

Removal of Reactive Blue 82 dye from Aqueous Solution with Adsorption Technique using Organic Adsorbents

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Abstract—This study was aimed to use *Gigantia Leaves (GL)*, *Curcuma Longa Leaves (CLL)*, *Morienga Oleifera (MO)* and *Citrus Sinensis (CS)* as a potential adsorbents to remove C.I. Reactive Blue 82 dye from aqueous solution. The adsorption of Reactive Blue 82 on adsorbents was studied as a functions of dose (50-300 g/L), pH solution (2-12), contact time (30 min). The influence of these parameters on the adsorption capacity was studied using the batch process. The corresponding results showed that excellent colour removal of Reactive Blue 82 can be achieved with adsorbents at optimum pH of 2. The maximum colour of *Gigantia Leaves*, *Curcuma Longa Leaves*, *Morienga Oleifera* and *Citrus Sinensis* was 90.36%, 80%, 75.81% and 70.90% respectively. The experimental data were analyzed by the Langmuir, Freundlich isotherms, Kinetic studies, and Interruption studies. Results show that the data fitted well with the Freundlich isotherm. The kinetics of Reactive Blue 82 adsorption onto adsorbents was examined using the pseudo-first and pseudo-second order. The adsorption kinetics followed the pseudo-second order kinetic model which implies that chemisorption is the rate limiting step. Pore diffusion seems to be the rate controlling in the sorption process as indicated by interruption studies.

Keywords— Adsorption, C.I. Reactive Blue 82, *Gigantia Leaves*, *Curcuma Longa Leaves*, *Moringa Oleifera*, *Citrus Sinensis*

I. INTRODUCTION

Synthetic dyes are widely used in industries, producing a large amount of toxic, carcinogenic, mutagenic, bio-accumulative wastewaters that pollute the environment [1]. Their discharges into effluents involve a significant source of pollution due to their recalcitrance nature. Furthermore dyes may impart toxicity to aquatic and plants biota and may be mutagenic and carcinogenic, causing severe damage to human life; such as disfunction of kidneys, reproductive system, liver, brain, and central nervous system [2]-[3]-[4]. A majority of the used dyes are azo dyes which are bright in colour due to the presence of one or several azo ($-N=N-$) groups associated with substituted aromatic structures [5]. Therefore, efficient and effective treatment approaches are necessary to overcome these problems.

At present, many treatment technologies, such as adsorption, flocculation, super filter film, oxidation and electrolysis, have been employed for dye removal from wastewaters. Among them, adsorption is considered to be superior because of the high efficiency and subsequently economical value [6]. Activated carbon, the prevalent adsorbent, is effective for dye removal. However, because of its high price and hard regeneration the wide applications of activated carbon were limited [7]-[8]-[9]-[10]. Thus, more economic, efficient and practical adsorbents are necessary for the dye removal.

In recent years, many plant materials have been tested as low-cost adsorbents for various dyes. For instance, wheat straw [11], barley straw [12], rice straw [13], rice husks [14], sawdust [15], tea waste [16], peanut husks [17], spent coffee grounds [18], coffee husks [19], spent grain [20], fruit peels [21] and sugarcane bagasse [22] have been successfully used for dye removal.

The present investigation was conducted to remove C.I. Reactive Blue 82 dye colour employing *Gigantia Leaves*, *Curcuma Longa Leaves*, *Morienga Oleifera* and *Citrus Sinensis*. Scope of the study includes kinetics and isothermal equilibrium studies, effect of adsorption process parameters such as pH, contact time and adsorbent dose on colour removal. Interruption studies were carried in order to know the sorption mechanism involved in the adsorption process.

II. MATERIALS AND METHODS

A. Adsorbent

Adsorbents like *Gigantia Leaves*, *Curcuma Longa Leaves*, *Morienga Oleifera* and *Citrus Sinensis* collected from the local areas are used in the present study. The four organic adsorbents were washed with distilled water to remove dirt and other particulate matter. The washed peels and leaves are dried at low temperature ($<105^{\circ}\text{C}$) to remove moisture content. After drying process, peels and leaves were grounded to fine powder and sieved through 75 μ size. Adsorbents size of 75 μ is used in the study.

B. Adsorbate

C.I. Reactive Blue 82 was used as adsorbate. Chemical structure of the dye:

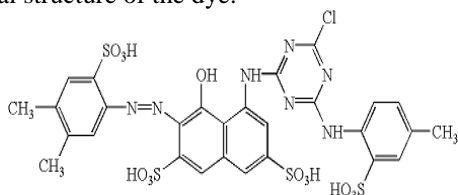


Fig.1. Chemical structure of C.I. Reactive Blue 82

C. Analysis and Characterization

The maximum wavelength of C.I. Reactive Blue 82 (570 nm) was observed using Thermo make UV VIS Spectrophotometer of Evolution 201 Model. All the analyses were done in accordance with standard methods [23].

III. BATCH ADSORPTION EXPERIMENT

Experiments were conducted for dye solution of pH from 2 to 12. The adsorbent dose and pH at which maximum colour removal of dye were determined, which was adopted as favourable dose and favourable pH. Agitated, non-flow batch sorption studies were conducted by bottle point method using reagent bottles of 250 mL capacity. To a 100 mL of test dye solution (optimum pH) of 50 mg/L concentration taken in the reagent bottle, premeasured quantity of adsorbent was added and the resultant mixture was agitated in a horizontal shaker at a rate of 125 rpm for varying time intervals of 1, 3, 5, 7, 9, 12, 15, 30, 45 and 60 minutes. The bottles were withdrawn from the shaker at designated time intervals and the reagent bottles were kept undisturbed for 4 hours for sedimentation, at the end of which, samples were withdrawn by carefully pipetting out 10 ml portion and are analyzed for colour content remaining in the test dye solution. The time at which maximum removal of colour takes place and no further significant difference in colour removal occurs from that time, was taken as the equilibrium contact time and used in all further studies. Equilibrium Isothermal studies were conducted by adding varying doses of adsorbents such as 50, 100, 150, 200, 250, and 300 mg/L to the test dye solution and contacted for equilibrium time. The residual colour was analyzed with a Spectrophotometer by measuring OD/%T at respective maximum wavelength (570 nm) of dye solution and computing concentrations from the calibration curve.

IV. RESULTS AND DISCUSSION

A. Effect of pH

The effect of initial pH on adsorption of dye was studied from pH 2 to 12, at dye concentration of 50 mg/L, contact time 30 min and 300 mg/L dosage. The percentage of colour removal of dye at different pH is as shown in Fig.2.

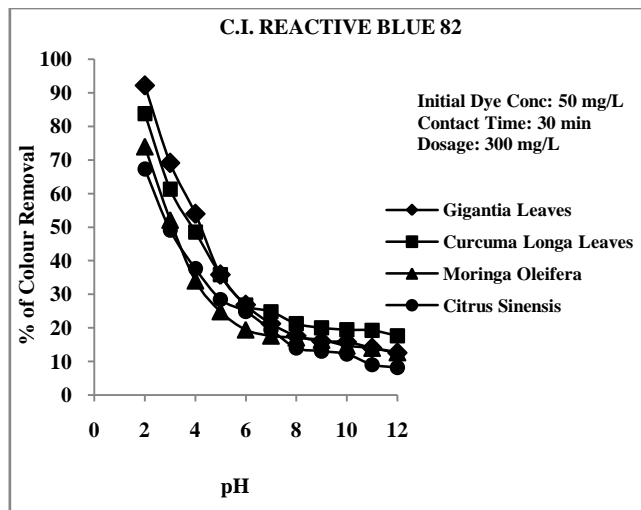


Fig.2. Response of C.I. Reactive Blue 82 onto Adsorbents at Different pH

From Fig.2, it was observed that maximum colour removal of C.I. Reactive Blue 82 with all adsorbents was obtained at pH of 2. Hence favourable pH of 2 was considered to the dye C.I. Reactive Blue 82.

B. Effect of Adsorbent Dosage

Equilibrium isothermal adsorption studies were conducted by varying the amount of adsorbent dose from 50 to 300 mg/L and the results are presented graphically as % colour removal at different doses for C.I. Reactive Blue 82, at pH 2 as shown in Fig.3.

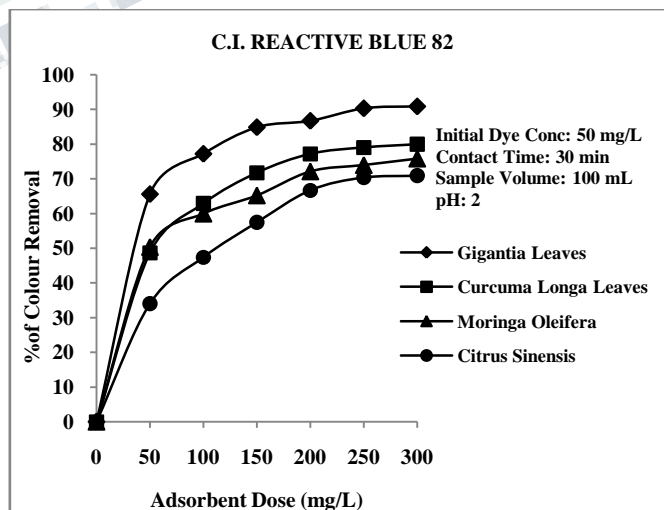


Fig.3. Response of C.I. Reactive Blue 82 to adsorbents at different dosages (pH=2)

From Fig.3, it was observed that C.I. Reactive Blue 82 responded favourably to all adsorbents investigated, exhibited Excellent colour removal of 90.36% with Gigantia Leaves, Good colour removal of 80%, 75.81%, and 70.90% with Curcuma Longa Leaves, Moringa Oleifera and Citrus Sinensis at pH of 2.

plane.

The linear form of Langmuir isotherm is given as;

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L C_e}$$

Where K_L is the energy constant of the sorption, q_m is the maximum value of sorption capacity (mg g^{-1}), C_e is the equilibrium conc. of sorbate in solution after adsorption (mg L^{-1}), q_e is the mass of sorbate adsorbed per unit mass of sorbent (mg g^{-1}). The plot between $1/q_e$ and $1/C_e$ is as shown in the Fig.5.

C. Effect of contact time

The influences of contact time vis-à-vis kinetics of colour removal by adsorbents are presented in Fig.4. It may be observed from figures that the rate of colour removal was rapid initially. The rate leveled off gradually and then attained a more or less constant value (equilibrium) beyond which there was no significant increase in colour removal. The time required to attain equilibrium was 30 minutes.

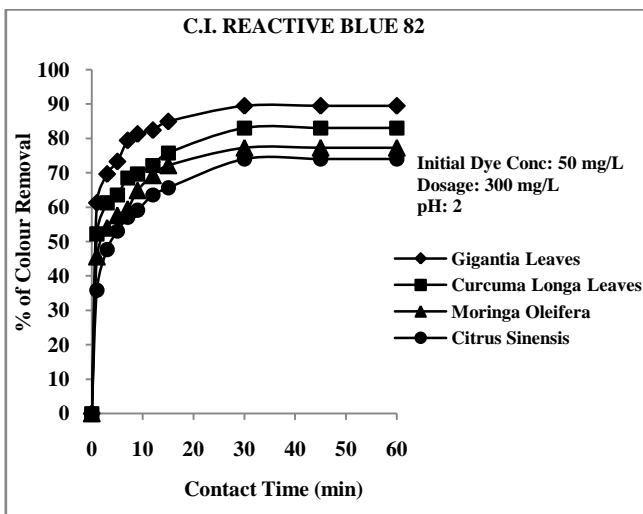


Fig.4. Kinetics of Sorption of C.I. Reactive Blue 82 onto Adsorbents at Different Contact Times (pH=2).

It follows from the experimental results that percentage removal of colour increased with an increase in mixing time; however, the difference is not much beyond a mixing time of 30 min. Therefore, an equilibrium mixing time of 30 min was adopted in all subsequent experiments.

V. EQUILIBRIUM STUDY

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and adsorbent, based on a set of assumptions that are mainly related to the homogeneity/heterogeneity of adsorbents, the type of coverage and possibility of interaction between the adsorbate species. Adsorption data are usually described by adsorption isotherms, such as Langmuir, Freundlich isotherms. These isotherms relate dye uptake per unit mass of adsorbent, q_e , to the equilibrium adsorbate concentration in the bulk fluid phase C_e .

A. The Langmuir isotherm

The **Langmuir model (1918)** is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface

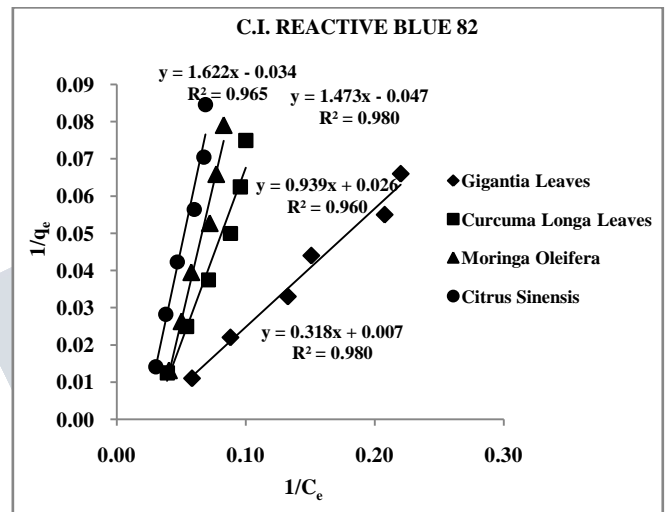


Fig.5. Linearised Plot of Sorption Isotherm of Langmuir Model for Various Adsorbents

The values of sorption capacities and coefficient of correlation of Langmuir Isotherm are presented in Table I.

Table I. Langmuir Adsorption Isotherm Constants and Coefficient of Correlation (R^2) for all the Adsorbents

Dye	Langmuir Isotherm											
	Coefficient of Correlation (R^2)				$q_m(\text{mg/g})$				$K_L(\text{L/mg})$			
	GL	CLL	MO	CS	GL	CLL	MO	CS	GL	CLL	MO	CS
C. I. Reactive Blue 82	0	0	0	0	1	3	2	2	0	0	0	0
	4	8.	9.	1.
	9	9	9	9	2.	4	4	2	0	0	0	0
	8	6	8	6	8	6	1	7	2	2	2	2
					5							

B. The Freundlich isotherm

Freundlich isotherm mode (1906) is applicable for non-ideal sorption on heterogeneous surfaces and multilayer sorption.

The nonlinear and linearised forms of the equation are as follows:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

where C_e is the equilibrium conc. of sorbate in solution after adsorption (mg L^{-1}), q_e is the mass of sorbate adsorbed per unit mass of sorbent (mg g^{-1}). The constants in the Freundlich isotherms can be determined by plotting $\log q_e$ versus $\log C_e$ which gives a straight line with slope of $1/n$ and a intercept equal to the value of $\log K_F$, where K_F (L g^{-1}) is the Freundlich constant related to the adsorption capacity and n is the constant for intensity. Plot between $\log C_e$ and $\log q_e$ was drawn to generate the intercept value of K_F and the slope of n as shown in the Fig.6.

The values of $n < 1$ indicate a favourable adsorption comparable with other researches. It is observed that all the adsorbents satisfy the condition of heterogeneity.

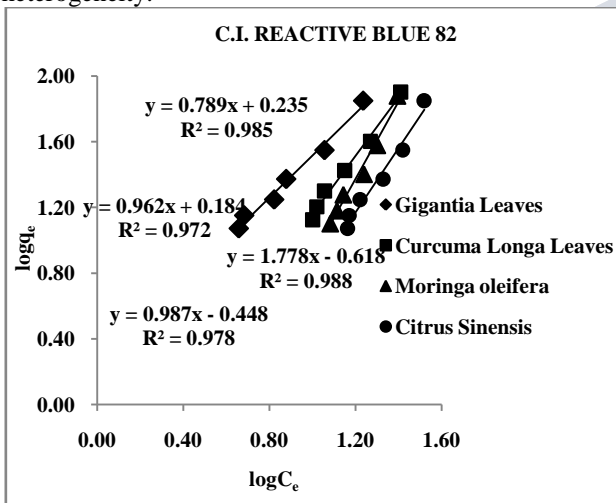


Fig.6. Linearised Plot of Sorption Isotherm of Freundlich Model for Various Adsorbents

The isothermal equilibrium sorption data were fitted into linearised Freundlich equation and the values of sorption capacities and coefficient of correlation are presented in Table II.

Table II: Isotherm model constants and correlation coefficients for adsorption of dye from aqueous solution

Dye	Freundlich isotherm														
	Coefficient of Correlation (R^2)		K_f (L/g)				Slope (n)								
	GL	CL	L	MO	CS	GL	CL	L	MO	CS	GL	CL	L	MO	CS

C.I	0	0	0	0	1	1	1	1	1	1	1	1
Reactive Blue 82	9	9	9	9	2	8	5	2	2	2	0	0
	8	8	7	7	6	5	6	0	6	8	1	3

From Table II, the value of coefficient of correlation (R^2) obtained was nearly equal to one for all adsorbents giving a best fit for Freundlich equation compared to Langmuir Isotherm. It follows from the data that equilibrium adsorption of colour on to all adsorbents follows Freundlich isotherm model, which implies multilayer sorption, with lateral interactions between the adsorbed molecules or ions in the case of Freundlich models; the energetic distribution of sites is heterogeneous due to the diversity of sorption sites.

C. Kinetic study

In order to investigate the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, the pseudo-first-order and pseudo-second-order equations are applied to model the kinetics of dye adsorption on to the adsorbents.

The **Pseudo-First-Order (1898)** rate equation is given as:

$$\log(q_e - q_t) = \log q_e - \left(\frac{K}{2.303}\right)t$$

where q_e is the amount of adsorbed adsorbate on the adsorbent at equilibrium ($\text{mg adsorbate g}^{-1}$ adsorbent), q_t is the amount of adsorbed adsorbate on the adsorbent at time t , K_1 is the adsorption rate constant for pseudo first-order. To determine the correlation coefficients, graph was drawn between $\log(q_e - q_t)$ and time as shown in the Fig.7.

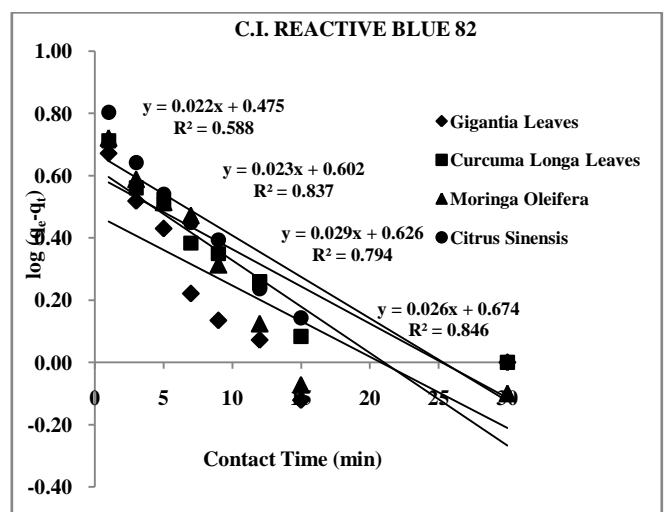


Fig.7. Pseudo-First-Order plot for C.I. Reactive Blue 82 Adsorbed onto Different Adsorbents.

Calculated values of K_1 and q_e along with correlation coefficient (R^2) are summarized in Table III.

Table III: The Adsorption Rate Constants, q_e and Coefficient of Correlation (R^2) for Pseudo-First-Order Kinetic Model

Dye	Pseudo-First-Order Kinetic Model															
	Coefficient of Correlation (R^2)				q_e .cal(mg/g)				Rate Constant K_1 (min ⁻¹)				q_e .exp (mg/g)			
	GL	CLL	MO	CS	GL	CLL	MO	CS	GL	CLL	MO	CS	GL	CLL	MO	CS
C.I. Reactive Blue 82	0.588	0.839	0.784	0.889	2.348	3.929	4.272	4.525	0.005	0.005	0.006	0.005	1.490	1.348	12.980	12.333

The pseudo first-order kinetic model of Lagergren was not fitted well with the experimental data of q_e .

The **Pseudo-Second Order (Ho, 1995)** kinetics is expressed as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e}$$

The initial adsorption rate, h , (mg g⁻¹ min) is expressed as $h = k_2 q_e^2$, Where k_2 is the rate constant of Pseudo-second-order adsorption (min⁻¹) and q_e is the equilibrium adsorption capacity (mg g⁻¹).The graph between t/q_t versus t was drawn as shown in the Fig.8, to determine the values of q_e , k and h from the slope and intercept of the plot.

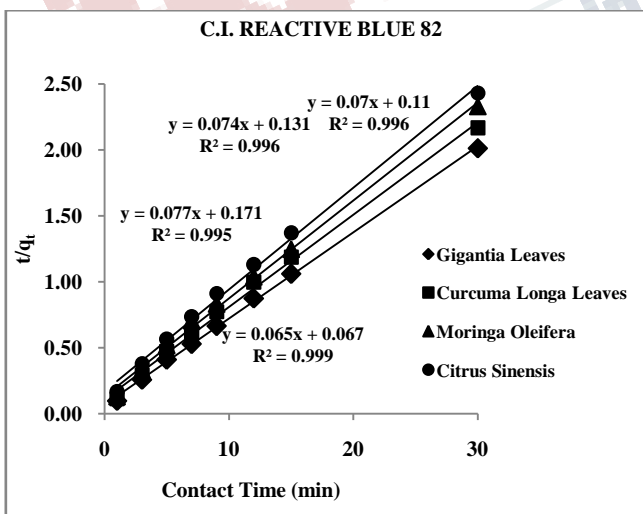


Fig.8. Pseudo-Second-Order Plot for C.I. Reactive Blue 82 Adsorbed onto Different Adsorbents.

Table IV: The Adsorption Rate Constants, q_e and Coefficient of Correlation and (R^2) for Pseudo-Second-Order Kinetic Model.

Dye	Pseudo-First-Order Kinetic Model																			
	Coefficient of Correlation (R^2)				q_e .cal (mg/g)				Rate Constant (K_2) (min ⁻¹)				h (mg/g min)				q_e .exp (mg/g)			
	GL	CLL	MO	CS	GL	CLL	MO	CS	GL	CLL	MO	CS	GL	CLL	MO	CS	GL	CLL	MO	CS
C.I. Reactive Blue 82	1.0	1.0	1.0	1.0	1.15	1.14	1.13	1.12	0.000	0.000	0.000	0.000	1.48	1.87	7.54	7.54	1.49	1.35	12.98	12.33

From Table IV, it was observed that R^2 is equal to 1.0 with respect to pseudo-second-order, moreover the experimental values of q_e is nearer to the values obtained in pseudo-second-order, indicating that pseudo-second-order model is well fitted to the data than pseudo-first-order model, which implies that chemisorption is the rate limiting step.

VI. INTERRUPTION STUDIES

In order to probe into the nature of the sorptive uptake of dye colour by the adsorbents, interruption studies were conducted by interrupting the ongoing process of adsorption for 30min in a batch system. For film diffusion controlled process, the interruption does not affect the rate of uptake, since there is no increase in concentration gradient on the sorbent after the interruption.

However, in the case of pore diffusion to be rate controlling step, the concentration gradient increases immediately after interruption compared to that of before interruption and this may result in a higher uptake. Result of interruption tests are presented in Fig.9, for various dyes using different adsorbents.

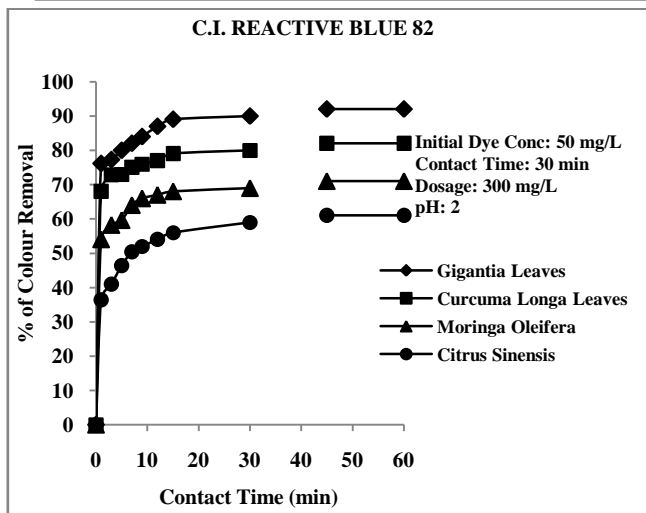


Fig.9. Interruption Kinetic Plot of C.I. Reactive Blue 82

It is evident from the Fig.9, that there is slight increase in the slope of the concentration gradient curve after interruption and hence it indicates the possibility of pore diffusion to be the rate controlling in the sorption process.

CONCLUSIONS

The present investigation shows that organic adsorbents can be effectively used as an adsorbent for the removal of C.I. Reactive Blue 82 from aqueous solutions. The amount of dye uptake was found to increase with increase in dose from 50 to 300 mg⁻¹L. Excellent colour removal can be achieved with adsorbent of Gigantia Leaves, Curcuma Longa Leaves, Moringa Oleifera and Citrus Sinensis at pH of 2. The maximum colour of Gigantia Leaves, Curcuma Longa Leaves, Moringa Oleifera and Citrus Sinensis was 90.36%, 80%, 75.81% and 70.90% respectively. The data fitted well to Freundlich model, which implies that the possibility of multilayer adsorption with a heterogeneous energy distribution of the active sites, accompanied by interaction between the adsorbed molecules. Kinetic studies data of all the sorbents are fitted well to pseudo-second-order, which implies that chemisorption is the rate limiting step. Further Interruption Studies implies that pore diffusion to be the rate controlling one in the adsorption process.

ACKNOWLEDGEMENTS

The authors are very grateful to the principal and to the Head of the Department of Civil Engineering, S. V. University, Tirupati, for providing with the necessary facilities to carry out the research work successfully.

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