



Adsorptive Removal of Colour from Aqueous Solution of Disazo Dye by Using Organic Adsorbents

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Abstract : Aqueous C.I. Direct Blue 77 dye was decolourized by adsorption onto Gigantia Leaves (GL), Curcuma Longa Leaves (CLL), Morienga Oleifera (MO) and Citrus Sinensis (CS). To understand the potentiality of organic adsorbents, experiments were conducted to determine equilibrium time, optimum dose of adsorbent, optimum pH, adsorption isotherms, kinetic studies, desorption studies and interruption studies. The corresponding results showed that excellent colour removal of Direct Blue 77 can be achieved with adsorbents at optimum pH of 4. The maximum colour of Gigantia Leaves, Curcuma Longa Leaves, Morienga Oleifera and Citrus Sinensis was 81%, 79%, 70% and 59% respectively. The isothermal equilibrium sorption data was well fitted into the Freundlich Isotherm. Kinetic studies which implies that chemisorption is the rate limiting step. Desorption studies, it states that physisorption plays a significant role in the colour removal of dyes. Pore diffusion seems to be the rate controlling in the sorption process as indicated by interruption studies.

Keywords: Adsorption, C.I. Direct Blue 77, Gigantia Leaves, Curcuma Longa Leaves, Moringa Oleifera, Citrus Sinensis.

1. Introduction

Annually, over seven million tons of dyes are produced in the world and widely utilized in different industries, including paper, plastics, leather, pharmaceutical, food, cosmetics, dyestuffs, and textiles industries¹. In these dyes, azo dyes are the largest class of dyes and up to 60–70% of industrially synthetic dyes. Considerable amount of dye-contaminated wastewater discharge in these industries resulted in a potential risk to human health and ecosystem, since coloured dye effluents would interfere with light penetration in the receiving water bodies and the degraded by-products had toxic effects on mammals and aquatic organisms². Due to the resistance of most azo dyes to normal treatment process, disposal of azo dye wastewater poses a major environmental problem³. 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 these methods, adsorption process provides an attractive alternative for the treatment of dye wastewater, especially the inexpensive adsorbent⁴. 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 limited⁵. Thus, more economic, efficient and practical adsorbents are necessary for the dye removal.

Recently, numerous approaches have been studied for the development of cheaper and effective adsorbents. Many non-conventional low-cost adsorbents, including natural materials, biosorbents and waste materials from industry and agriculture, where these materials could be used as adsorbents for the colour removal of dyes from aqueous solution. Some of the adsorbents include clay materials (bentonite, kaolinite), zeolites, siliceous material (silica beads, alunite, perlite), agricultural wastes (bagasse pith, maize cob, rice husk, coconut shell), industrial waste products (waste carbon slurries, metal hydroxide sludge), biosorbents (chitosan, peat, biomass) and others (starch, cyclodextrin, cotton).

The present investigation was conducted to remove C.I. Direct Blue77 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. Desorption studies and Interruption studies were also carried in order to know the sorption mechanism involved in the adsorption process.

2. Materials and methods

2.1. 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°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.

2.2. Adsorbate

C.I. Direct Blue 77 was used as adsorbate. Chemical structure of the dye:

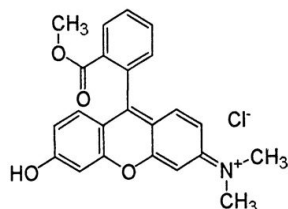


Fig.1. Chemical structure of C.I. Direct Blue 77

2.3. Analysis and Characterization

The maximum wavelength of C.I. Direct Blue 77 (470 nm) was observed using Thermo make UV VIS Spectrophotometer of Evolution 201 Model. All the analyses were done in accordance with standard methods⁶.

3. 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 10ml 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 (470 nm) of dye solution and computing concentrations from the calibration curve.

4. Results and discussion

4.1 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.

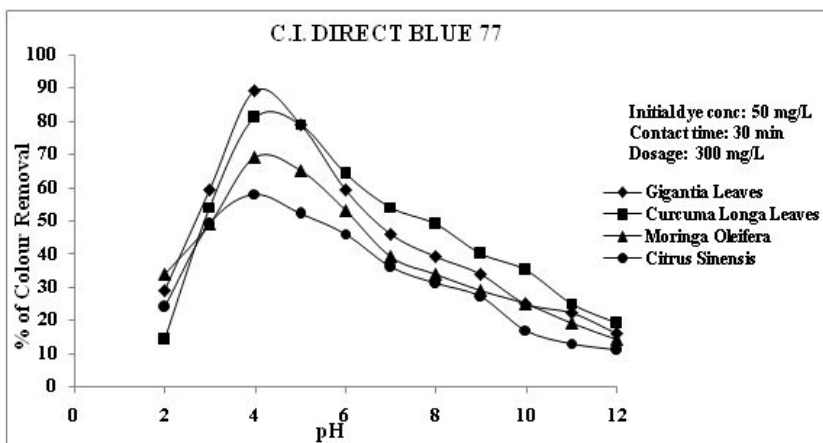


Fig.2. Response of C.I. Direct Blue 77 onto Adsorbents at Different pH

From Fig.2, it was observed that maximum colour removal of C.I. Direct Blue 77 with all adsorbents was obtained at pH of 4. Hence favourable pH of 4 was considered to the dye C.I. Direct Blue 77.

4.2. 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. Direct Blue 77, at pH=4 as shown in Fig.3.

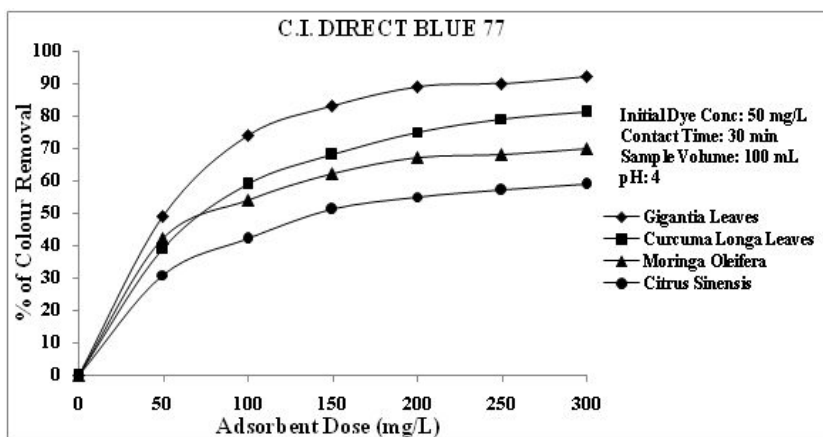


Fig.3. Response of C.I. Direct Blue 77 to adsorbents at different dosages (pH=4)

From Fig.3, C.I. Direct Blue 77 responded favourably to all adsorbents, exhibited Excellent colour removal of 81% with Gigantia Leaves and 79% with Curcuma Longa Leaves, Good colour removal of 70% with Moringa Oleifera and a Moderate colour removal of 59% with Citrus Sinensis at pH of 4.

4.3. 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.

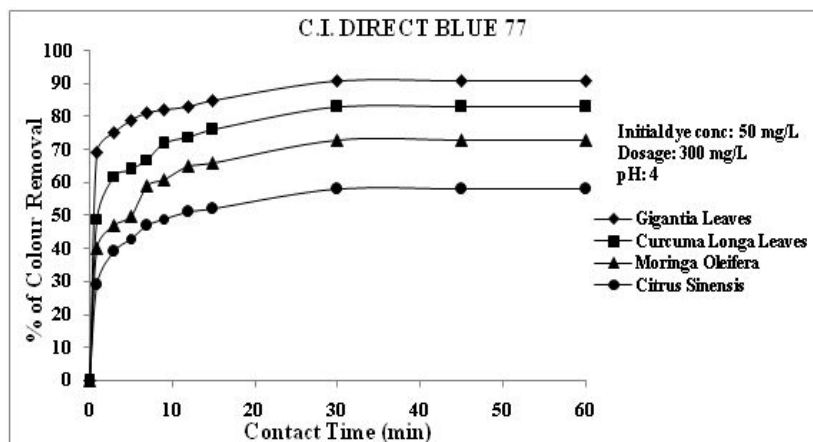


Fig.4. Kinetics of Sorption of C.I. Direct Blue 77 onto Adsorbents at Different Contact Times (pH=4)

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.

4.4. 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 .

4.4.1. 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 plane.

The linear form of Langmuir isotherm is given as;

$$1/q_e = 1/q_m + 1/(q_m K_L) 1/C_e$$

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

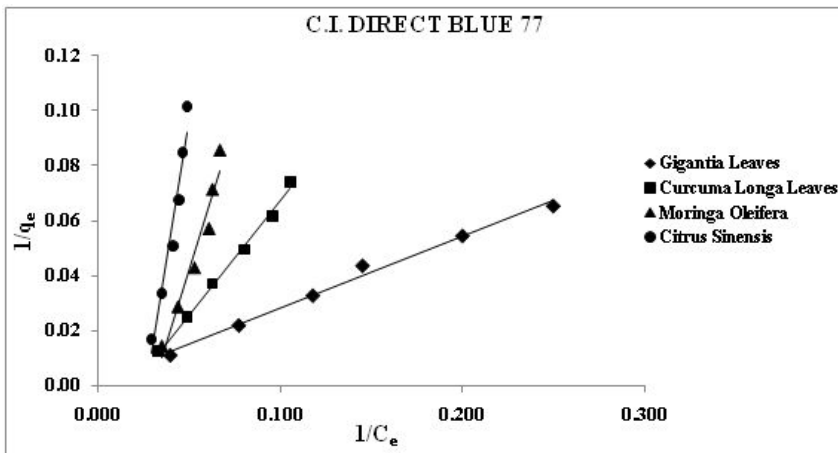


Fig.5. Linearised Plot of Sorption Isotherm of Langmuir Model for Various Adsorbents (C.I. Direct Blue 77)

4.4.2. 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:

$$\log q_e = \log(K_F + 1/n \log C_e)$$

where C_e is the equilibrium conc. of sorbate in solution after adsorption (mg/L), q_e is the mass of sorbate adsorbed per unit mass of sorbent (mg/g). 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) 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.

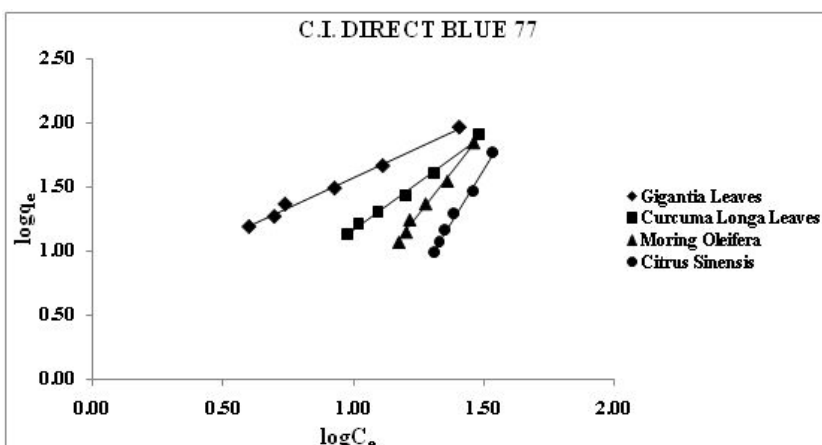


Fig.6. Linearised Plot of Sorption Isotherm of Freundlich Model for Various Adsorbents (C.I. Direct Blue 77)

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.1.

Table 1: Isotherm model constants and correlation coefficients for adsorption of dye from aqueous solution

Adsorbents	Langmuir Coefficients			Freundlich Coefficients		
	R ²	q _m (mg/g)	K _L (L/mg)	R ²	n	K _F (mg/g)
Gigantia Leaves	0.99	500	0.001	0.994	1.053	1.85
Curcuma Longa Leaves	0.99	66.66	0.001	0.994	0.92	1.40
Morienga Oleifera	0.95	16.12	0.002	0.990	0.62	7.22
Citrus Sinensis	0.95	9.43	0.002	0.991	1.24	7.71

From Table.1, the value of coefficient of correlation (R²) 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.

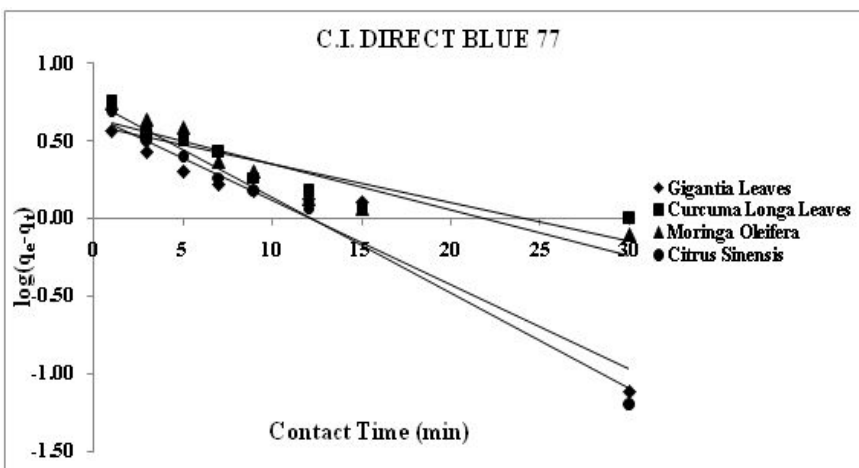
4.5. Kinetic study

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:

$$\log(q_e - q_t) = \log q_e - (K_1/2.303)t$$

where q_e is the amount of adsorbed adsorbate on the adsorbent at equilibrium (mg adsorbate/g 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. Direct Blue 77 Adsorbed onto Different Adsorbents**

Calculated values of K_1 and q_e along with correlation coefficient (R²) are summarized in Table.2. The pseudo first-order kinetic model of Lagergren was not fitted well with the experimental data of q_e .

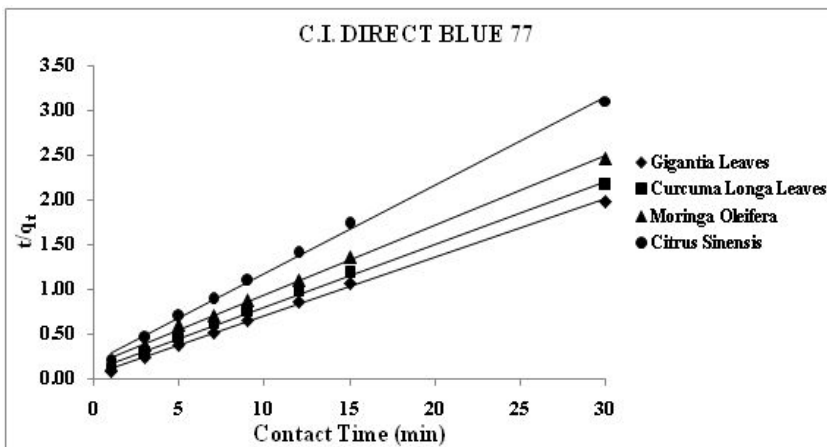
Table 2: Comparison between the Adsorption Rate constants, q_e , and correlation co-efficient associated with Pseudo-first order and Pseudo-second order equations

Adsorbents	Pseudo-first-order equation				Pseudo-second-order equation				
	R^2	q_e cal (mg/g)	q_e exp (mg/g)	K_1 (L/mg)	R^2	q_e cal (mg/g)	q_e exp (mg/g)	h	K_2 (mg/g)
Gigantia Leaves	0.76	3.91	15.16	0.05	0.99	15.38	15.16	16.56	0.07
Curcuma Longa Leaves	0.93	4.52	13.83	0.12	0.99	14.49	13.83	8.39	0.04
Morienga Oleifera	0.83	4.39	12.16	0.06	0.99	12.82	12.16	6.24	0.03
Citrus Sinensis	0.96	5.54	9.67	0.14	0.99	10.1	9.67	5.32	0.05

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

$$t/q_t = 1/h + t/q_e$$

The initial adsorption rate, h , (mg/g 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). 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. Direct Blue 77 Adsorbed onto Different Adsorbents**

From Table 2, 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.

4.6. Desorption studies

Desorption studies are useful in the elucidation of the mechanism of adsorption reaction and also to assess the regeneration capacity of the sorbent for reuse in a more economic manner. The amount of desorption provides an insight into the nature of sorbent-sorbate bonding.

Desorption is generally studied by employing a solvent (dispersion media) like Distilled water, 0.1N NaOH and 0.1N HCL. If the dye bound to the sorbent is desorbed by distilled water, then it may be deduced that the dye molecule is attached to sorbent surface by weak bonds and that sorption can be said to be of

physical in nature. If the inorganic solvents are required to desorb, then the adsorption is attributed to be the type of ion-exchange.

In the present study, desorption studies were conducted for C.I. Direct Blue 77 and sorbents by dispersing the (adsorbed) loaded sorbent in distilled water and inorganic solvents like 0.1N NaOH, 0.1N HCL and agitated for a period of 30min.

Tables.3. represents the percentage of desorption of dye C.I. Direct Blue 77 from GL, CLL, MO, and CS with distilled Water, 0.1N NaOH and 0.1N HCL.

Table 3: Desorption Data of Four Adsorbents by Various Inorganic Solvents

Adsorbents	Percentage of desorption		
	Distilled Water	0.1N HCl	0.1N NaOH
Gigantia Leaves	50	20	10
Curcuma Longa Leaves	63	14	28
Morienga Olefiera	68	12	NIL
Citrus Sinensis	92	17	NIL

From the above Table.3, the percentage of C.I. Direct Blue 77 dye adsorbed on to adsorbents was easily desorbed in distilled water. Desorption was significant (50-92%) with the distilled water indicating that the dye molecules in its original form are desorbing into solution. This type of dye-adsorbent interaction may be attributed to a physisorption type reaction in which dye molecules are bound to the surface by some type of weak bonding perhaps due to hydrogen bonding.

4.7. 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 (Helffirich 1962).

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.

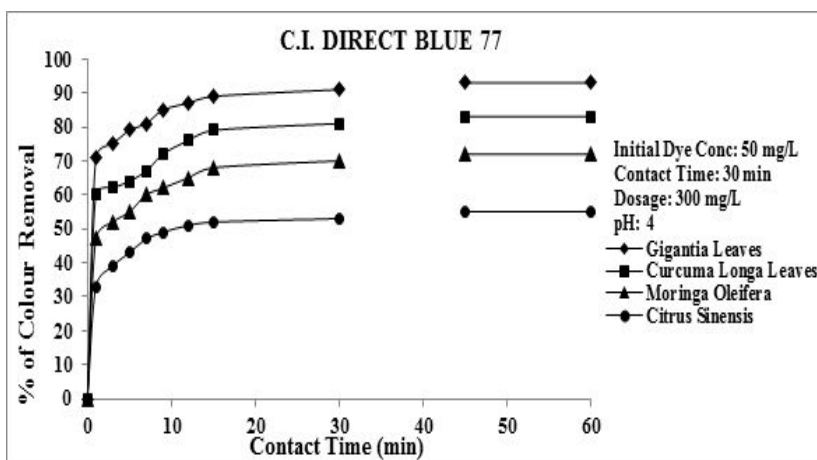


Fig.9. Interruption Kinetic Plot of C.I. Direct Blue 77

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.

5. Conclusions

Adsorption studies have been conducted for the different organic adsorbents to assess their capability to remove C.I. Direct Blue 77 in the aqueous phase. Excellent colour removal can be achieved with adsorbent of Gigantia Leaves, Curcuma Longa Leaves, Moringa Oleifera and Citrus Sinensis at pH of 4. 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. Attempts to desorb the sorbed dye molecules with distilled water preclude the possibility of physisorption playing significant role in the colour removal of dye. Further Interruption Studies implies that pore diffusion to be the rate controlling one in the adsorption process.

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