fig.11-Jovanovic adsorptio isotherm

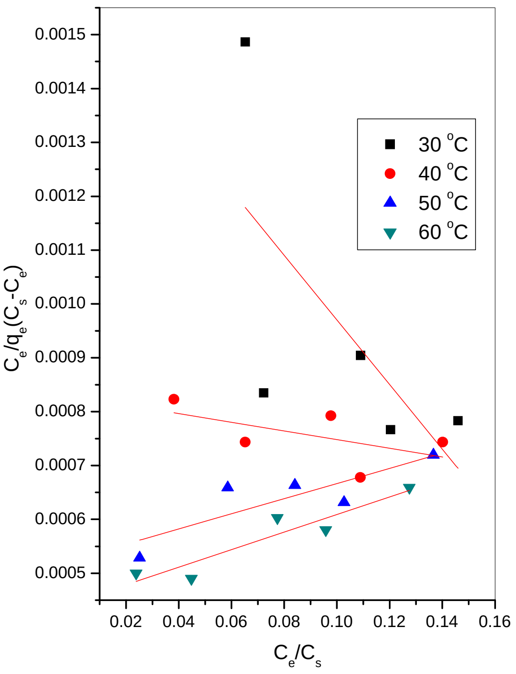


Fig.12- BET adsorption isotherm

REFERENCES:

[1] K. Ramesh, A. Rajappa, V. Nandhakumar, Research Journal of Chemical Sciences, July 2014, 4(7), 36-42.

[2] P. Manivannan, S. Arivoli, Raja Mohammed, Research Journal of Chemical and Environmental Sciences, December 2015, 3(6), 50-58.

[3] C. Pragathiswaran, N. Anantha Krishnan, B. MahinAbbubakkar, P. Govindhan, K. A. Syed Abuthahir, International Journal of Research in Pharmacy and Chemistry, 6(1), 95-103.

[4] A. Janet, R. Kumaresan, S. Uma Maheswari, Middle-East Journal of Scientific Research, 2015, 23(2), 308-317.

[5] Sachin, M. Kanawade, R.W. Gaikwad, International Journal of Chemical Engineering and Applications, October 2011, 2(5).

[6] M. Jerald Antony Joseph, N.Xavier, International Journal of Applied Biology andPharmaceutical Technology, July-Sep 2012,3(3).

[7] P. Srinivasan, P. Sivakumar, S. Raja, Arch. Appl. Sci. Res., 2013, 5(6), 132-140.

[8] Koninika Tanzim, M.Z. Abedin, International Journal of Scientific & Technology, December 2015, 4(12).

[9] S.E. Abechi, C.E. Gimba, A. Uzairu, J.A. Kagbu,O.J. Ocholi, International Refereed Journal of Engineering and Science, May 2013, 2(5), 38-45.

[10] Obuge, A. Macaulay, O.B Evbuomwan, International Journal of Engineering and Technical Research, October 2014, 2(10).

[11] C.Theivarasu, S. Mylsamy, N. Sivakumar,Universal Journal of Environmental Research and Technology, 2011, 1, 70-78.

[12] O. A. Gulnaz,F. Kaya, F. Matyar,B.Arikan, et al., J.Hazardous Materials, 2004, 108, 183-188.

[13] M. Zhao, Z. Tang, P. Liu, J.Hazardous Materials,2008, 158, 43-51.

[14] T. Robinson, B.Chandran, P.Nigam,Environ. Int.,2002, 28, 29-33.

[15] S. Wnag, Y. Boyjoo, A. Choueib, Chemosphere 60,2005, 1401-1407.

[16] A. O”zer, G. Dursun, J. Hazard Materials,2007, 146, 262-269.

[17] K.A. Strivastava, S.K. Gupta, M.V.S. Iyer, J. of Inst. Public Health Eng. India, Part 2/3, 1984,59-64.

[18] D.Nevskaia. A. Saantianes. V. Munoz, A. Guerrero-Ruiz et al., Carbon 37, 1999, 1065-1074.

[19] M.F. Froix, R. Nelson,Macromolecules 8, 1975,726-730.

[20] S.S. Barton,Carbon 25, 1987,343-350.

[21] M.A.M. Al- ghouti, S.J. Allen, M.N. Ahmed et al, Journal of EnvironmentalManagement,2003,69, 229-238.

[22] S. Arivoli, K. Kalpana, R. Sudha, T. Rajachandrasekar, E.J Chem. 2007, 4, 238-254.

[23] Renmin Gong, yingzhi Sun, Jian Chen, Huijun Liu, and Chao yang, Dyes and Pigments, 2005, 67,179.

[24] V. Vadivelan, K.J Vasanthkumar, J. Colloid Interface Sci.,2005, 286, 91.

[25] S.H Chien, W.R Clayton, Soil Sci. Sco, Am. J., 1980, 44, 265-268.

[26] W.J Weber, J.C Morris, J, Sanitary Eng, Div.1964, 90, 79.