Removal Of Crystal Violet Dye Using A Low-Cost Activated Carbon By Adsorption

By

MEERA MADHAVAN

(11PCM 05)

A dissertation submitted to the

AVINASHILINGAM INSTITUTE FOR HOME SCIENCE AND HIGHER EDUCATION FOR WOMEN-COIMBATORE -43

In partial fulfillment of the Requirements

FOR THE DEGREE OF MASTER OF SCIENCE

IN

CHEMISTRY

MAY-2013

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Certified as Bonafied Research Work

R. Shyamala

N. Renugadevi

Signature of the Head of Department

Signature of the Guide

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MEERA MADHAVAN

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1.INTRODUCTION

Water is one of the basic requirements for life on earth. Due to industrialization, urbanization and domestic activities water is polluted everywhere (**Shouman *et al.*, 2012)**.

The polluted water contains both organic and inorganic pollutants, dyes and heavy metals like cadmium, chromium, lead, copper etc. Dyes are used in paper and pulp, leather, polymer, pharmacological and in food industries (**Esther forgan *et al*.**, **2009).**

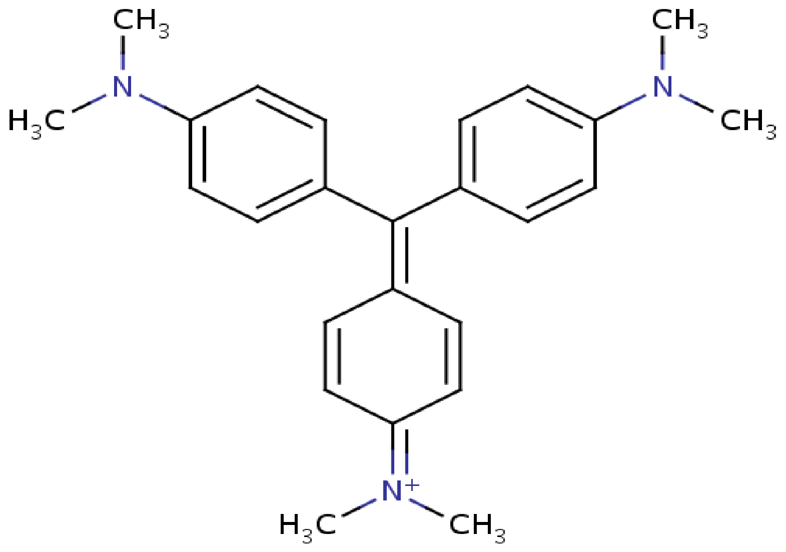
The usage of synthetic dyes is increased globally. The discharge of dyes in to waste water cause serious health problems. Over 10,000 dyes with an annual production of over 7x 10^5 metric tons worldwide are commercially available and 5-10% of the dye is lost in the industrial effluent (**Sunil Kumar and Arthi Jain, 2010**).

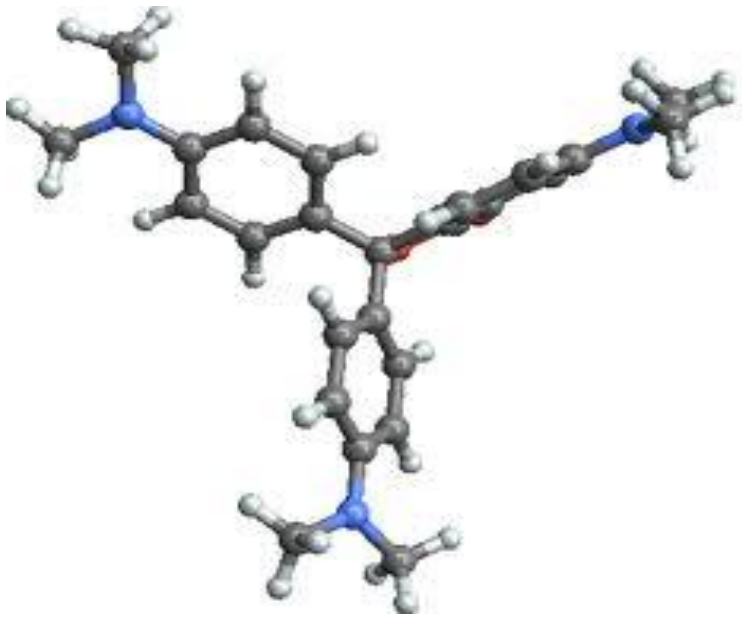
The dyes in colored effluents are stable, resistant towards light and moderate oxidizing agents. These dyes are toxic in nature and they have high chemical oxygen demand (COD) and biological oxygen demand (BOD).It affects living organisms which include human beings, flora, fauna and aquatic organisms (**Ramel *et al*** .,**2009)**.

CRYSTAL VIOLET

Crystal Violet is a cationic triphenyl methane dye with molecular formula $C_{25}N_3H_{30}Cl$ and it is highly water soluble and gives a very bright color. At room temperature it appears as a green powder and gives a violet solution when dissolved in water.

STRUCTURE OF CRYSTAL VIOLET DYE





PROPERTIES OF CRYSTAL VIOLET DYE

C.I No	:	42555
CAS No	:	548-62-49
Molar mass	:	407.97g/mol
Melting point	:	205^{o}C
λ_{max}	:	591 nm
Other names	:	Methyl violet 10B, Gentian violet

USES : It is used as a histological stain and Gram's Method for classifying bacteria. It finds application in textile industry for dyeing cotton, wool, silk and leather.

HAZARDS : It is carcinogenic and mutagenic. It causes moderate eye irritation tow ards light, cause bladder cancer, kidney failures and also cancer in the digestive system of animals.

The waste water from dyeing industry cause serious environmental hazards. Hence the removal of dye from waste water takes important environment necessity.

REMOVAL TECHNIQUE

Dyes can be removed from waste water using various methods like precipitation, coagulation, flocculation, ion-exchange and adsorption technique. Among these adsorption has greatest importance because of its simplicity, low-cost and ease of operation (**Theivarase *et al*.**, **2012**).

The removal of dyes by adsorption using commercial activated carbon is used widely, because of its high adsorption capacity, large surface area and micro porous structure. Due to the high cost of manufacturing of commercial activated carbon adsorption technique using commercial carbon is expensive (**Shouman *et al*.**, **2012**).

Many investigators have studied the feasibility of using economical and low-cost adsorbent from agricultural and industrial waste products. It include spent tea leaves ,pumpkin seed hull, wheat straw, pinecone, coir pith, crude oil residue, coconut shell etc. These are found effective in the adsorption capacities for the removal of dyes from waste water (**Narayanasaibaba *et al*., 2011**).

Hence in this study a low-cost adsorbent prepared from Water Hyacinth is used for the removal of Crystal Violet dye from aqueous solution. Water Hyacinth was converted in to activated carbon using conc.sulphuric acid and tested its ability to remove Crystal Violet dye from aqueous solution. The parameters which influence the adsorption process such as initial dye concentration, adsorbent dosage and pH are systematically analyzed.

Objectives:

- To prepare a low-cost and eco-friendly activated carbon from Water Hyacinth.
- To determine the effect of variation of initial concentration of Crystal Violet dye solution on the adsorption of dye from aqueous solution.
- To determine the effect of optimum contact time for the effective adsorption of Crystal Violet dye from aqueous solution.
- To determine the effect of pH variation on the adsorption of Crystal Violet dye from aqueous solution.
- To find out the variation of adsorbent dosage on the removal of Crystal Violet dye from aqueous solution.
- To interpret the results of the study in terms of
  - Lagergren kinetic equation
  - Intraparticle diffusion rate equation
  - Langmuir adsorption isotherm
  - Freundlich adsorption isotherm

2.REVIEW OF LITERATURE

Dyes are used in textile, paper, pulp, leather and plastic industries. These industries use large amount of water for their processes and produce waste water containing large amount of dyes. Most of the dyes are completely resistant to biodegradation and also toxic in nature. Hence their removal before disposal of the waste water is necessary.

2.1 Waste water treatment

Various methods have been employed for the removal of dyes from waste water. The methods include adsorption, coagulation, flocculation, sedimentation, filtration, reverse osmosis and ion exchange etc..

The treatment processes are generally divided in to three namely

- Primary treatment process
- Secondary treatment process
- Tertiary treatment process

2.1.1Primary treatment process

It involves the physical separation of suspended solids from the waste water. It reduces the total solids as well as the biological oxygen demand (http//www.watersiemens.com).

Sedimentation

It is a physical water treatment process using gravity to remove suspended solids from water (http//en.wikipedia.org/wiki. sedimentation).

Flocculation

It is a process of contact and adhesion where by the particle of a dispersion form larger size clusters (en.wikipedia.org/wiki/flocculation).

Filtration

It is the mechanical or physical operation which is used for the separation of solids from fluids by interposing a medium through which only fluid can pass.

2.1.2 Secondary treatment process

The processes consist of reducing or removing contaminants. Usually biological treatment is used to treat waste water. It involves the removal of biodegradable organic matter or suspended solids (www.gov.mb.ca/conservation).

Coagulation

Coagulation removes small particles that are made up of microbes, slit and other particles suspended in water.

Chlorination

Chlorination is a water treatment method that destroys disease causing bacteria, nuisance bacteria, parasite and other organisms (http://www.extension.umn.edu/distribution natural resources).

2.1.3 Tertiary treatment process

It is the final waste water treatment process. It removes stubborn contaminants which are not removed by secondary treatment (www.water.siemens.com).

Reverse osmosis

A method of producing pure water by forcing saline or impure water through a semipermeable membrane across which salt or impurities cannot pass. It is used for filtration and desalination of sea water. (http:/www.thefreedictionary.com/reverse osmosis)

Ion exchange

It is a reversible chemical reaction where an ion from solution is exchanged for a similarly charged ion attached to an immobile solid particle .These solid ion exchange particles are either naturally occurring inorganic Zeolite or synthetically produced organic resins. .(http:/www.remco.com/ix.htm)

Adsorption

It is the most popular treatment process for the removal of non-biodegradable organic from aqueous solution. Activated carbon is the common adsorbent for this process. **(Yue-ming *et al.*,2011).**

- **Verma and Mishra, (2010)** studied the removal of Crystal Violet, Direct orange and Magenta dyes from aqueous solution onto a low-cost adsorbent, rice husk carbon. The removal of dyes followed by pseudo first order rate equation and Freundlich adsorption isotherm.

- **Gamel O.El. Sayed *et al*., (2011)** carried out the adsorption of basic dyes(Crystal Violet and Methylene Blue)using sugarcane stalks by batch adsorption method. Removal of dyes increased with increased pH from aqueous solution. The results showed that Langmuir adsorption isotherm was fitted well for adsorption compare to Freundlich adsorption isotherm.

- The adsorption of Crystal Violet dye from waste water onto a low-cost material was investigated by **AbdoTaher *et al*., (2012).**Adsorption studies were carried out by varying the parameters such as pH, adsorbent dosage, contact time and temperature The results showed that removal of dye decreases with increase in initial concentration of dye. The adsorption followed pseudo second order rate equation.

- Adsorption of cationic dyes (Crystal Violet, Methylene Blue and Malachite Green) from aqueous solution onto a activated bottom ash was carried out by **Gandhimathi *et al.*, (2012).** Langmuir and Freundlich adsorption isotherms fitted well for the adsorption of dyes from aqueous solution.

- Removal of crystal violet dye from aqueous solution by adsorption using Gmelinaarborea bark was studied by **Angelie Jover and Jonathan Salvcion, (2012)**. The results revealed that increase in temperature and agitation time increased the percentage of adsorption of dye and the adsorption process was found to be spontaneous and exothermic in nature.

- **Nausha *et al*., (2011)** used papaya seed and chemically modified papaya seed by esterification in the removal of cationic and anionic dye (Congo Red and Methylene Blue) from aqueous solution by adsorption. The adsorption isotherm data for Methylene Blue best fitted for the Langmuir adsorption isotherm and for Congo Red the best fitted isotherm was Freundlich adsorption isotherm. The adsorption followed pseudo second order.

- Adsorption of Crystal Violet on CitullusLanatus Rind was carried out by **Bharathy Kandasamyand Ramesh SrikrishnaPerumal, (2012).** The effect of various factors such as contact time, adsorbent dosage, pH, initial dye concentration and temperature were studied. The adsorption followed pseudo second order rate with good correlation coefficient. . The order of adsorption isotherms followed Freundlich>Tempkin> Harkins > Jura > Langmuir isotherms.

- **Atmani *et al*., (2009)** studied the adsorption of Crystal Violet and Methyl Orange using an activated carbon prepared from skin almond waste. The results showed that the adsorption followed pseudo second order kinetics and also intra particle diffusion rate equation. The thermodynamic parameters showed that the adsorption of both dyes were exothermic in nature.

- **SemraCorush *et al*., (2012)** studied the removal of Crystal Violet dye from aqueous solution using fly ash as an adsorbent.The results showed that the adsorption followed pseudo first order, pseudo second order rate and also intraparticle diffusion rate equation.

- **Jayaraj *et al.*, (2012)** studied the removal of dyes (Crystal Violet, Methylene Blue and Malachite Green) from aqueous solution using activated carbon prepared from chlor-alkali waste. The experimental data reveals that adsorption followed pseudo second order kinetics and data fitted well with the Langmuir and Freundlich adsorption isotherms.

- **Meenakshi Sundaram and ShahulHameed (2012)** investigated the potential use of activated carbon prepared from Syzygium Cumini seed as a low-cost adsorbent for the removal of crystal violet dye from aqueous solution. The results revealed that the adsorption followed first order kinetics, Langmuir and Freundlich adsorption isotherms.

- **Nidheesh e*t al*., (2012)** successfully removed Crystal Violet dye from aqueous solution using bottom ash as an adsorbent. The percentage removal of Crystal Violet dye decreases with increase in concentration of dye solution and increases with decrease in particle size of the adsorbent.

- **Narayanasaibaba et al., (2011)** studied the adsorption of Crystal Violet dye using waste prawn shells as an adsorbent. The results showed that prawn shell can be used as a low-cost alternative adsorbent for the removal of Crystal Violet dye from aqueous solution.

- **Theivarasce *et al.*, (2011**) investigated the ability of cocoa shell activated carbon to absorb Crystal Violet dye from aqueous solution. Adsorption experimental data fitted well with pseudo second order rate equation. Equilibrium data were well represented by Langmuir adsorption isotherm .

- **Tolga DEPCI *et al.*, *(*2012)** studied the removal of Crystal Violet dye from aqueous solution using an activated carbon prepared from golbasilignite. The experimental results reveal that the adsorption followed pseudo second order kinetic equation and Langmuir adsorption isotherm. Thermodynamic parameters indicate that the adsorption process is endothermic in nature.

- Plant cellulose waste was used as an adsorbent for the removal of Crystal Violet dye from aqueous solution. The experimental data fitted well with Freundlich adsorption isotherm (**Mahesh *et al.*, 2010).**

- Batch adsorption studies were carried out for the removal of Crystal Violet dye from aqueous solution using chitosan as an adsorbent. Equilibrium experimental data were better represented by Langmuir adsorption isotherm showing maximum adsorption capacity of 28.5 mg/g. Adsorption kinetics was studied using pseudo second order kinetic equation and intraparticle diffusion rate equation. The results revealed that the chitosan can be used as an effective adsorbent for the removal of crystal violet dye from aqueous solution(**Mona Shouman *et al* ., 2012).**

- **Suteu *et al*., (2009)** studied the removal of Reactive Orange, Reactive Violet, Methylene Blue and Crystal Violet dyes from aqueous solution using hydrolyzed polyacrylonitrile textile fibers. The adsorption followed Langmuir, Freundlich and Dubinium-Radushkevich adsorption isotherms.

- **Shoumanand Rashwan, (2012)** have reported that phragmitiesaustralis is a potential low-cost adsorbent for the removal of basic dyes(Crystal Violet and Rhodamine B)from aqueous solution. The dye adsorption was well described by Langmuir adsorption isotherm and the adsorption process followed pseudosecond order rate equation. Thermodynamic parameters indicated that the adsorption is spontaneous and endothermic in nature.
- **AshlyLeena Prasad and Thirumalaisamy Santhi,(2012)** investigated the adsorption potential of Acacia nilotica leaves towards Crystal Violet and RhodamineB dyes from aqueous solution. The results showed that Acacia nilotica leaves can be used as an effective and low-cost adsorbent for the removal of both the dyes used in this study.

- **Malik *et al*., (2006)** studied the removal of Malachite Green dye from aqueous solution using an activated ground nut shell. Adsorption behaviour was compared with the commercially activated carbon. The results indicated that the ground nut shell can be used as a low-cost adsorbent for the removal of malachite green dye from aqueous solution.

- The removal of textile dye Malachite Green from aqueous solution was studied by **Rajesh kannan *et al*., (2010)** by adsorption technique using a low-cost adsorbent prepared from tamarind seed. The results showed that the adsorption process followed pseudo first order and intraparticle diffusion rate equation.

- **Sonawane *et al.*, (2009)** studied the ability of maize cob powder carbon in the removal of Malachite Green from aqueous solution. The experimental results revealed that the adsorption data followed both Langmuir and Freundlich adsorption isotherm.

- Adsorption of Malachite Green dye using treated Borassuraethiopum was carried out by **Nethaji *et al*., (2010).**The results showed that the adsorption followed pseudo second order rate equation and the adsorption was due to both film diffusion and intraparticle diffusion.
- The rattan(stems of climbing palm)was used as an adsorbent for the removal of malachite Green dye from aqueous solution. The results showed that rattan saw dust can be used as a low-cost alternative adsorbent for the removal of Malachite Green dye from aqueous solution **(Hameed *et al*., 2008).**

- **Rais Ahmed et al., (2010**) studied the adsorption of malachite green dye on treated ginger waste by batch adsorption studies. The various parameters such as initial dye concentration, contact time, pH and temperature which affect the adsorption process were studied. The experimental results indicated that the adsorption followed pseudo second order rate equation.

- **Mouzdahir *et al*., (2007)** have reported the removal of Methylene Blue from waste water using Moroccan clay as an adsorbent. The results showed that Moroccan clay could be used as a low-cost adsorbent for the removal of Methylene Blue from waste water.

- **Pavel (2003)** investigated that Iron-hamates can be used as a low-cost adsorbent for the removal of basic dyes (Methylene Blue, Methyl violet, Crystal Violet, Malachite Green and Rhodamine B)from waste water. The results showed that the presence of anionic substances increases the adsorption of Methylene Blue.

- Adsorption of Rhodamine B ,Fast Green and Methylene Blue from waste water on to has been carried out by **Gupta *et al*., (2004).**The results indicated that the adsorption was exothermic in nature.

- **Shri ram *et al* ., (2007)** used rice husk saw dust , wood coal and boiler bottom ash to remove Methylene blue from aqueous solution. The results showed that boiler bottom ash can be used as a low –cost alternative material for the removal of dyes.

- .The removal of Methylene Blue dye from aqueous solution using jack-fruit peel was carried out by **Hameed (2009).**The results showed that the jack fruit peel could be used as an effective low-cost alternative adsorbent for the removal of Methylene Blue dye.

- **Erdal (2009)** investigated the adsorption of Crystal Violet dye from aqueous solution using raw and manganese dioxide-modified bentonite sample.The results showed that manganese dioxide modified bentonite could be used as an effective low-cost alternative adsorbent for the Crystal violet dye removal.

- Spent tea leaves for the removal of Crystal Violet dye have been investigated by **Sunil kumarBajpai and Arti Jain, (2010).** Batch experiments were conducted to study the effect of initial concentration of dye, pH, adsorbent dosage, temperature and agitation time on the removal of Crystal Violet from aqueous solution. The dynamic data were analyzed by using pseudo first order, pseudo second order and Elovich equations. The results showed that the spent tea leaves have greatest efficiency for the removal of Crystal Violet from aqueous solution.

  Removal of cationic dyes (Crystal Violet, Malachite Green and Rhodamine B) from aqueous solution by adsorption using agro residue corncorb was conducted by **Yakout and Ali, (2011)** by varying pH and contact time. The experimental data fitted well the pseudo second order kinetic model. Increase in adsorption of the cationic dyes noticed as the pH increased from 2 to 4 and further increase in pH from 4 to 10 there was no change in the adsorption of the dyes.
- Adsorption of Crystal Violet dye on to a activated mango kernel was analyzed By **Prasad e*t al*., (2012**).The parameters like pH, temperature, initial concentration of the dye and adsorbent dosage on the adsorption of dye were tested. The percentage removal of Crystal Violet dye increases with increase in pH from 3 to 9 and the maximum adsorption of Crystal Violet dye at all the concentrations(50,75,100,125 mg/L) noticed at pH 9.
- Soil nano clays used as a low-cost adsorbent for the removal of Crystal Violet dye and Methylene Blue by **YE-Mingchen *et al*., (2011).**The results showed that soil nano clays could be used as an alternative effective low-cost adsorbent for the removal of cationic dyes.
- **Ramel *et al*., (2011)** studied the removal of Crystal Violet dye from aqueous solution by adsorption using ChaetophoraElegans algae. The effect of dye concentration, pH, adsorbent dosage and salinity have been studied. Adsorption kinetic data were modeled using pseudo first order and pseudo second order. The Langmuir and Freundlich adsorption isotherms model fitted well for the adsorption.

3. MATERIALS AND METHODS

3.1 Project plan

The present investigation has been carried out to study the efficiency of a low-cost, eco-friendly adsorbent prepared from Water Hyacinth in the removal of a basic dye, Crystal Violet by adsorption technique. Batch adsorption studies were carried out by varying the initial concentration of dye solution, $_{P}$H and adsorbent dosage.

3.2 Description of the adsorbent

COMMON NAME : Water Hyacinth

BOTANICAL NAME : Eichornia Crassipes

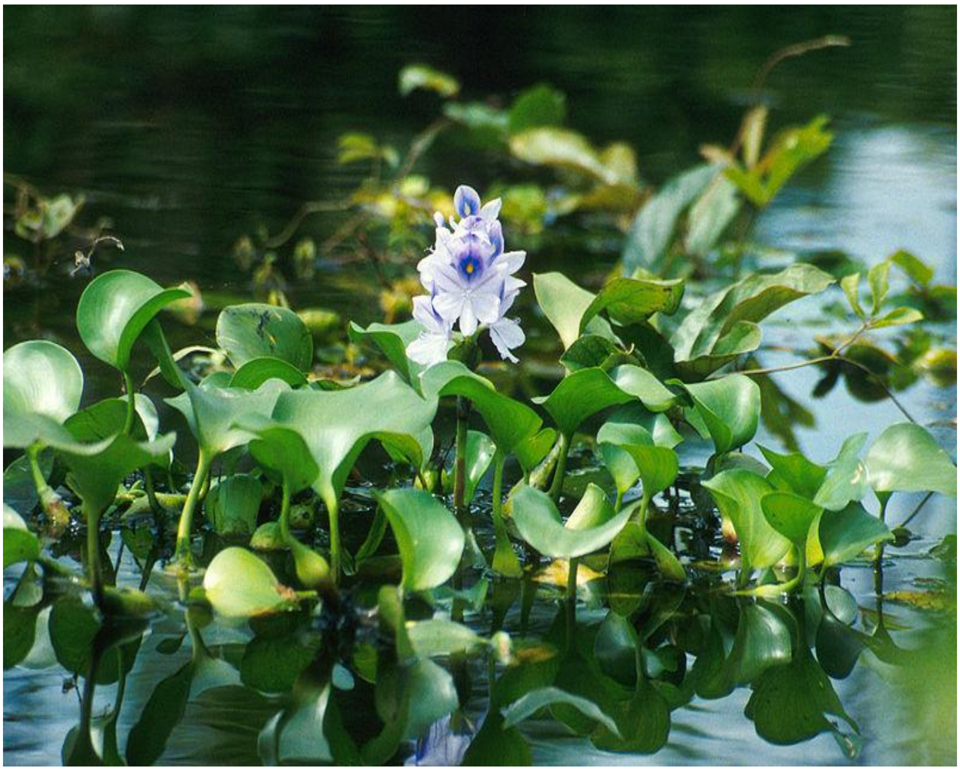
FAMILY : Pontderiaceae

3.3Parameters studied

Batch adsorption studies were conducted with a low-cost activated carbon prepared from Water Hyacinth. The adsorption technique was used owing to its simplicity and ease of evaluating some basic parameters which influence the adsorption process.

- Determination of the effect of variation of initial concentration of dye solution on the percentage adsorption of dye from aqueous solution.
- Determination of the effect of variation of pH on the effective removal of dye from aqueous solution.
- Determination of the variation of adsorbent dosage on the percentage adsorption of dye from aqueous solution.
- The experimental data obtained in the adsorption of dye was interpreted using the Lagergren first order kinetic equation, Intra particle diffusion rate equation, Langmuir and Freundlich adsorption isotherms.

WATER HYACINTH



3.4 Preparation of the adsorbent

Water Hyacinth plants were collected from Singanallur pond and cut in to small pieces, dried in sunlight for 10 days and further dried in hot air oven at 60^{0}C for 24 hours. The completely dried material was powdered well. The powdered raw material was chemically activated by treating it with conc. Sulphuric acid with constant stirring and kept for 24hours.The carbonized material obtained was washed well with plenty of water several times to remove excess acid and then dried at 105^{o}C-110^{o}C in a hot air oven. The adsorbent thus obtained was ground well and sieved through a 250 mesh and kept in an air tight container for further use.

3.5 REAGENTS

The dye solution was prepared by dissolving 20g of Crystal Violet in distilled water and diluted to 1000ml.The stock solution was diluted to appropriate concentrations.

3.6 Equipment

Elico pH meter was used to measure pH

- Photo colorimeter was used for spectro-colorimetric work
- Genuine equipment manufacture’s mechanical horizontal bench shaker was used for shaking of solution containing adsorbent and adsorbate.

pH METER

PHOTO COLORIMETER

MECHANICAL HORIZONTAL BENCH SHAKER

3.7 Effect of variation of initial concentration of the dye on the adsorption

The dye solution of different concentrations containing 20,30,40,50mg of dye in 100ml was added with 100mg of the adsorbent taken in pyrex bottles and shaken in a bench shaker for various time intervals (10.20,30,40,50,60,90,120,150 and 180 minutes) at room temperature. The solutions were filtered and the dye concentrations of the filtrates were estimated colorimetric ally at 590 nm.

3.8 Effect of variation of pH on the adsorption of dye

The optimum pH for the maximum dye adsorption was found by varying the pH from 6 to 9.The pH of the prepared original Crystal Violet solution was 3.21.Therefore pH of the solution for this pH variation study was adjusted using sodium hydroxide solution.100ml of the dye solution containing 50mg of the dye were contacted with 100mg of the adsorbent and batch mode experiments conducted by varying the pH from 6 to 9.These solutions were shaken using mechanical horizontal bench shaker for various time intervals(10,20,30,40,50,60,90,120,150 and 180 minutes).The solutions were filtered and the filtrates obtained were analyzed colorimetrically to find the amount of dye adsorbed.

3.9 Effect of variation of adsorbent dosage on the adsorption of dye

100ml of the dye solution containing 50 mg of the dye were shaken in pyrex bottles and batch adsorption studies conducted by varying the adsorbent dosage (100,150,200 and 250 mg).The pyrex bottles containing adsorbent and adsorbate were shaken using mechanical horizontal bench shaker at room temperature for various time intervals (10,20,30,40,50,60,90,120,150 and 180 minutes).The solutions were filtered and the filtrates were analyzed colorimetrically to find the amount of dye adsorbed.

4.RESULTS AND DISCUSSION

The experimental data obtained and the findings of the present study are presented and discussed in the light of the objectives set forth. Batch experiments were carried out for the removal Crystal Violet dye by adsorption. The results were used to evaluate the optimum conditions for the removal of the dye, Crystal Violet and to examine the efficiency of the low-cost adsorbent prepared from Water Hyacinth for the removal of Crystal Violet dye from aqueous solution by adsorption. The parameters which influence the extent of adsorption such as concentration of the adsorbate, contact time, pH and adsorbent dosage were investigated.

4.1 EFFECT OF VARIATION OF INITIAL CONCENTRATION OF CRYSTAL VIOLET DYE SOLUTION ON THE ADSORPTION OF CRYSTAL VIOLET DYE FROM AQUEOUS SOLUTION

The adsorbate concentrations were varied from 200 to 500mg/L and batch experiments were performed. The percentage removal of Crystal Violet dye with the variation in initial concentration of Crystal Violet dye solution is depicted in figure I and the data are given in table 1. An increase in percentage removal (86.77 to 29.04%) of Crystal Violet was noticed when the initial concentration of the adsorbate was varied from 500 to 200mg/L. This may be probably due to the fact that for a fixed adsorbent dose, the total available adsorption sites are limited there by adsorbing almost the same amount of Crystal Violet dye corresponding to an increased initial concentration of the adsorbate.

4.2 EFFECT OF CONTACT TIME ON ADSORPTION OF CRYSTAL VIOLET

Effect of agitation time on adsorption is one of the factors affecting adsorption potential. The percentage adsorption of Crystal Violet dye increases with increase in contact time. From the table 1, it is evident that for maximum removal of dye by adsorbent, the solution should be equilibrated for 180 minutes and consequently it was decided that to maintain 180 minutes for all other studies. The Crystal Violet removal curves (figure 1) are smooth and continuous indicating the formation of monolayer coverage of adsorbate on outer surface of adsorbent. The percentage of dye removed by adsorption increased from 29.04 to 86.77%, when the contact time was varied from 10 to 180 minutes using 100 ml of the dye solution containing 200mg/L and 100mg adsorbent

Table 1

ADSORPTION OF CRYSTAL VIOLET WITH THE VARIATION OF INITIAL CONCENTRATION OF CRYSTAL VIOLET SOLUTION

Conditions:

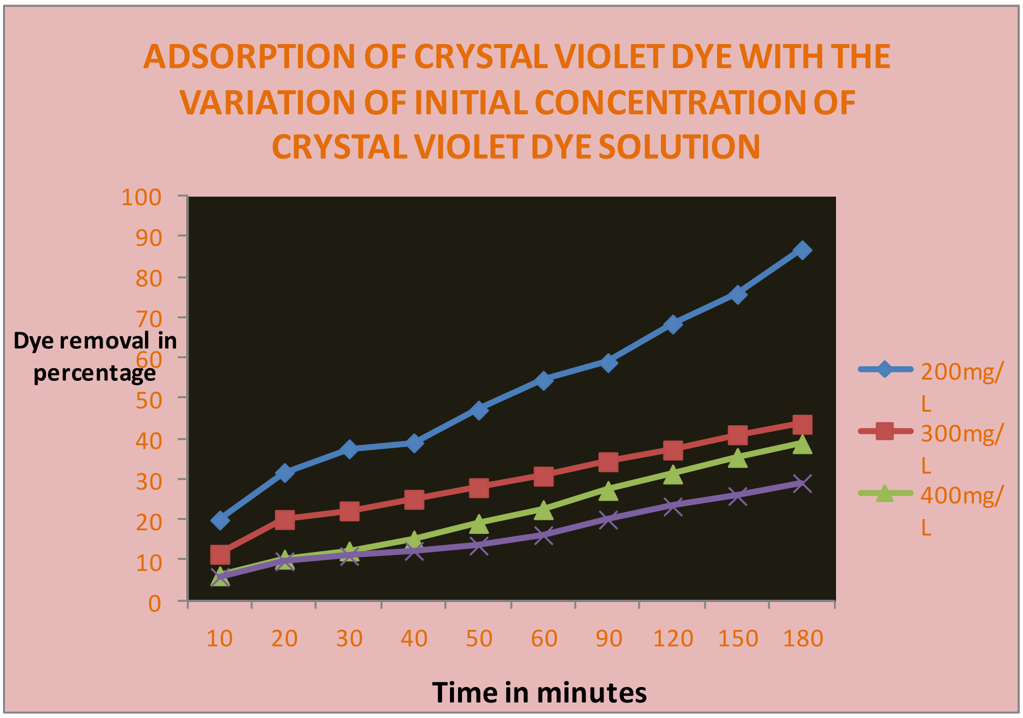
Adsorbent dosage : 100mg

Temperature : 27^{o}C

Contact time :10 to 180 minutes

Time in minutes	% of adsorption of Crystal Violet Initial concentration of Crystal Violet dye solution			
	200mg/L	**300mg/L**	**400mg/L**	**500mg/L**
10	19.9	11.43	6.12	5.82
20	31.65	20.03	10.22	9.7
30	37.52	22.16	12.25	11
40	39	25.03	14.97	12.28
50	47.1	27.9	19.07	13.58
60	54.45	30.76	22.47	16.16
90	58.85	34.33	27.22	20.02
120	68.39	37.2	31.3	23.26
150	75.75	41	35.4	25.84
180	86.77	43.6	38.8	29.04

Figure 1


ADSORPTION OF CRYSTAL VIOLET DYE WITH THE VARIATION OF INITIAL CONCENTRATION OF CRYSTAL VIOLET DYE SOLUTION
Dye removal in percentage
100
90
80
70
60
50
40
30
20
10
0
10
20
30
40
50
60
90
120
150
180
Time in minutes
200mg/L
300mg/L
400mg/L

4.3 EFFCT OF pH VARIATION ON THE ADSORPTION OF CRYSTAL VIOLET DYE

In order to optimize the pH for maximum Crystal Violet dye removal experiments were conducted with 100ml of aqueous solution of the dye containing 500mg/L of Crystal Violet dye with 100mg adsorbent. For this study pH was varied from 6 to 9. The results are depicted in table2 and figure2.The percentage adsorption of dye increased from 20.8 to 37.84%,when the pH is varied from 6 to 8. As the pH of the sorbate solution increases number of H^+ions decreases thus making the adsorption process favourable.(**Sunil kumarBajpal and Arti Jain, 2012).**

4.4 EFFECT OF ADSORBENT DOSAGE ON THE ADSORPTION OF CRYSTAL VIOLET

The effect of variation of adsorbent dosage was determined by varying the adsorbent dosage from 100 to 250mg.The results are tabulated in table3.It is evident from that adsorption potential of the adsorbent increases with increasing adsorbent dosage. The dye adsorbed increased from 37.84 to 40.88% when the adsorbent dosage was increased from 100 to 250mg.The increase in the adsorption of dye with increase in the adsorbent dosage may be due to the availability of more surface area of the adsorbent for adsorption of more number of Crystal Violet dye.

Table 2

ADSORPTION OF CRYSTAL VIOLET DYE WITH THE VARIATION OF pH

Conditions:

Adsorbent dosage	:	100mg
Temperature	:	27^{o}C
Concentration of dye solution	:	500mg/L
Contact time	:	10 to 180 minutes

Time in minutes	**% adsorption of Crystal Violet dye**		
	pH6	**pH 7**	**pH 8**
10	6.5	7.22	7.82
20	7.82	8.54	9.21
30	9.12	9.84	10.1
40	9.78	10.5	12.22
50	10.42	11.8	14.66
60	11.06	12.9	18.32
90	13.02	18.98	23.2
120	15.62	22.26	28.08
150	19.7	24.86	32.34
180	20.8	26.82	37.84

Figure 2

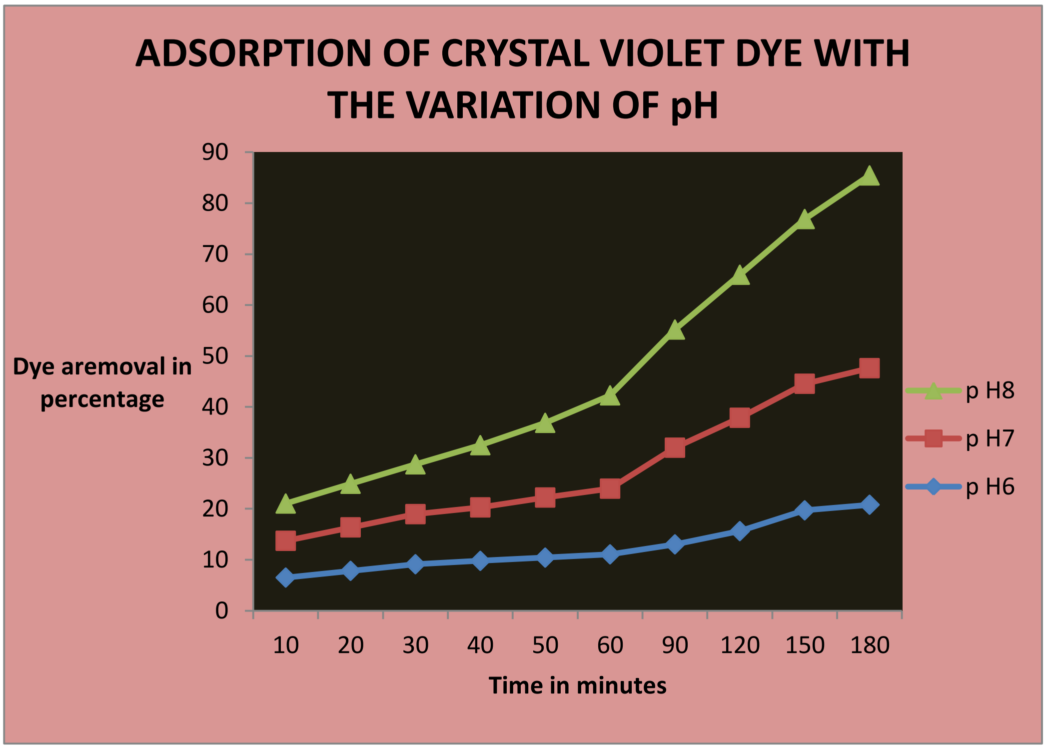
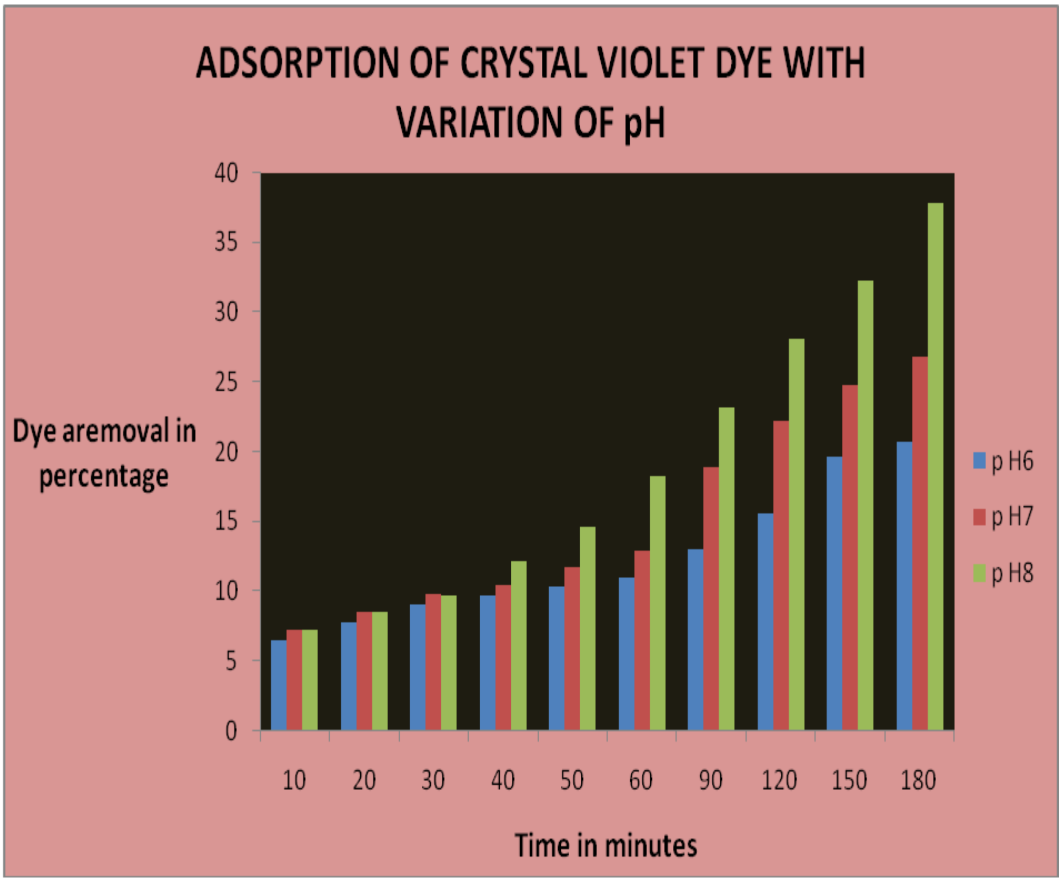

ADSORPTION OF CRYSTAL VIOLET DYE WITH THE VARIATION OF pH
Dye aremoval in percentage
90
80
70
60
50
40
30
20
10
0
10
20
30
40
50
60
90
120
150
180
Time in minutes
p H8
p H7
p H6

Figure 2.1



ADSORPTION OF CRYSTAL VIOLET DYE WITH VARIATION OF pH
Dye aremoval in percentage
40
35
30
25
20
15
10
5
0
10
20
30
40
50
60
90
120
150
180
Time in minutes
p H6
p H7
p H8

Table 3

ADSORPTION OF CRYSTAL VIOLET DYE WITH THE VARIATION OF ADSORBENT DOSAGE

Conditions:

Temperature : 27^0C

Concentration of dye solution : 500 mg/L

Contact time : 10 to 180 minutes

Time in minutes	**% Adsrption of Crystal Violet**			
	100mg	**150mg**	**200mg**	**250 mg**
10	7.32	10.98	13.44	15.88
20	8.56	13	14.66	17.1
30	9.78	14.66	16.5	18.32
40	12.22	14.80	17.72	20.76
50	14.66	17.1	19.54	21.38
60	18.32	19.54	21.38	23.2
90	23.2	23.8	25.64	26.86
120	28.08	29.3	30.3	30.52
150	32.34	33.56	35.56	36.82
180	37.84	38.44	39.66	40.88

Figure 3

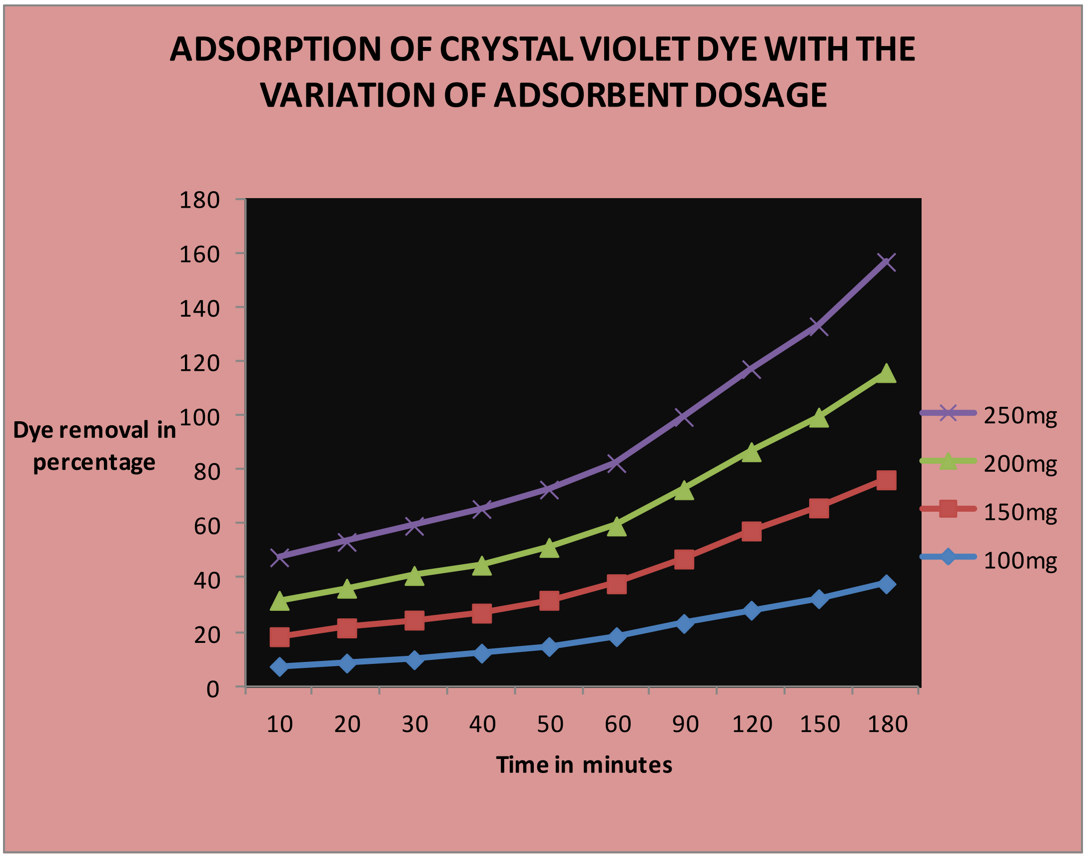
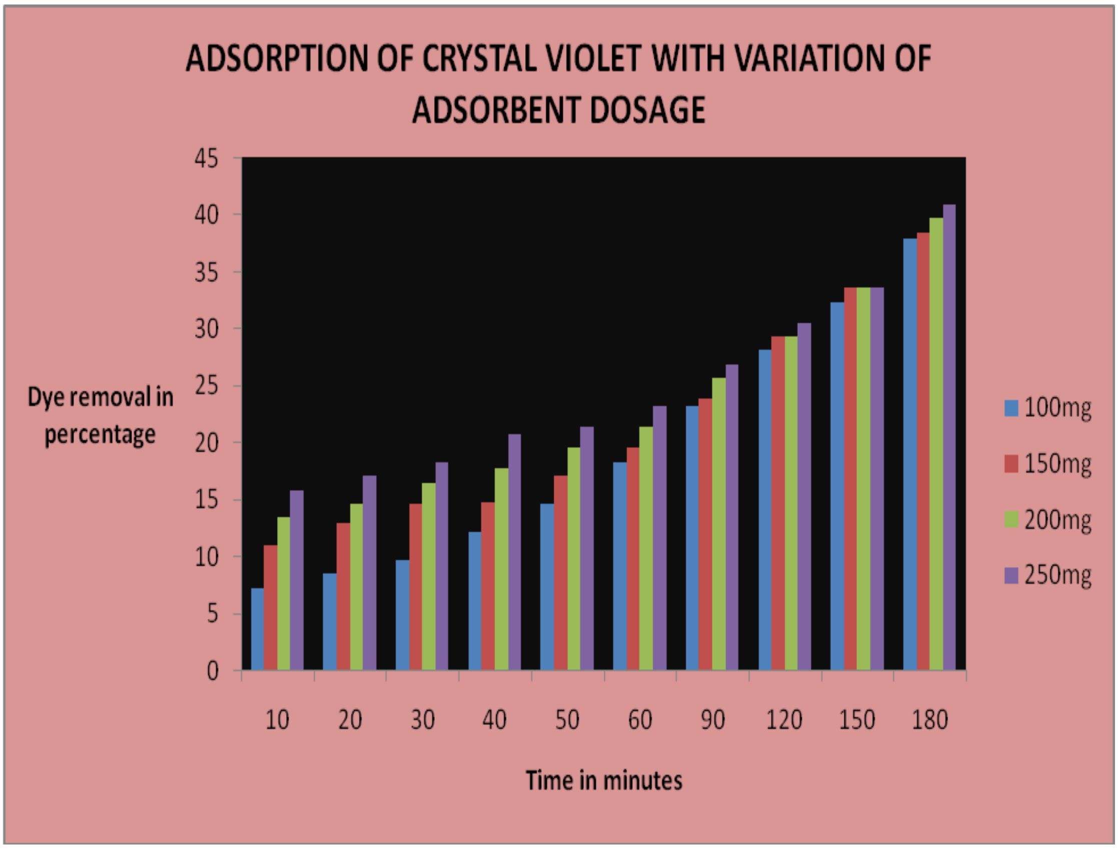

ADSORPTION OF CRYSTAL VIOLET DYE WITH THE VARIATION OF ADSORBENT DOSAGE
180
160
140
120
100
80
60
40
20
0
Dye removal in percentage
10
20
30
40
50
60
90
120
150
180
Time in minutes
250mg
200mg
150mg
100mg

Figure 3.1


ADSORPTION OF CRYSTAL VIOLET WITH VARIATION OF ADSORBENT DOSAGE
Dye removal in percentage
45
40
35
30
25
20
15
10
5
0
10
20
30
40
50
60
90
120
150
180
Time in minutes
100mg
150mg
200mg
250mg

4.5 KINETIC MODELLING FOR CRYSTAL VIOLET DYE ADSORPTION USING LAGERGREN EQUATION (VARIATION OF INITIAL CONCENTRATION OF DYE SOLUTION)

The chemical kinetics reaction path ways, along times to react the equilibrium.In this study Lagergren pseudo first order kinetic equation and intra particle diffusion rate equation were studied in the adsorption of Crystal Violet dye from aqueous solution. The Lagergren pseudo first order rate equation is as follwos.

$$\text{Log } (q_e - q_t) = \log q_e - K_a t/2.303$$

Where qe and qt are the amount of Crystal Violet dye adsorbed at time t and at equilibrium time .Ka is the rate constant. The rate constant Ka is calculated from the slopes of the linear plots of log (qe-qt) versus t. The Lagergren plots Crystal Violet dye adsorption are shown in figure5.The rate constant of Ka for different concentrations of dye solution used in this study is given in table 5..The Ka values obtained indicates that the adsorption of the dye followed Lagergren pseudo first order rate equation.

Concentration of dye in mg/L	**Kax 10^{-2}**
200	1.204
300	1.612
400	1.545
500	1.358

Table 4

KINETIC MODELLING FOR CRYSTAL VIOLET DYE ADSORPTION USING LAGERGREN EQUATION (VARIATION OF INITIAL CONCENTRATION OF DYE SOLUTION)

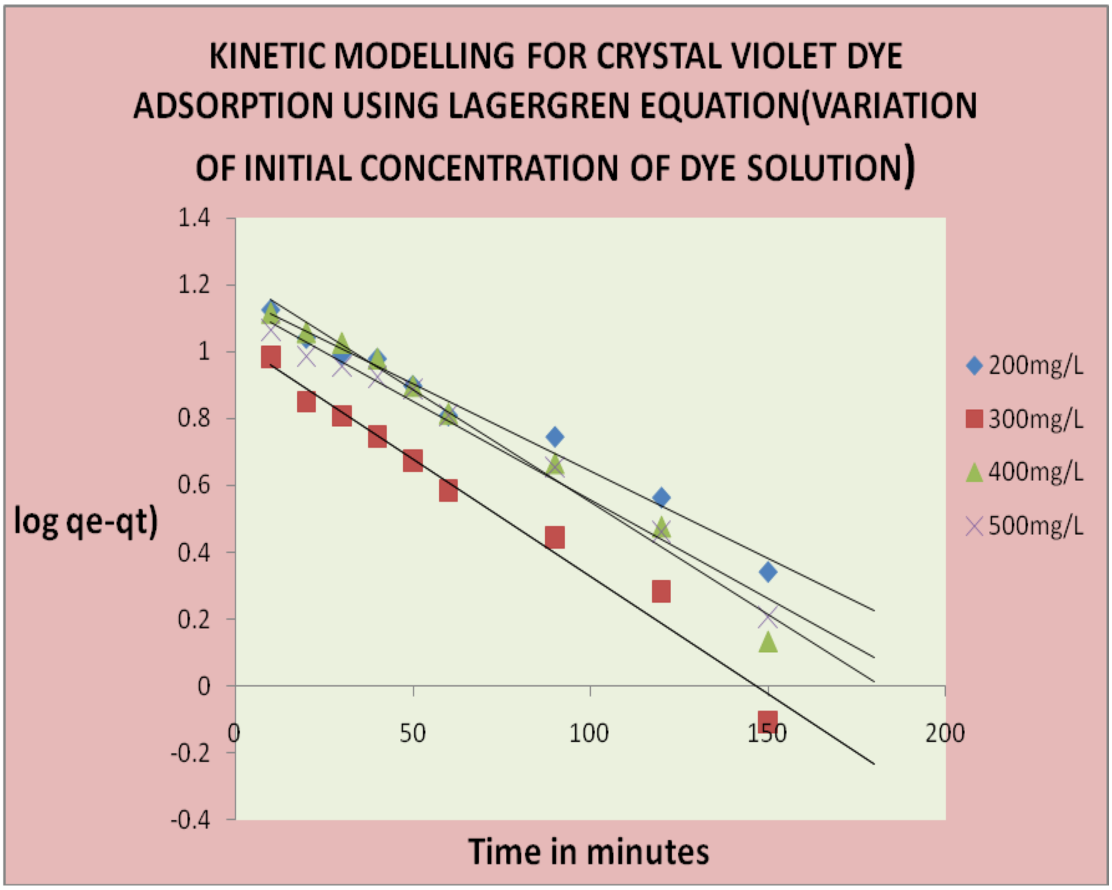
Conditions:

Adsorbent dosage : 100 mg

Temperature : 27^0 C

Time in minutes	Log (q_e-q_t)			
	Concentration of the dye solution in mg/L			
	200mg/L	**300mg/L**	**400mg/L**	**500mg/L**
10	1.1262	0.9845	1.1162	1.0468
20	1.0423	0.8494	1.0581	0.9854
30	0.9934	0.8083	1.0261	0.9552
40	0.9801	0.7459	0.9791	0.9232
50	0.8994	0.6730	0.8971	0.8881
60	0.8105	0.5856	0.8150	0.8088
90	0.7469	0.8105	0.6665	0.6539
120	0.5653	0.2833	0.4771	0.4608
150	0.3432	-0.1079	0.1335	0.2041
180	-	-	-	-
intercept	1.1656	1.0286	1.2213	1.1451
slope	-0.00523	-0.007	-0.00671	-0.0059
Ka x 10^{-2}	1.204	1.612	1.545	1.358

Figure 4



KINETIC MODELLING FOR CRYSTAL VIOLET DYE ADSORPTION USING LAGERGREN EQUATION(VARIATION OF INITIAL CONCENTRATION OF DYE SOLUTION)
log qe-qt)
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
0
50
100
150
200
Time in minutes
200mg/L
300mg/L
400mg/L
500mg/L

4.6 INTRA PARTICLE DIFFUSION RATE EQUATION FOR ADSORPTION OF CRYSTAL VIOLET DYE

Due to rapid stirring in batch reactors there is a possibility of transport of dye species from the bulk in to pores of the adsorbent as well as adsorption at outer surface of the adsorbent. The rate limiting step may be either film diffusion or intra particle diffusion. As they act in series, the slower of the two will be the rate determining step. The possibility of Crystal Violet species to diffuse in to the interior sites of the particle of adsorbent was tested with Weber-Morris equation given as follows

$$q = K_p t^{1/2}$$

Where q is the amount Crystal Violet adsorbed in mg, Kp is the intraparticle diffusion rate constant and‘t’ is the time(agitation time) in minutes.

In order to study the diffusion process batch adsorption experiments were carried out at 27^0C at by varying the initial concentration of Crystal Violet dye solution. The results are given in the table5 graphically shown in the figure 5.

Table 5

INTRAPARTICLE DIFFUSION RATE EQUATION FOR THE ADSORPTION OF CRYSTAL VIOLET DYE

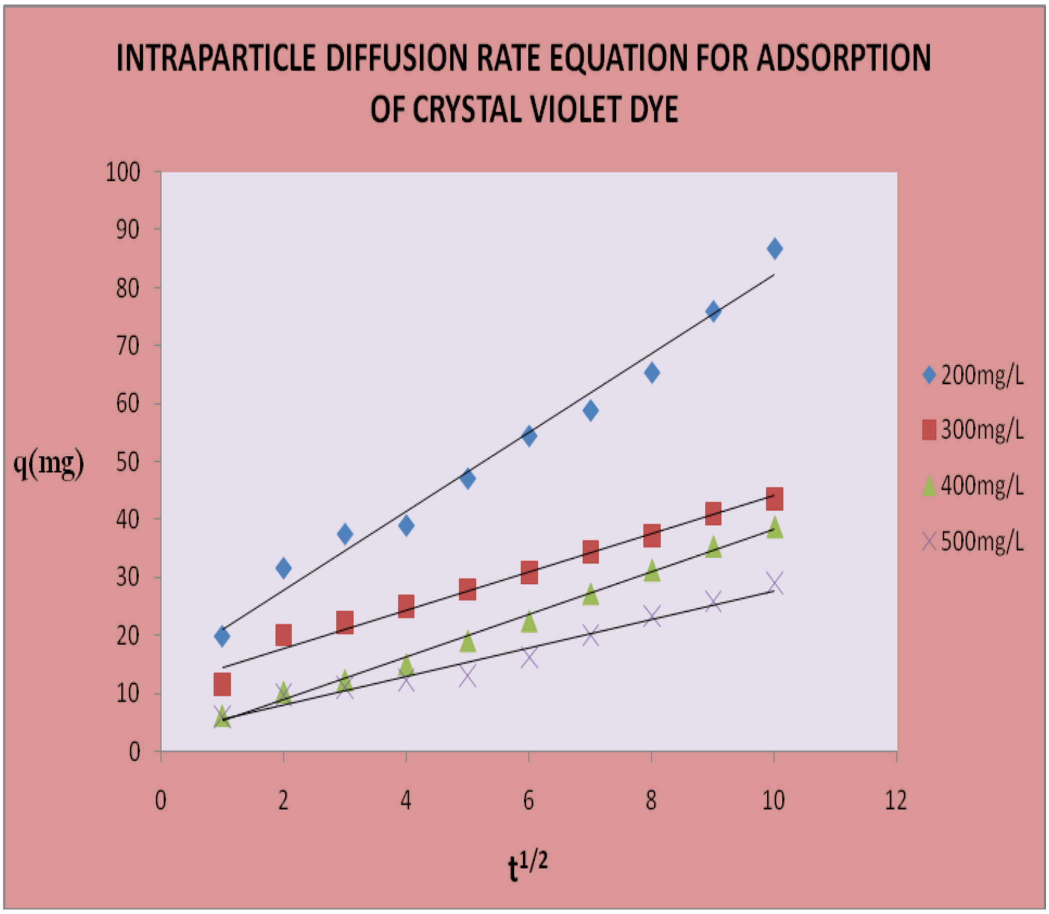
Conditions :

Adsorbent dosage :100mg

Temperature : 27^0C

Time in minutes	**$t^{1/2}$**	**Initial concentration of Crystal Violet dye in mg/L**			
		Amount of dye adsorbed(q) in mg			
		200mg/L	**300mg/L**	**400mg/L**	**500mg/L**
10	3.162	19.9	11.43	6.12	5.82
20	4.472	31.65	20.03	10.22	9.7
30	5.472	37.52	22.16	12.25	11
40	6.324	39	25.03	14.97	12.28
50	7.071	47.1	27.9	19.07	13.58
60	7.745	54.85	30.76	22.47	16.16
90	9.486	58.85	34.33	27.22	20.02
120	10.954	65.39	37.2	31.3	23.26
150	12.247	75.75	41	35.4	25.84
180	13.416	86.77	43.6	38.8	29.04
Slope		0.3487	0.1641	0.1883	0.1294
intercept		25.4997	17.0335	7.6587	6.9616

Figure 5



INTRAPARTICLE DIFFUSION RATE EQUATION FOR ADSORPTION OF CRYSTAL VIOLET DYE
q(mg)
100
90
80
70
60
50
40
30
20
10
0
0
2
4
6
8
10
12
t1/2
200mg/L
300mg/L
400mg/L
500mg/L

4.7 ADSORPTION ISOTHERMS

The results obtained in the study by varying the initial concentration of Crystal Violet solution were interpreted in terms of Langmuir and Freundlich adsorption isotherms.

4.7.1 LANGMUIR ADSORPTION ISOTHERMS

Langmuir adsorption isotherm is based on the assumption that points of valency exist s on the surface of the adsorbent and that each of these site is capable of adsorbing one molecule. The Langmuir model assumes that uptake of Crystal Violet molecule occurs on a homogeneous surface by monolayer adsorption. Thus the adsorbed layer will be one molecule thick. Further , It is assumed that all the adsorption sites have equal affinities for the adsorbent and that the presence of adsorbed molecule at one site will not affect the adsorption of a molecule at an adjacent site. The Langmuir adsorption isotherm is given as follows,

$x/m=(k^1Ce/1+k_1Ce)$ **(Gamel O.sayed *et al*., 2011)**

where,

x= Amount of Crystal Violet adsorbed(mg/L)

m= Weight of adsorbent(mg)

Ce= Concentration of Crystal Violet at equilibrium

k_1^1 and k_1=Langmuir constants(adsorption capacity and energy of adsorption)

On re arranging

$1/x/m \quad = \; 1/k_1^1 + 1/k_1Ce$

A plot of 1/x/m Vs 1/Ce is linear with slope equal to $1/k^1{}_1$ and intercept [$1/k_1^1/k_1$]. The slope, intercept and separation values are calculated and given in the table 6.

4.7.2 SEPARATION FACTOR R_L

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

$$R_L = 1/(1+bCi)$$

Where

Ci = initial concentration of the dye solution in mg/L

b= Langmuir constant (k^1_1)

R_L Value	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$R_L < 1$	Favourable

Table 6

INTERPRETATION OF RESULTS OF ADSORPTION OF CRYSTAL VIOLET DYE IN TERMS OF LANGMUIR ADSORPTION ISOTHERM FOR VARIATION IN INITIAL CONCENTRATION OF THE DYE SOLUTION

Time in minutes	Initial Conc. of dye in mg/L	Amount of dye left (Ce)	1/Ce	m/x	Separation factor R_L	Intercept	Slope
	200	16.02	0.0624	0.0251	-0.0015		
	300	26.57	0.0376	0.0291	-0.0010	0.0435	0.3038
10	**400**	37.55	0.0266	0.0408	-0.00075		
	500	47.09	0.0212	0.0343	-0.000607		
	200	13.67	0.0731	0.0151	-0.000669		
	300	23.99	0.0416	0.0164	-0.000461	-0.0247	-0.1339
20	**400**	35.91	0.0278	0.0244	-0.000334		
	500	45.15	0.0221	0.0206	-0.000267		
	200	12.49	0.0800	0.0133	-0.000136		
30	**300**	23.35	0.0424	0.0148	-0.000091	0.01601	-0.0273
	400	35.1	0.0284	0.0204	-0.000068		
	500	44.5	0.0224	0.0181	-0.000054		
	200	12.2	0.0819	0.0128	-0.00013		
40	**300**	22.49	0.0444	0.0131	-0.000091	0.0175	-0.0636
	400	34.01	0.0294	0.0167	-0.000068		
	500	43.86	0.0227	0.0162	-0.000054		
	200	10.58	0.0945	0.0106	-0.000317		
50	**300**	21.68	0.0462	0.0118	-0.000212	0.019	-0.0496
	400	32.37	0.0308	0.0131	-0.000159		
	500	43.21	0.0231	0.0147	-0.000127		

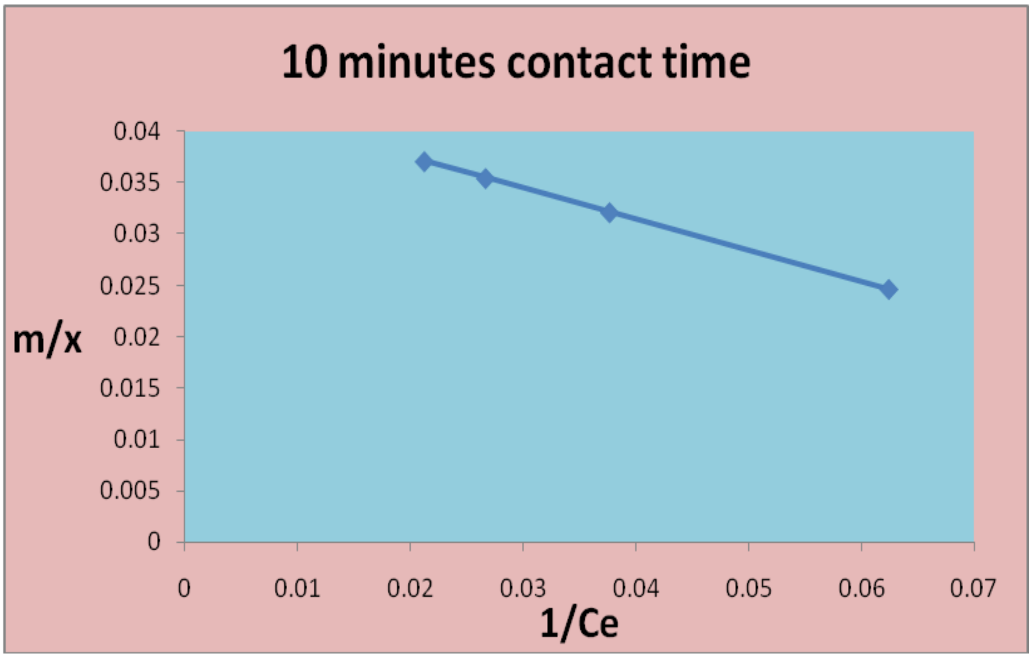
Table 6

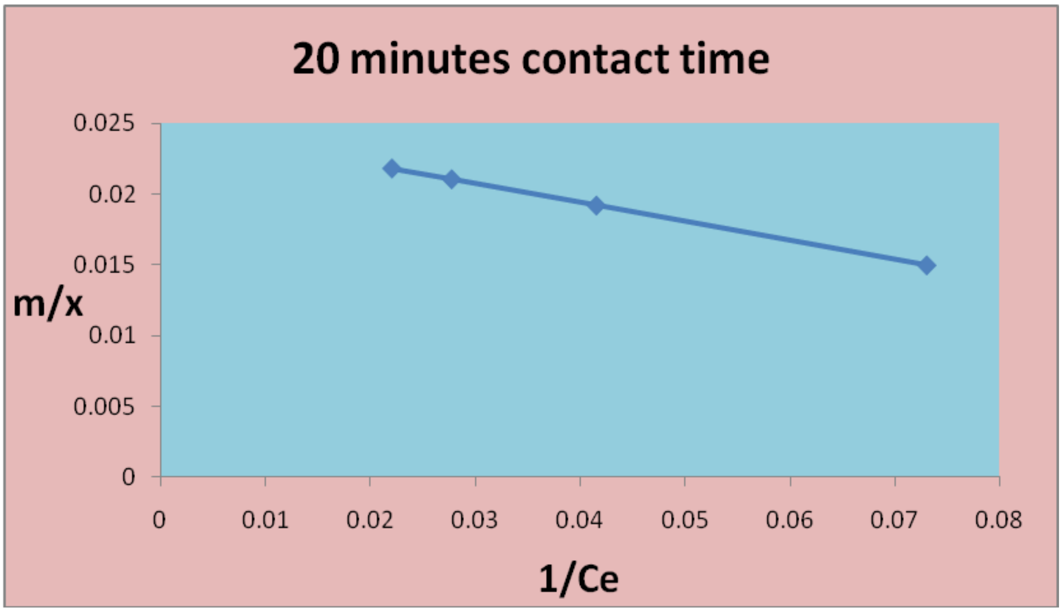
INTERPRETATION OF RESULTS OF ADSORPTION OF CRYSTAL VIOLET DYE IN TERMS OF LANGMUIR ADSORPTION ISOTHERM FOR VARIATION OF INITIAL CONCENTRATION OF THE DYE SOLUTION

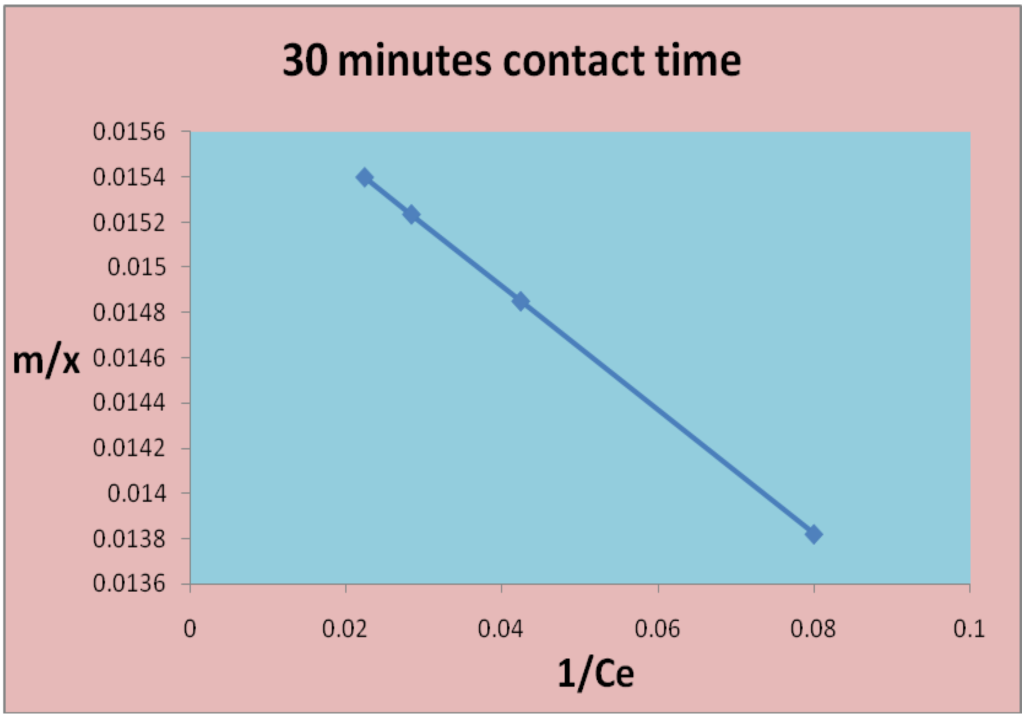
Time in minutes	Initial concentration of dye mg/L	Amount of dye left (Ce)	1/Ce	m/x	Separation factor RL	Intercept	Slope
	200	9.11	0.1097	0.0091	-0.000248		
60	**300**	20.77	0.0481	0.0107	-0.000165	0.0122	-0.0322
	400	31.01	0.0322	0.111	-0.000124		
	500	41.92	0.0238	0.0123	-0.000099		
	200	8.23	0.1215	0.0096	0.000027		
90	**300**	19.70	0.0507	0.00840	0.000017	-0.0100	0.0054
	400	29.11	0.0343	0.0091	0.000013		
	500	39.99	0.024	0.0099	0.000010		
	200	6.23	0.0605	0.0087	0.000025		
120	**300**	18.84	0.0530	0.0073	0.000017	-0.0086	0.0051
	400	2.48	0.0363	0.0079	0.000012		
	500	38.37	0.0260	0.0085	0.000010		
	200	4.85	0.2061	0.0080	0.000021		
150	**300**	17.7	0.0564	0.0066	0.000014	-0.0077	0.0042
	400	25.84	0.0386	0.0070	0.0000010		
	500	37.08	0.0269	0.0077	0.000085		
	200	2.64	0.3787	0.0075	0.000016		
180	**300**	16.92	0.0591	0.0057	0.000010	-0.0070	0.0032
	400	24.68	0.0405	0.0064	0.000008		
	500	35.48	0.0281	0.0068	0.000006		

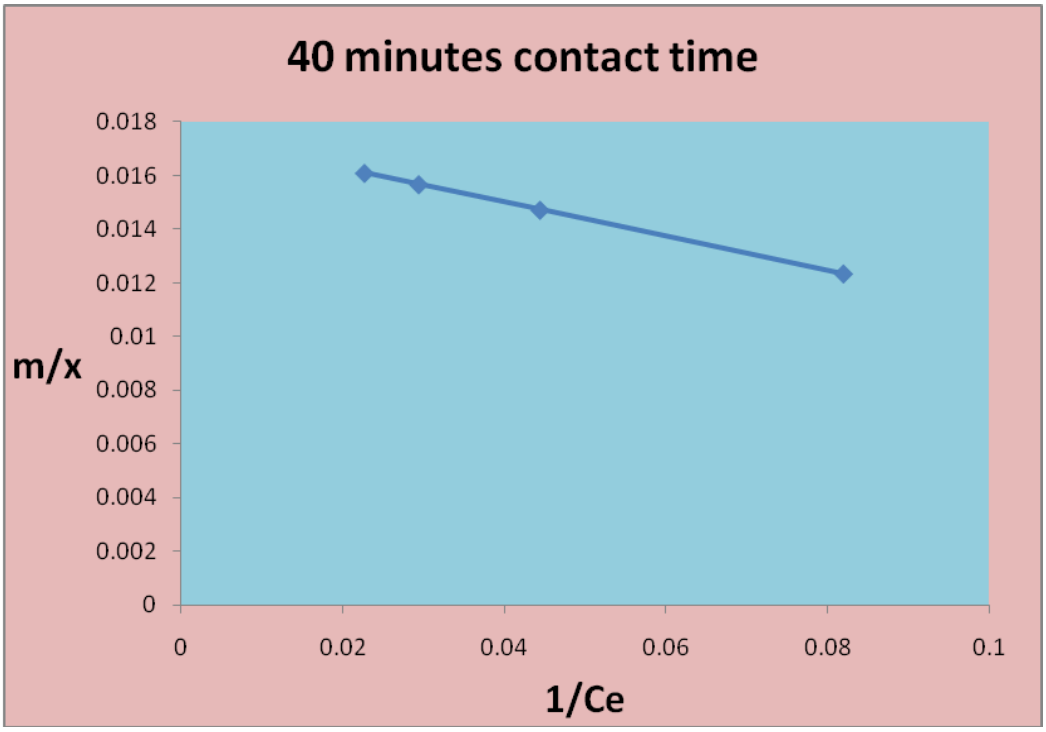
Figure 6

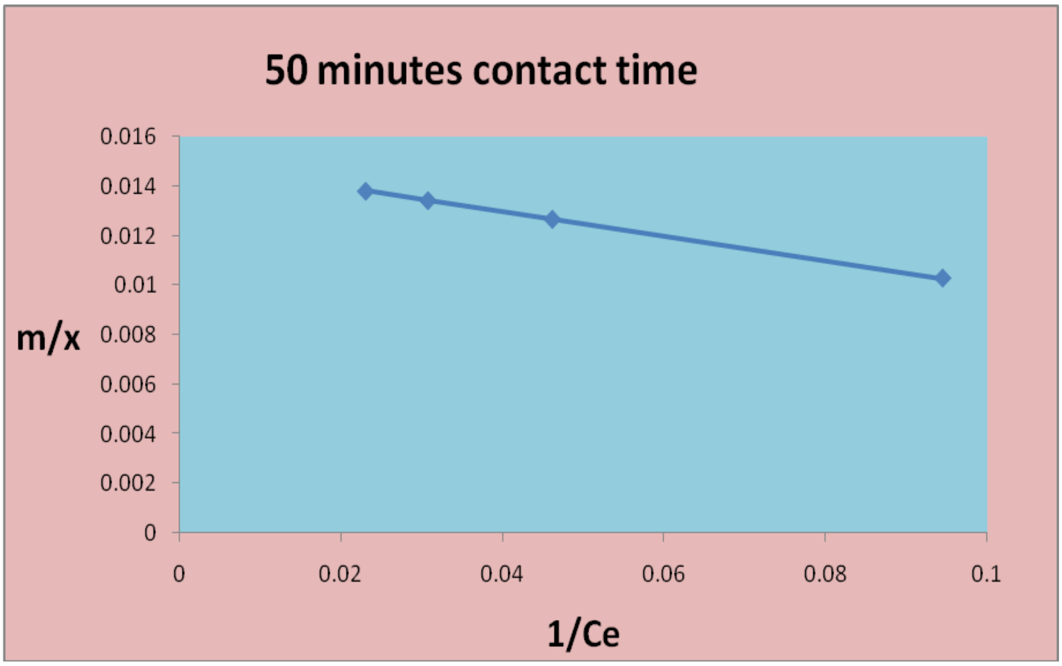
LANGMUIR ADSORPTION ISOTHERM PLOTS

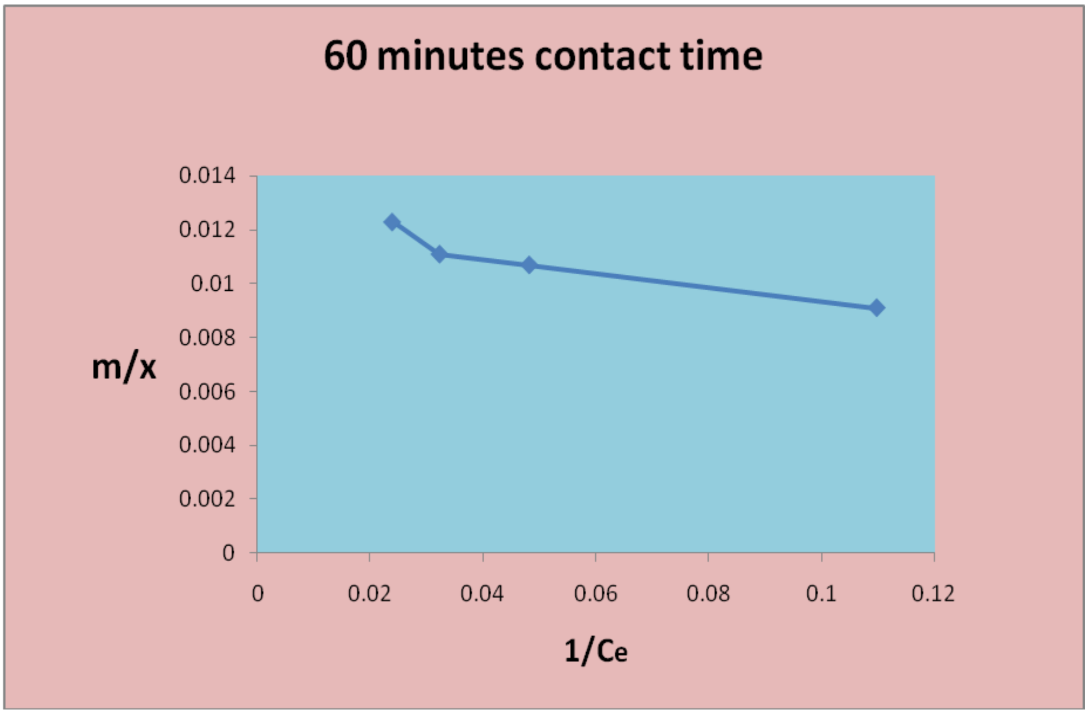


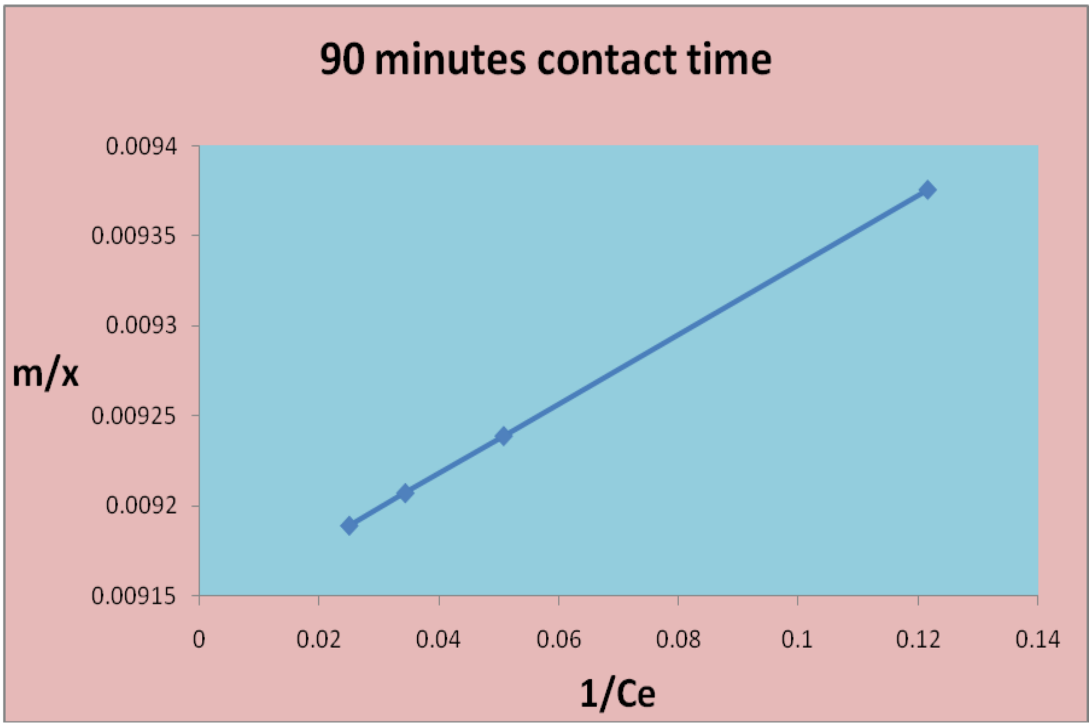


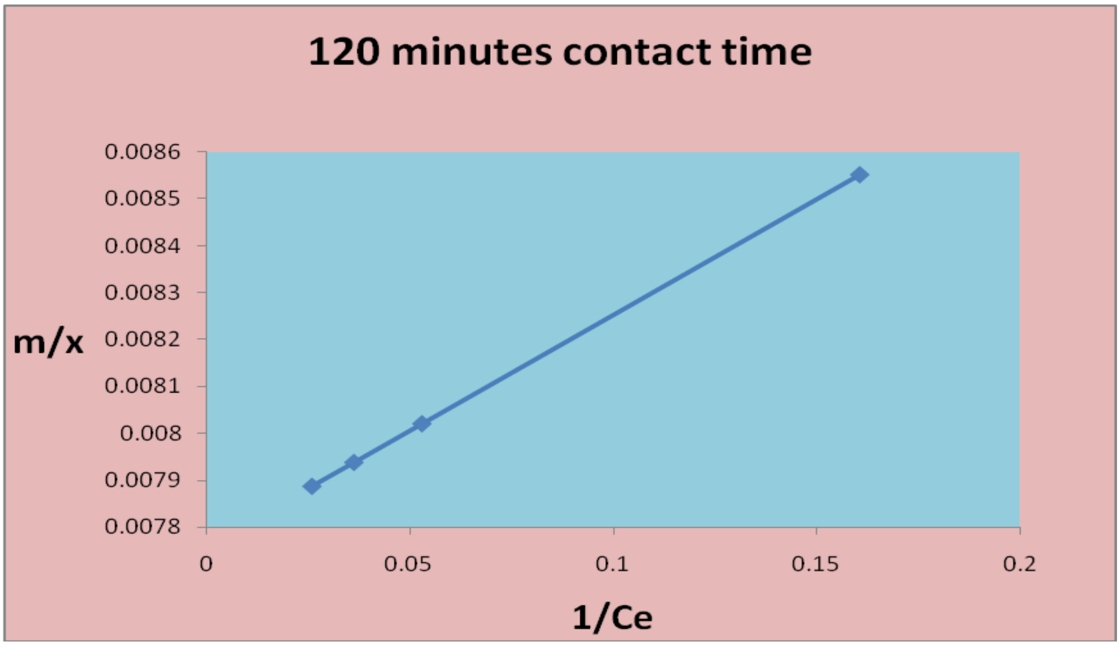

30 minutes contact time
m/x
0.0156
0.0154
0.0152
0.015
0.0148
0.0146
0.0144
0.0142
0.014
0.0138
0.0136
0
0.02
0.04
0.06
0.08
0.1
1/Ce

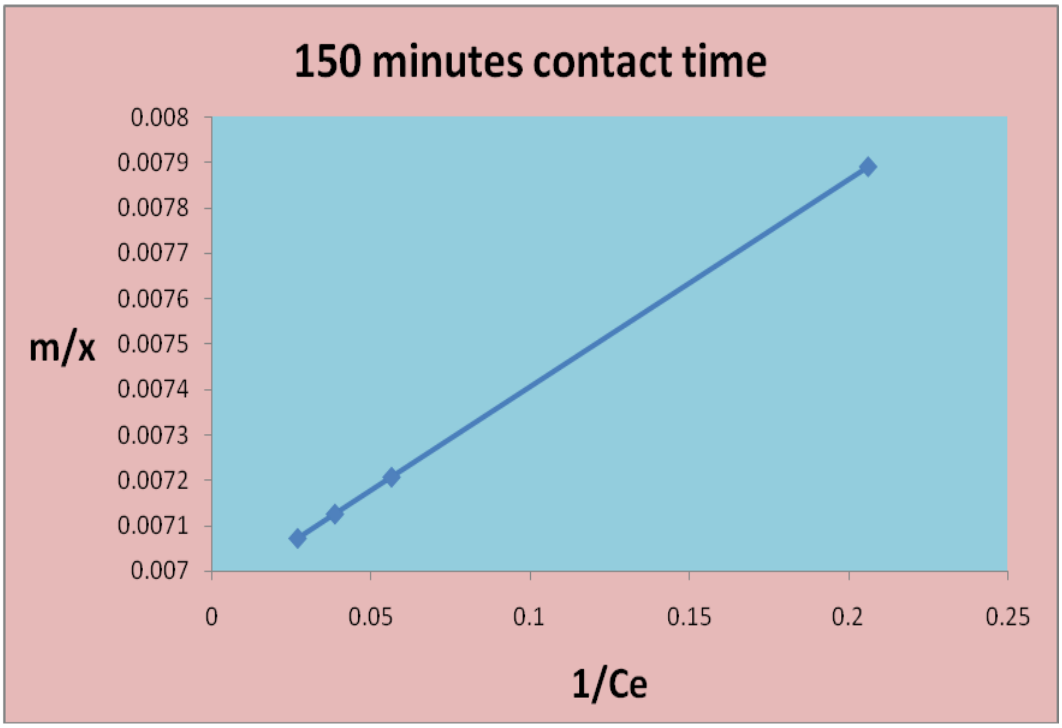

40 minutes contact time
m/x
0.018
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
0
0.02
0.04
0.06
0.08
0.1
1/Ce


50 minutes contact time
0.016
0.014
0.012
0.01
m/x
0.008
0.006
0.004
0.002
0
0
0.02
0.04
0.06
0.08
0.1
1/Ce

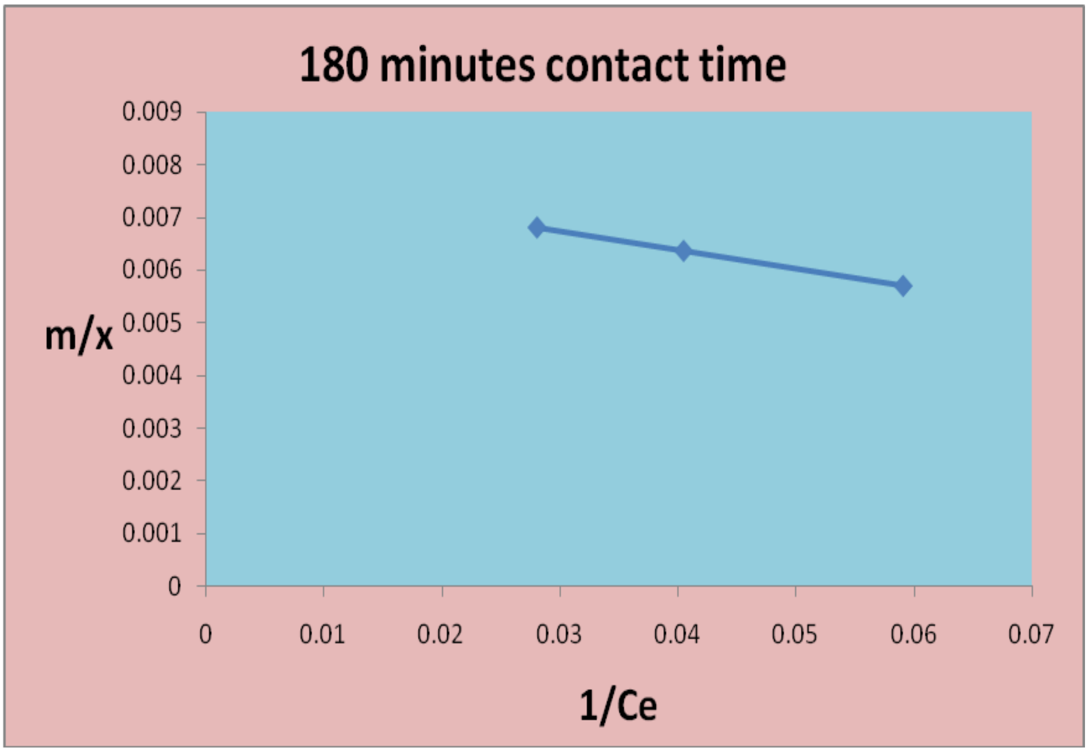

60 minutes contact time
0.014
0.012
0.01
0.008
m/x
0.006
0.004
0.002
0
0
0.02
0.04
0.06
0.08
0.1
0.12
1/Ce


90 minutes contact time
m/x
0.0094
0.00935
0.0093
0.00925
0.0092
0.00915
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
1/Ce


120 minutes contact time
m/x
0.0086
0.0085
0.0084
0.0083
0.0082
0.0081
0.008
0.0079
0.0078
0
0.05
0.1
0.15
0.2
1/Ce



150 minutes contact time
m/x
0.008
0.0079
0.0078
0.0077
0.0076
0.0075
0.0074
0.0073
0.0072
0.0071
0.007
0
0.05
0.1
0.15
0.2
0.25
1/Ce



180 minutes contact time
m/x
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
1/Ce

4.7.3 FREUNDLICH ADSORPTION ISOTHERM

The Freundlich adsorption isotherm equation is given as follows

$x/m = K_F C_e^{1/n}$

The linear form of Freundlich adsorption is given as

$\text{Log } x/m = \log K_F + 1/n \log Ce$

Where x/m is the amount of Crystal Violet adsorbed on unit weight of the adsorbent at equilibrium and Ce is the concentration of Crystal Violet dye at equilibrium (**Jambulingam *et al*.**, 2006).

The Freundlich adsorption isotherm plots at room temperature is plotted between log x/m Vs log Ce for different concentration of the aqueous solution of Crystal Violet dye solution are shown in figure .K_F and 1/n values are evaluated from the slope and intercept respectively.

The Freundlich parameters K_F and 1/n are indicators of adsorption capacity and adsorption intensity respectively.The values have been encorporated in T able 7

Table 7

INTERPRETATINOF RESULTS OF ADSORPTION OF CRYSTAL VIOLET IN TERMS OF FREUNDLICH ADSORPTION ISOTHERM FOR VARIATION OF INITIAL CONCENTRATION OF THE DYE SOLUTION

Time in minutes	Initial conc. Of dye mg/L	Log Ce	Log x/m	Intercept	Slope 1/n	n
10	200 300 400 500	1.2046 1.4243 1.5746 1.6729	1.6003 1.5360 1.3891 1.4646	2.0521	-0.3776	-2.6483
20	200 300 400 500	1.1357 1.3800 1.5552 1.6546	1.8040 1.7832 1.6125 1.6860	2.1732	-0.3156	-3.1685
30	200 300 400 500	1.0965 1.3682 1.5453 1.6483	1.8761 1.8296 1.6902 1.7422	2.2164	-0.3053	-3.2754
40	200 300 400 500	1.0863 1.3519 1.5316 1.6420	1.8927 1.8800 1.7772 1.7883	2.1457	-0.2218	-4.4286
50	200 300 400 500	1.0244 1.3350 1.5101 1.6355	1.9746 1.9280 1.8826 108320	2.2137	-0.2248	-4.5085

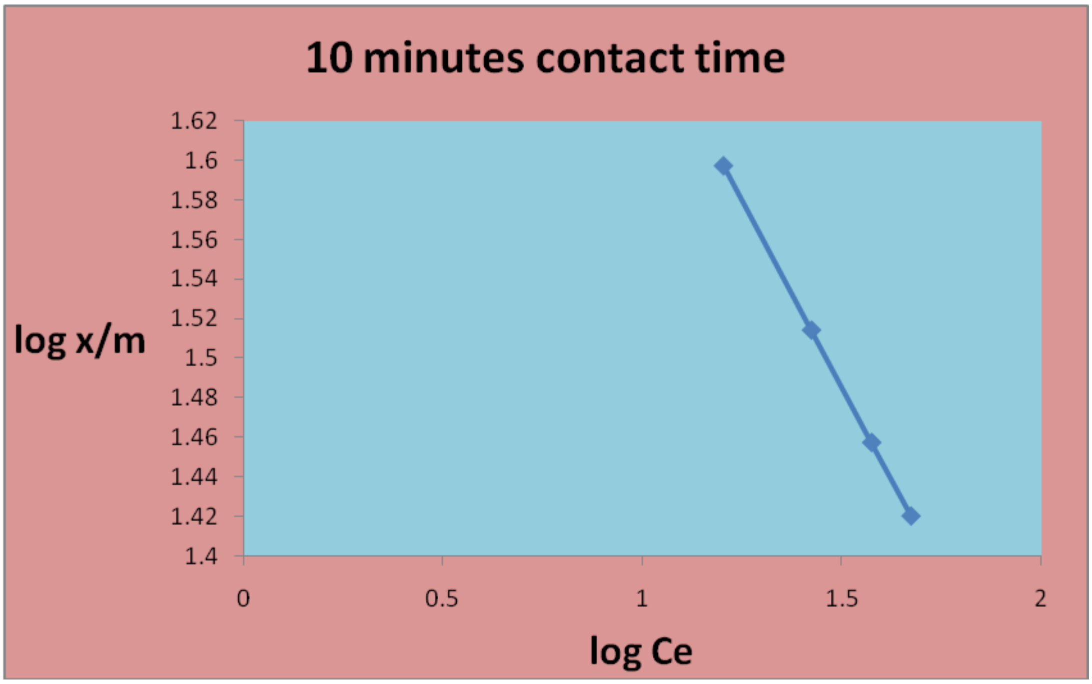
Table 7

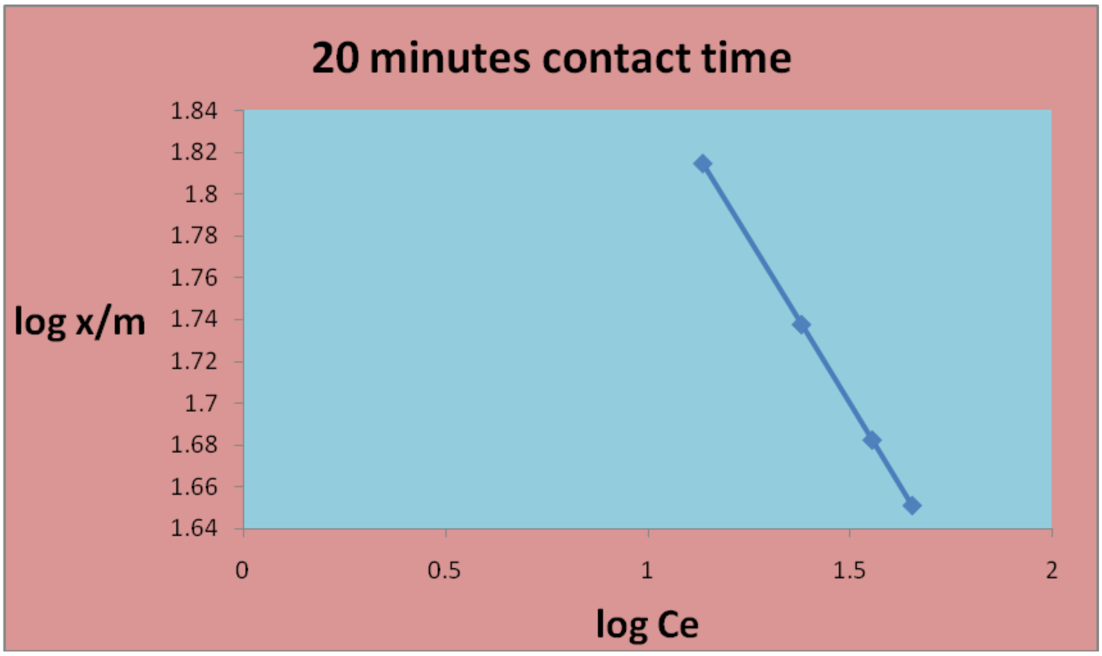
INTERPRETATINOF RESULTS OF ADSORPTION OF CRYSTAL VIOLET IN TERMS OF FREUNDLICH ADSORPTION ISOTHERM FOR VARIATION OF INITIAL CONCENTRATION OF THE DYE SOLUTION

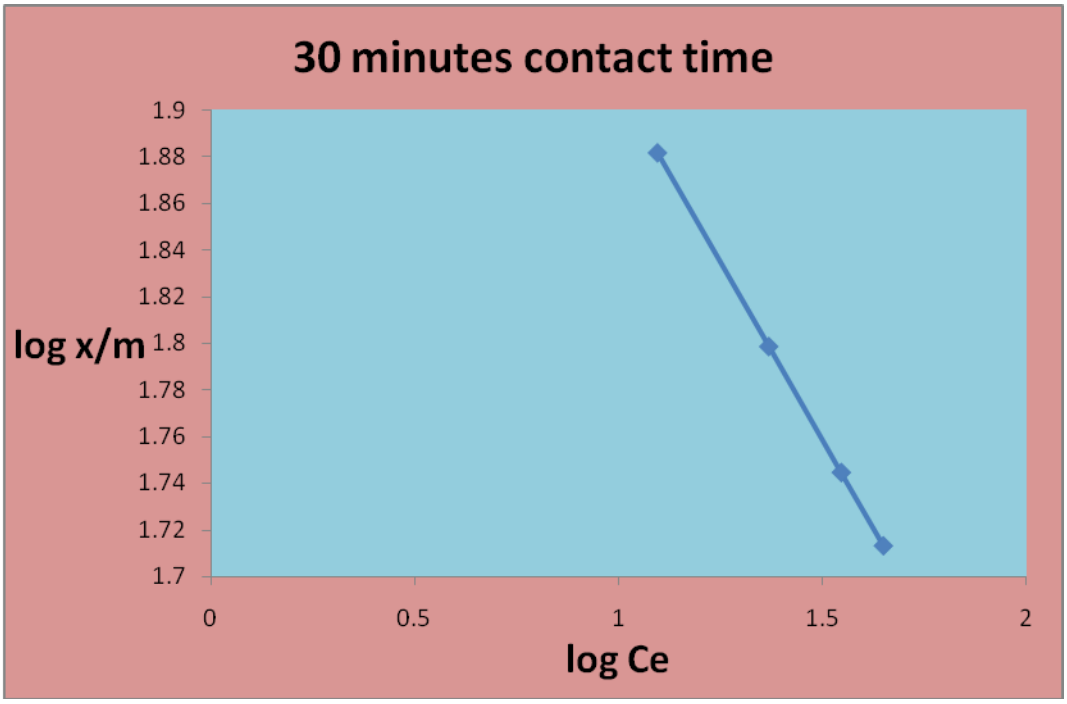
Time in minutes	Initial conc. Of dye mg/L	Log Ce	Log x/m	Intercept	Slope 1/n	n
60	200 300 400 500	0.9545 1.3174 1.4915 1.6224	2.0370 1.9697 1.9546 1.9160	2.0101	-0.3806	-26.084
90	200 300 400 500	0.0244 1.3350 1.4640 1.6355	1.9746 1.9280 1.8826 1.8320	2.0062	-0.0701	-14.417
120	200 300 400 500	0.08007 1.2750 1.4390 1.5893	2.1360 2.0604 2.0979 2.0659	2.1927	-0.08053	-12.417
150	200 300 400 500	10.6857 1.2479 1.4122 1.5691	2.1794 2.0947 2.1511 2.5691	2.2168	-0.0672	-14.880
180	200 300 400 500	1.4219 1.2284 1.3923 1.5499	2.2395 2.1214 2.1938 2.1623	2.2068	-0.0735	-13.653

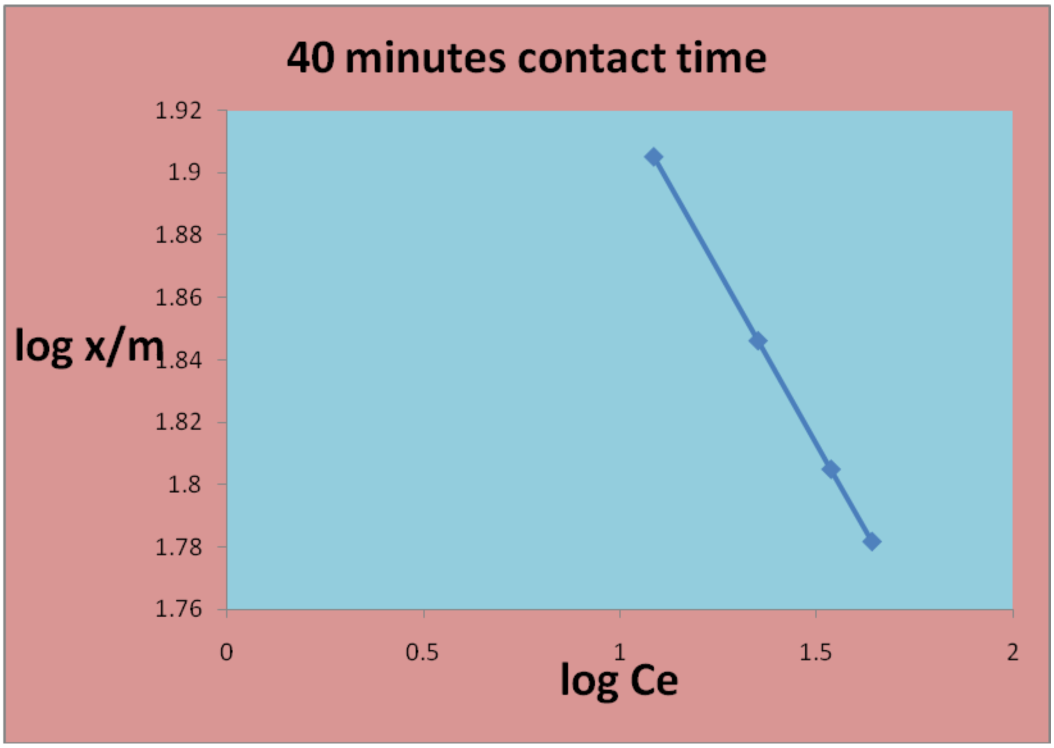
Figure 7

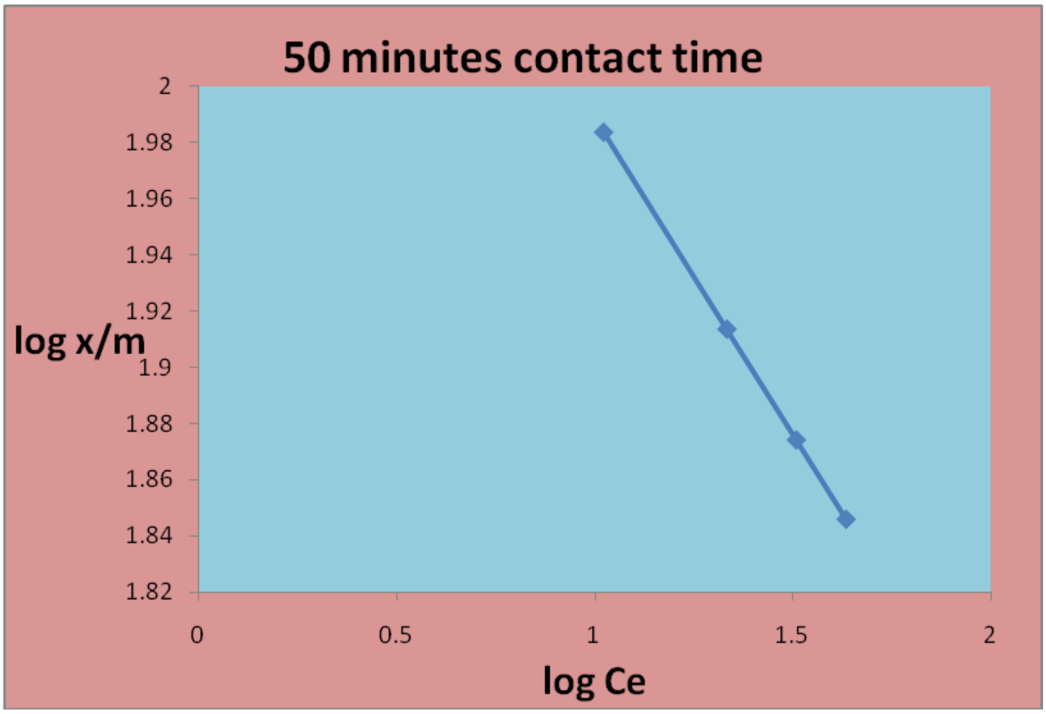
FREUNDLICH ADSORPTION ISOTHERM PLOTS

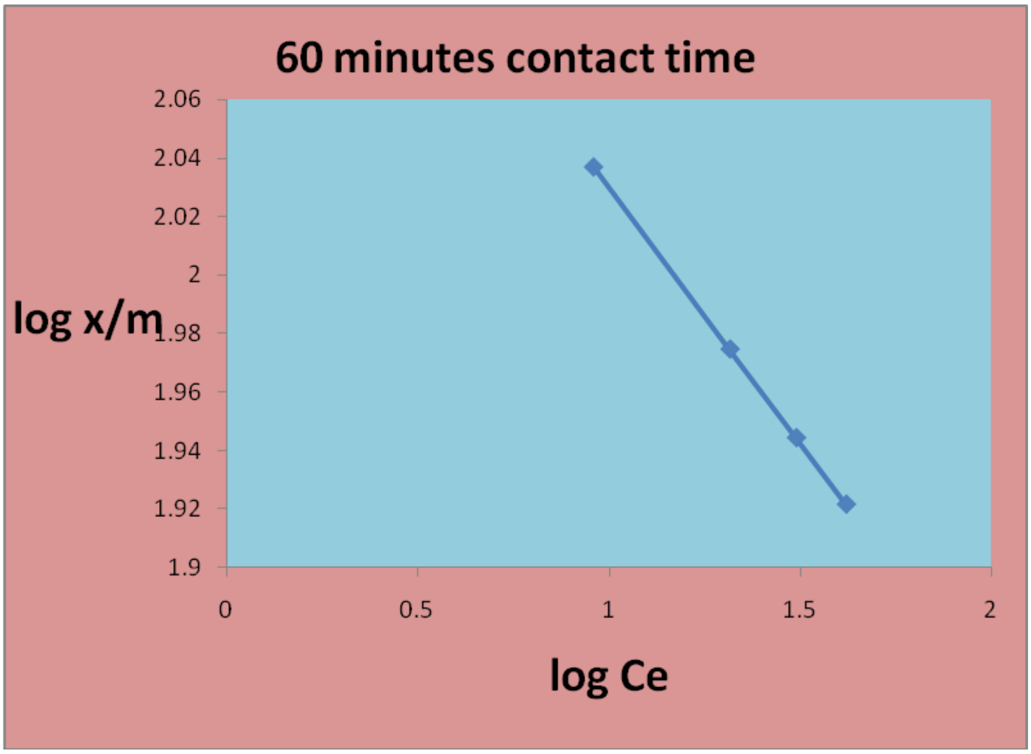


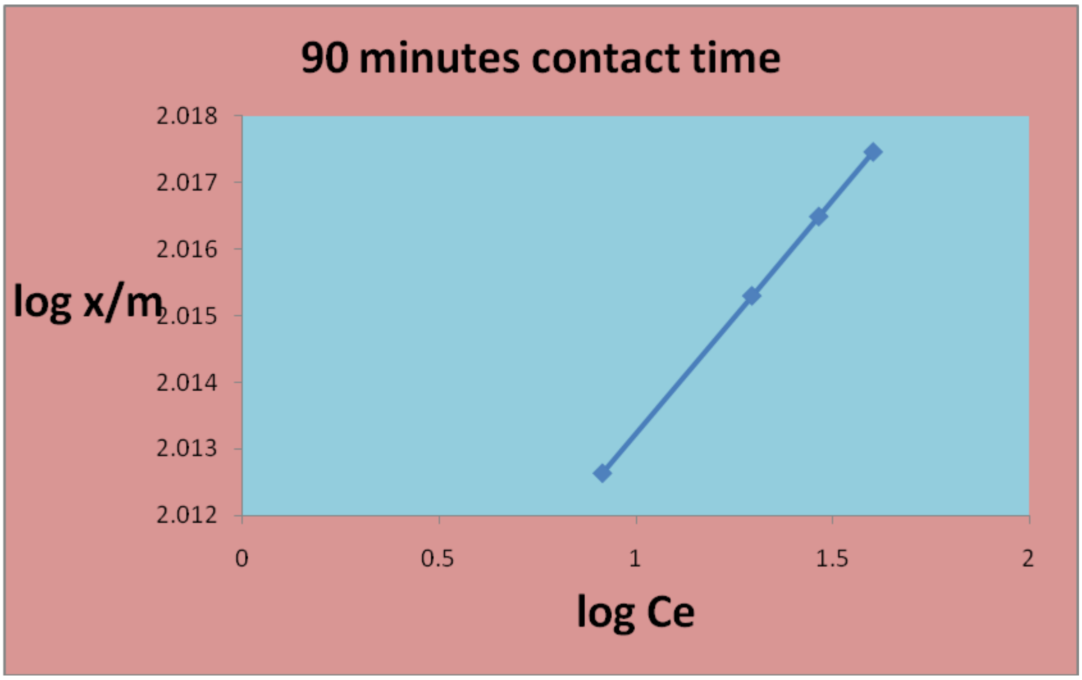


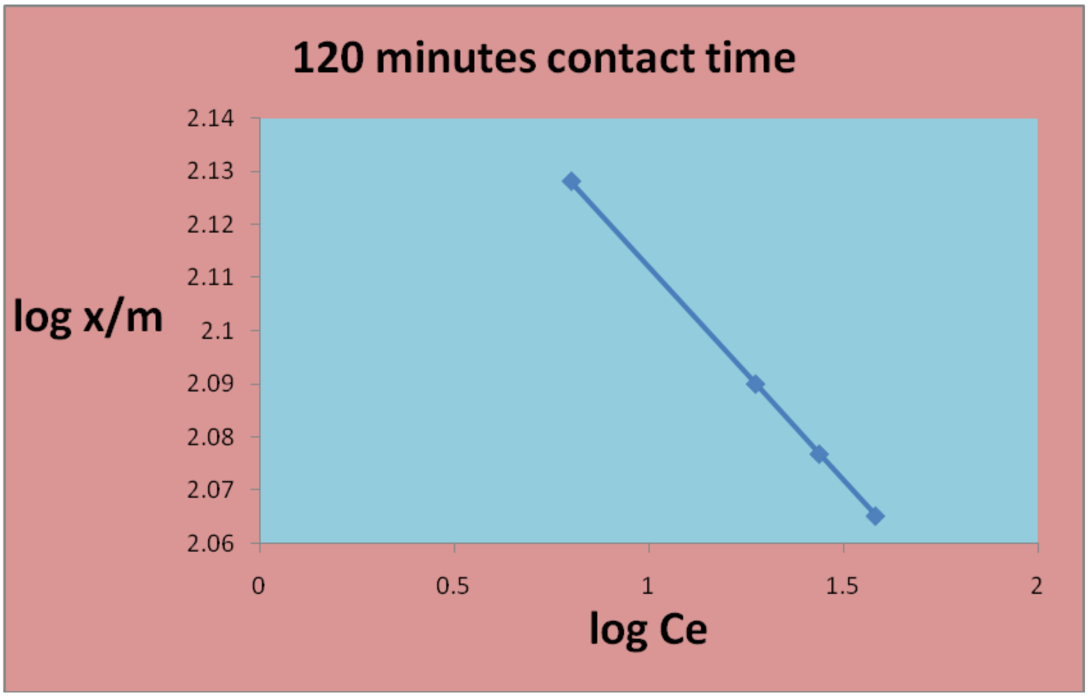

30 minutes contact time
log x/m
1.9
1.88
1.86
1.84
1.82
1.8
1.78
1.76
1.74
1.72
1.7
0
0.5
1
1.5
2
log Ce

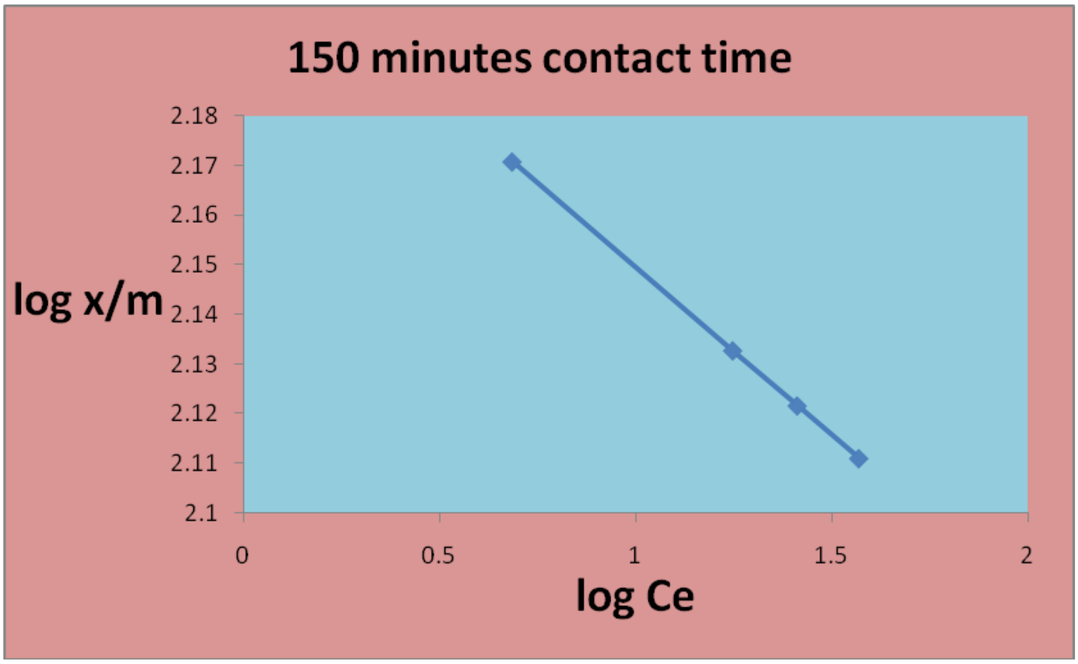

40 minutes contact time
log x/m
1.92
1.9
1.88
1.86
1.84
1.82
1.8
1.78
1.76
0
0.5
1
1.5
2
log Ce

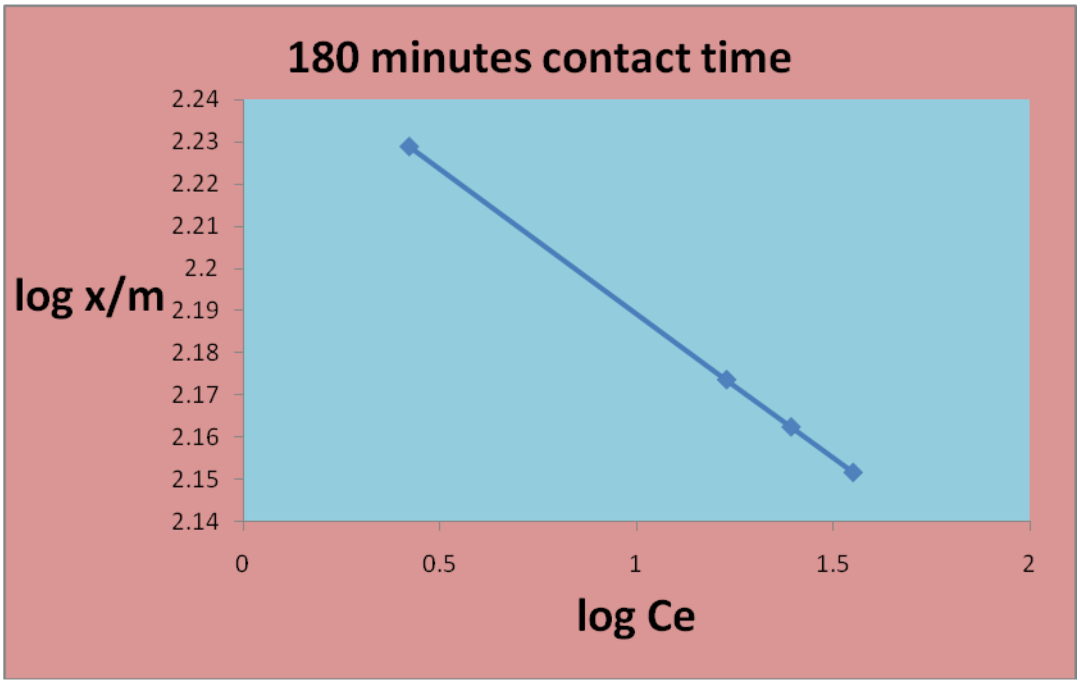

50 minutes contact time
log x/m
2
1.98
1.96
1.94
1.92
1.9
1.88
1.86
1.84
1.82
0
0.5
1
1.5
2
log Ce


60 minutes contact time
log x/m
2.06
2.04
2.02
2
1.98
1.96
1.94
1.92
1.9
0
0.5
1
1.5
2
log Ce


90 minutes contact time
2.018
2.017
2.016
2.015
2.014
2.013
2.012
log x/m
0
0.5
1
1.5
2
log Ce


120 minutes contact time
2.14
2.13
2.12
2.11
2.1
2.09
2.08
2.07
2.06
log x/m
0
0.5
1
1.5
2
log Ce


150 minutes contact time
log x/m
2.18
2.17
2.16
2.15
2.14
2.13
2.12
2.11
2.1
0
0.5
1
1.5
2
log Ce


180 minutes contact time
log x/m
2.24
2.23
2.22
2.21
2.2
2.19
2.18
2.17
2.16
2.15
2.14
0
0.5
1
1.5
2
log Ce

SUMMARY AND CONCLUSION

- The low-cost activated carbon prepared from Water Hyacinth can be used as an effective adsorbent for the removal of basic dye, Crystal Violet from aqueous solution.

- The percentage removal of Crystal Violet dye increases from 29.04 to 86.77% in 180 minutes of contact time when the concentration of the dye solution was varied from 500 to 200mg/L with 100mg adsorbent used in this study.

- Removal of Crystal Violet dye increases with increase in pH. The percentage removal of the dye by adsorption increased from 20.8 to 37.84%, when the pH of the dye solution was varied from 6 to 8 in 180 minutes of contact time with 100mg of the adsorbent.

- Removal of Crystal Violet dye increased from 37.84 to 40.88% with increasing adsorbent dosage from 100 to 250mg in 180 minutes contact time, using 100ml of the dye solution of initial concentration of 500mg/L.

- The adsorption kinetics of Crystal Violet dye onto low-cost adsorbent used in this study followed Lagergren pseudo first order rate equation.

- The intra particle diffusion study shows that the rate constant (Kp) for intra particle diffusion increased with the increase in initial concentration of Crystal Violet dye solution.

- Langmuir adsorption isotherm plots obtained by plotting 1/Ce vs m/x are linear. R_L values obtained in this study are below one indicated that the adsorption of Crystal Violet dye on to low-cost adsorbent is favourable.

- Freundlich adsorption isotherms obtained in this study are linear indicating the feasibility of the Crystal Violet dye adsorption onto the low-cost adsorbent used in this study.

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