

ADSORPTION CHARACTERISTICS OF JACKFRUIT LEAF POWDER (JLP) FOR THE REMOVAL OF DYES

*Thesis submitted in partial fulfillment of the requirement
for the award of the degree of*

*Master of Technology
in
Chemical Engineering*

Submitted By:

Amit Kumar Ojha

Roll No.: 601111018

Under the Guidance of:

Dr. Vijaya Kumar Bulasara

Assistant Professor

Department of Chemical Engineering



Department of Chemical Engineering

Thapar University, Patiala

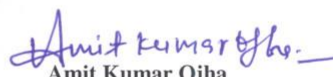
Patiala – 147004, Punjab, India

June 2013

CERTIFICATE

This is certified that the thesis entitled “**Adsorption characteristics of Jackfruit leaf powder (JLP) for the removal of dyes**” is an authentic record of my own work carried out as requirements for the award of the degree of M. Tech. (Chemical engineering) at Thapar University, Patiala, under the guidance of **Dr. Vijaya Kumar Bulasara** (Assistant Professor, ChED) during January to June 2013.

Date:- 14-06-2013


Amit Kumar Ojha

Roll No. 601111018

It is certified that the above statement made by the student is correct to the best of our knowledge and belief.



Dr. Vijaya Kumar Bulasara

Assistant Professor

Department of Chemical Engineering

Thapar University, Patiala

Countersigned by:


09.07.13

Dr. Rajeev Mehta

Head of the Department

Department of Chemical Engineering



Dr. S. K. Mohapatra

Dean of Academic Affairs

Thapar University, Patiala

ACKNOWLEDGEMENTS

At first, my heartfelt thanks to the almighty for his abundant blessing showered on me throughout this endeavor to complete this successful work of mine. I am thankful to my parents for their great support throughout my life. I would cherish every moment where my parents were so keen and curious to know about the details and progress of my work which boosted my confidence. I express my deep sense of gratitude to them. My honorable guide **Dr. VIJAYA KUMAR BULASARA**, Assistant Professor, Department of Chemical Engineering, Thapar University, is a person to whom I will always remain grateful for his excellent guidance, valuable discussions, encouragement, constructive criticism and his insights have strengthened this study significantly. He gave me a complete freedom to use my opinion, correcting whenever necessary in my dissertation.

I would like to thank my Head of Department **Dr. RAJEEV MEHTA**, who has at all times been very supportive and accommodating.

I thank **Dr. RAJ KUMAR GUPTA**, my P.G. Coordinator for his terrific guidance regarding the thesis writing and sir has provided us much time to write thesis.

I would like to thank **all the faculty members** of the department of chemical engineering for encouraging me to write the seminar report.

I would like to thank the most senior person, **Dr. P.K. BAJPAI** (Distinguished Professor) for his guidance and blessings.

I would like to thank all my **colleagues** at Thapar University, Patiala for their support and encouragement in carrying out my research smoothly.

ABSTRACT

Adsorption process is one of the superior methods for the dye removal from wastewater; generally the dyes are removed by using synthetic adsorbent such as activated carbon, zeolite and many other adsorbent. But, the synthetic adsorbent is too costly and is not readily available. That's why we are looking forward for the natural adsorbents. Whose are readily available and the adsorbent does not have any commercial value. In this work we have used JLP (Jackfruit leaf powder) synthesized from mature Jack fruit leaf, having high adsorption capacity for dye and it is relatively cheap. This work presents the experimental studies on the adsorptive removal of Amido Black 10 B dye and Crystal violet dye using a natural adsorbent JLP. Preparation methodology for JLP involved grinding, drying (sun drying), boiling and drying in hot air oven at 105 °C. The synthesized JLP was then used to study the effect of various parameters namely pH, temperature, agitation speed, adsorption time, JLP loading and initial dye concentration on the dye removal efficiency. Then, the optimal process parameters for the dye–JLP system were determined. Each experiment was carried out thrice and the average values were reported to ensure the consistency, repeatability and accuracy of the results. It was observed from the experimental analysis that the dye removal efficiency increases with increasing the adsorbent dosage, adsorption time as well as stirrer speed and the optimal values of JLP dosage, adsorption time and stirrer speed were found to be 10 g/L, 6 h and 275 rpm respectively for Amido black and 10g/L, 4h and 200 rpm respectively for Crystal violet. On the other hand, the dye removal efficiency decreased with increasing the initial dye concentration in the solution as well as temperature, indicating that the adsorption process using JLP is exothermic and is effective for the treatment of solutions with low concentrations of adsorbate. The effect of pH on the dye removal efficiency did not show any regular trend. Maximum dye removal was obtained at low pH values (between 2–4) indicating the fact that the JLP surface is positively charged. During comparison analysis JLP shows the greater removal efficiency than synthetic zeolite. Finally, the data were fitted with various equilibrium and kinetic models and the model parameters were obtained by curve fitting and regression analysis.

CONTENTS

Chapter	Title	Page No.
	Abstract	i
	Contents	ii-iii
	List of figure	iv-vi
	List of Tables	vii-viii
	Symbols/Abbreviation	xi
1.	Introduction	1-6
	1.1. Adsorption	1
	1.2. Jackfruit leaf powder (JLP)	3
	1.3. Objectives of the present investigation	3
	1.4. Application of Jackfruit leaf powder (JLP) for the adsorption dyes.	4
	1.4.1 Amido Black dye	5
	1.4.2 Crystal Violet dye	6
2.	Literature Review	7-20
	2.1. Dye removal by various natural adsorbent	7
	2.2. Literature on the removal of Amido Black and Crystal Violet dye	16
	2.3. Summary of Literatures	19
3.	Experimental Methodology	21-23
	3.1. Synthesis of Jackfruit leaf Powder (JPL)	21
	3.2. Procedure for adsorption experiment	21
4.	Result and discussion	24-58
	4.1. JLP properties	24
	4.1.1 Morphological analysis by scanning electron Microscopy (SEM)	24

COTENTS CONTINUED....

Chapter	Title	Page No.
	4.2. Determination of λ_{\max} for Amido Black and Crystal violet dye solution	26
	4.3. Calibration curve for Amido Black and Crystal violet dye solution	28
	4.4. Adsorption experiments	29
	4.4.1. Effect of JLP loading	30
	4.4.2. Effect of solution pH	33
	4.4.3. Effect of stirrer speed	35
	4.4.4. Effect of dye concentration	38
	4.4.5. Effect of adsorption time	40
	4.4.6. Effect of temperature	42
	4.5. Thermodynamic, Kinetic and equilibrium studies	45
	4.5.1. Thermodynamics of adsorption	45
	4.5.2. Adsorption Kinetics	46
	4.5.2.1. Pseudo first-order kinetics	46
	4.5.2.2. Pseudo second-order kinetics	49
	4.5.2.3. Intra particle diffusion	51
	4.5.3. Equilibrium Adsorption isotherms	52
	4.6. Comparison of JLP performance with a commercial Adsorbent	57
5.	Conclusion and Future Work	59-60
	References	61-64

LIST OF FIGURES

Figure	Title	Page No.
1.1	Structure of Amido Black 10B dye.	5
1.2	Structure of Crystal violet dye.	6
3.1	Process diagram for JLP.	22
4.1(a)	SEM image JLP adsorbent.	24
4.1(b)	SEM image JLP adsorbent after adsorption of Amido black 10 B dye.	25
4.1(c)	SEM image JLP adsorbent after adsorption of Crystal violet dye.	25
4.2(a)	A plot of absorbance versus wavelength for Amido black dye solution.	27
4.2(b)	A plot of absorbance versus wavelength for Crystal violet dye solution.	27
4.3(a)	Calibration curve for Amido black dye solution.	28
4.3(b)	Calibration curve for Crystal violet dye solution.	29
4.4(a)	Variation of Amido black removal efficiency with JLP concentration.	31
4.4(b)	Variation of Crystal violet removal efficiency with JLP concentration.	32
4.4(c)	Variation of adsorptive capacity for Amido Black dye with JLP concentration.	32
4.4(d)	Variation of adsorptive capacity for Crystal Violet dye with JLP concentration.	33
4.5(a)	Variation of Amido black dye removal efficiency with pH solution.	34

LIST OF FIGURES CONTINUED....

Figure	Title	Page No.
4.5(b)	Variation of Crystal dye violet removal efficiency with pH solution.	35
4.6(a)	Variation of Amido black dye removal efficiency with stirrer speed.	37
4.6(b)	Variation of Crystal violet dye removal efficiency with stirrer speed.	37
4.7(a)	Variation of Amido black dye removal efficiency with initial dye concentration.	39
4.7(b)	Variation of Crystal violet dye removal efficiency with initial dye concentration.	39
4.8(a)	Variation of Amido black dye removal efficiency with time.	41
4.8(b)	Variation of Crystal violet dye removal efficiency with time.	42
4.9(a)	Variation of Amido black dye removal efficiency with temperature.	43
4.9(b)	Variation of Crystal violet dye removal efficiency with temperature.	43
4.10(a)	Plot of Amido black dye change in Gibbs free energy with temperature.	45
4.10(b)	Plot of Crystal violet dye change in Gibbs free energy with temperature.	46
4.11(a)	Pseudo first-order kinetic model for the adsorption of Amido black dye on JLP surface.	48
4.11(b)	Pseudo first-order kinetic model for the adsorption of Crystal violet dye on JLP surface.	48

LIST OF FIGURES CONTINUED....

Figure	Title	Page No.
4.12(a)	Pseudo second-order kinetic model for the adsorption of Amido black dye on JLP surface.	50
4.12(b)	Pseudo second-order kinetic model for the adsorption of Crystal violet dye on JLP surface.	50
4.13(a)	Intra-particle diffusion model for the adsorption of Amido black dye on JLP surface.	51
4.13(b)	Intra-particle diffusion model for the adsorption of Crystal violet dye on JLP surface.	52
4.14(a)	Plot of C_e/q_e versus C_e for the estimation of Amido black Langmuir isotherms constant.	53
4.14(b)	Plot of C_e/q_e versus C_e for the estimation of Crystal violet Langmuir isotherms constant.	54
4.15(a)	Variation of equilibrium adsorption intensity (R_L) with initial dye (Amido black) concentration (C_i).	54
4.15(b)	Variation of equilibrium adsorption intensity (R_L) with initial dye (Crystal violet) concentration (C_i).	55
4.16(a)	Equilibrium isotherm for the adsorption of Amido black on JLP.	56
4.16(b)	Equilibrium isotherm for the adsorption of Crystal violet on JLP.	56
4.17	Comparison of dye removal efficiency over JLP and synthesized Zeolite (ZX).	58

LIST OF TABLES

Table	Titles	Page No.
4.1(a)	EDXS analysis for JLP adsorbent.	26
4.1(b)	EDXS analysis for JLP adsorbent after adsorption Amido black dye.	26
4.1(c)	EDXS analysis for JLP adsorbent after adsorption Crystal violet dye.	26
4.2(a)	Calculation of Amido black dye removal efficiency from absorbance value at different JLP dosage.	30
4.2(b)	Calculation of Crystal violet dye removal efficiency from absorbance value at different JLP dosage.	30
4.3(a)	Calculation of Amido black dye removal efficiency from absorbance value at different pH values.	33
4.3(b)	Calculation of Crystal violet dye removal efficiency from absorbance value at different pH values.	34
4.4(a)	Calculation of Amido black dye removal efficiency from absorbance value at different stirrer speed.	36
4.4(b)	Calculation of Crystal violet dye removal efficiency from absorbance value at different stirrer speed.	36
4.5(a)	Calculation of Amido black dye removal efficiency from absorbance value at different dye concentration.	38
4.5(b)	Calculation of Crystal violet dye removal efficiency from absorbance value at different dye concentration.	38
4.6(a)	Calculation of Amido black dye removal efficiency from absorbance value at different adsorption time.	40
4.6(b)	Calculation of Crystal violet dye removal efficiency from absorbance value at different adsorption time.	41

LIST OF TABLES CONTINUED....

Table	Titles	Page No.
4.7(a)	Calculation of Amido black dye removal efficiency from absorbance value at different temperatures.	42
4.7(b)	Calculation of Crystal violet dye removal efficiency from absorbance value at different temperatures.	43
4.8(a)	Equilibrium parameters for Langmuir and Freundlich adsorption isotherms for Amido black dye.	57
4.8(b)	Equilibrium parameters for Langmuir and Freundlich adsorption isotherms for Crystal violet dye.	57

List of Symbols/Abbreviations

JLP	Jackfruit leaf powder (Adsorbent)
C_i	Initial dye concentration in the solution, mg/L
C_f	Dye concentration in the solution after adsorption with JLP, mg/L
C_j	Jackfruit leaf powder loading (adsorbent dosage), g/L
R	dye removal efficiency, %
q_t	Amount of dye adsorbed per unit weight of jackfruit leaf powder(JLP), mg/g
ΔG°	Change in Gibbs free energy, J
ΔH°	Change in enthalpy, J
ΔS°	Change in entropy, J K ⁻¹
R	Universal gas constant, J mol ⁻¹ K ⁻¹
q_e	Equilibrium dye adsorption capacity, mg/g
k_1	Pseudo first –order rate constant, min ⁻¹
k_2	Pseudo second- order rate constant, g.mg ⁻¹ .min ⁻¹
C_e	Liquid phase concentration of adsorbate at equilibrium, mg/L
Q_m	Maximum adsorption capacity of the adsorbent, mg/g
K_L	Equilibrium adsorption constant of the Langmuir isotherm, L/mg
R_L	Equilibrium adsorption intensity
K_F	Freundlich constant, (mg/g). (mg/L) ⁻ⁿ
n	Exponent in Freundlich isotherm equation
R^2	Correlation coefficient

1.1 Adsorption

Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances. Activated carbon is the most popular adsorbent and has been used with great success, but is expensive (Chakrabarty et al., 2003). A full description of low cost adsorbents for waste and wastewater treatment: a review has been presented by Yunus et al. (2006). A number of studies have been reported with regard to the adsorption equilibrium of dye removal processes using various adsorbents. In most adsorption systems of dyestuffs-adsorbent, Langmuir (Elbec et al., 1985; Fatma et al. 2006; Venkat et al., 2006), Freundlich (Pollock et al., 1973), and Redlich-Peterson (Hou et al. 2000; Chakrabarty et al., 2003; Purkait et al., 2003) isotherms have been applied to describe equilibrium between liquid–solid phases. Two intraparticle diffusion mechanisms are involved in the adsorption rate (a) diffusion within the pore volume known as pore diffusion, and (b) diffusion along the surface of pores known as surface diffusion (Gong et al., 2005). Some of the investigators have applied the pore diffusion model with and without film resistance. McKay has developed homogeneous solid phase diffusion model to describe systems dyes on bagasse pith (Purkait et al., 2003). The homogeneous solid phase diffusion model has been developed based on external mass transfer and surface diffusion by M.S.El-Geundi (Hau et al., 2000). He has applied this model for adsorption of basic dyes onto natural clay in a batch adsorber. The branched pore kinetic model was used to describe the adsorption of cobalt phthalocyanine dye onto active carbon and basic dyes onto natural clay (Pollock et al. 1973).

Research has already been carried out using different treatment technologies e.g. chemical coagulation-flocculation, different types of oxidation processes, biological processes (Ledakowicz et al. 2001) membrane based separation processes (Dey et al. 2006), adsorption (Dasgupta et al. 2006) etc. for the removal of colored dye from wastewater. Each of the above processes has its own benefits and limitations.

Adsorption on solid surface is of growing interest in this field because of its lower price. Activated carbon is one of the common adsorbents due to its high surface area and high

adsorption capacity. However, its high cost makes the process uneconomical for industrial applications. Therefore, the process of dye removal by adsorption is diverted to the use of lower cost adsorbents so that the process becomes economically feasible.

For this reason, research is focused on the use of low-cost, reusable, locally available, biodegradable adsorbents made from natural sources. Natural adsorbent Jackfruit leaf powder (JPL) and Neem leaf powder (NPL) are being considered as alternative very low-cost adsorbents. Adsorption of organic molecules to an adsorbent depends on various factors like temperature, pH of the solution, the structure and concentration of the adsorbing molecule, the ionic strength of the suspension, and the structure of the adsorbent.

However, adsorption over a surface with highly ionic character is mostly effective and very fast for a dye with opposite ionic character. Although very few works have been done on adsorption of dyes on Jack fruit Leaf (JLP), the present work gives detailed information about the adsorption of Methylene blue and Crystal violet on jackfruit leaf powder (JLP). No works on the adsorption of Amido Black dye on Jackfruit leaf powder (JLP) are reported. Jackfruit leaf is cationic in nature Tamez et al. (2008). Adsorption experiments using Jackfruit Leaf (JLP) as an adsorbent were carried out by Tamez et al. (2008) on different other basic dyes such as Methylene blue, Methyl Orange etc. They observed the usability of Jackfruit leaf powder (JLP) as an adsorbent for the removal of acidic and basic dyes only. Systematic experimentations that include characterization of adsorbent, stirring effect, role of pH, temperature, and the dose of the adsorbent as well as the adsorbate are yet to be done. Again, determination of various thermodynamic parameters, kinetic and equilibrium model parameter will also be the further scope of research.

The aim of this work is to study the ability of Jackfruit leaf powder (JPL) to remove the acidic dye Amido Black from aqueous solutions. This adsorbent was chosen because of its cheapness, very low cost, and readily availability. The main purpose of chosen adsorbent JLP is cationic in nature so we can get the better removal efficiency of Amido black anionic dye. The equilibrium isotherms and the kinetics for these systems have to be determined. The importance of such isotherms and kinetics curves lies in developing a model, which accurately represents both the obtained results, and could be used for design purposes.

1.2 Jackfruit leaf powder (JLP)

Jackfruit or *Artocarpus heterophyllus* is a tropical plant. It is common in backyards and waste places. Carbonised jackfruit peel has already been used as adsorbent for the removal of basic dyes (Inbaraj and Sulochana, 2006, 2002) and Cd (II) (Inbaraj and Sulochana, 2004). Activated carbon prepared from jackfruit peel has also been studied to remove phenol and chlorophenols from aqueous solution (Jain and Jayaram, 2007). However, no experiment has ever performed to use jackfruit leaf as adsorbent. In the present study column performance of jackfruit leaf powder (JLP) for the removal of methylene blue from an aqueous solution has been investigated. The adsorption capacity of some low cost adsorbents for methylene blue adsorption has been shown in our previous study (Uddin et al., 2009). During preliminary studies carried out at laboratory, jackfruit leaf powder had shown several folds higher adsorption capacity for methylene blue than the others. Moreover, it is available all over the year in Bangladesh. Due to its abundant availability and low-cost it can also be disposed off after use without need for expensive regeneration. The used adsorbent can be disposed after incineration to prevent the further impact on the environment. The ash obtained by incineration is not a pollutant rather it could be used as an adsorbent.

1.3 Objectives of the present investigation

Experimental investigations have been carried out to remove Amido Black and Crystal violet dyes from their aqueous solutions using jackfruit leaf powder (JLP) as the adsorbent. JLP is chosen because of its abundant availability without any commercial value. The overall objective of this work is to study the adsorption characteristics of JLP for the removal of dyes from aqueous solutions. The specific objectives of this work are as follows.

- To synthesize fine adsorbent powder (JLP) from jackfruit mature leaves.
- To characterize JLP by measuring its particle size distribution (using 150 nm sized sieve), microscopic analysis using scanning electron microscope and composition analysis by using EDAX analysis.
- To study the effects of solution pH, contact time, initial dye concentration, JLP loading, stirring speed, and temperature on the removal of Amido Black and Crystal violet dyes in batch mode.

- To compare the adsorption capacity of the prepared jackfruit leaf powder (JLP) with any other synthetic adsorbent such as a zeolite.
- To fit the adsorption isotherms and kinetic models for the experimental data.

1.4 Application of Jackfruit leaf powder (JLP) for the adsorption of dyes

Adsorption processes are important fields of study in physical chemistry. They form the basis for understanding phenomena such as heterogeneous catalysis, chromatographic analysis, dyeing of textiles, and clarification of various effluents.

Dyes are defined as colored substances which when applied to fibers give them a permanent color, i.e. resistant to action of light, water and soap. Practically every dyestuff is made from either one or more of the compounds obtained by the distillation of the coal tar. The chief of these are Benzene (C_6H_6), Toluene ($C_6H_5.CH_3$), Naphthalene ($C_{10}H_8$), Anthracene ($C_{14}H_{10}$), Phenol (C_6H_5OH), Cresol (C_7H_7OH), Acridine ($C_{13}H_9N$), and Quinoline (C_9H_7N).

Wastewaters from dyeing and finishing operations in the textile industry are generally high in both color and organic content. Color removal from textile effluent has been the target of great attention in the last few years, not only because of its potential toxicity, but also mainly due to its visibility problems. Recent estimate indicates that 20% of dyes enter the environment through effluent that result from the treatment of industrial wastewater. The existing technologies have certain efficiency in the removal of dyes but their initial and operational costs are very high. On the other hand, low cost technologies do not allow the desired degree of color removal or have certain disadvantage.

Oxidation (UV/ozone and UV/ H_2O_2) and adsorption are two major technologies that are used for wastewater treatment in the textile industry. Adsorption is rapidly becoming a prominent method of treating aqueous effluents and it has been extensively used in industrial processes for a variety of separation and purification purposes. This process has been found to be superior to other techniques for water re-use in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances.

Adsorption of dyes by natural adsorbents has evolved into one of the most effective physical process for the decolorization of textile wastewater. However, very little work has

been done using JLP as the adsorbent. Therefore, JLP is chosen in this work for the removal of two different dyes namely amido black and crystal violet. Some of the salient features of these dyes are presented below.

Dyes are an important class of pollutants, and can even be identified by the human eye. Disposal of dyes in precious water resources must be avoided, however, and for that various treatment technologies are in use. Among various methods adsorption occupies a prominent place in dye removal. The growing demand for efficient and low-cost treatment methods and the importance of adsorption has given rise to low-cost alternative adsorbents (LCAs).

1.4.1 Amido Black dye

Amido black 10B is an amino acid staining diazo dye. Its molecular formula is $C_{22}H_{14}N_6Na_2O_9S_2$. Amido Black 10B is a synthetic acid dye containing both NN and CC chromophore groups (pyrazolone dye). It is a dark red to black powder soluble in water and used as a stain for protein-containing. Its chemical designation is 4-amino- hydroxy- 3-(4-nitrophenyl) azo- 6-(phenylazo) - 2, 7-naphthalene disulfonic acid disodium salt. Acid dyes are water-soluble dyes employed mostly in the form of sodium salts of the sulfonic or carboxylic acids. They are anionic which attach strongly to cationic groups in the fibre directly. They can be applicable to all kind of natural fibres like wool, cotton and silk as well as to synthetics like polyesters, acrylic and rayon. However, they are not substantive to cellulosic fibres. They are also used in paints, inks, plastics and leather. Chemical structure of Amido Black dye is given below.

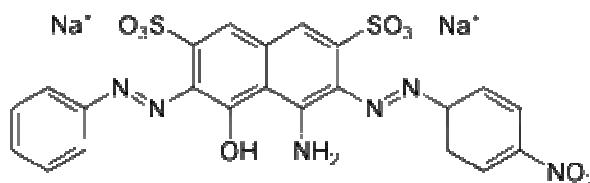


Figure 1.1: Structure of Amido Black 10B dye

1.4.2 Crystal violet dye

Crystal violet or Gentian violet it is also known as Methyl violet (hexamethyl pararosaniline chloride). Methyl violet is mixtures of tetramethyl, pentamethyl and hexamethyl pararosanilins. It's molecular formula is $C_{25}H_{30}N_3Cl$. Crystal violet (CV) or Genetian violet is widely used for dyeing of cotton and silk and in the manufacture of paints and printing inks. It also finds application as a biological stain and is the active ingredient in Gram's stain. The dye is used as a bacteriostatic agent in animal husbandry and veterinary practice and as an additive to poultry feed to inhibit propagation of mold, intestinal parasites and fungus. Crystal violet has antibacterial, antifungal, and anthelmintic properties and was formally superseded by more drugs, although it is still listed by the World Health organization. Being a protein dye, CV is also used as an enhancer for bloody fingerprints. The dye is also used on most types of adhesive tapes, because conventional powders adhere to the entire sticky side of the tape and are not selective to the latent prints.

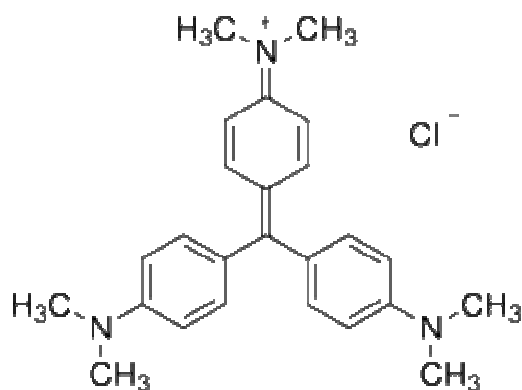


Figure 1.2: Structure of Crystal violet dye

2.1 Dye removal by various natural adsorbent

Yasmin et al. (2012) studied the kinetics, equilibrium and process design for the removal of Brilliant Blue Green (BBG) dye from aqueous solutions using marine *Aspergillus wentii* as the adsorbent. They were performed the sorption of BBG by dead biomass of marine fungus *Aspergillus wentii*, which was chemically modified by esterification of the carboxylic acids (CB), or methylation of amine (NB), or raw biomass (RB) with variation in the parameters of contact time (0–80 min), initial concentration of dye (119.3–544.8 mg/L) and solution pH (2–10). The contact time necessary to reach equilibrium was 180 min. The BBG biosorption was strictly pH dependent, and maximum uptake capacity of all three biosorbents was observed at initial pH 2. The biosorption isotherm data were fitted well to the Langmuir isotherm and the monolayer sorption capacity was found to be 384.6, 370.4 and 312.5 mg/L for CB, NB and RB, respectively.

Fernandez et al. (2012) studied the batch and dynamic biosorption of basic dyes from binary solutions by alkaline-treated cypress cone chips. They performed a simple alkaline pre-treatment of *Cupressus sempervirens* cone chips to improve their biosorption capacity towards methylene blue and rhodamine B from aqueous solutions, in batch and continuous modes. Biosorption kinetics were determined from single and binary dyes solutions, and properly described by the pseudo-second-order rate model. Experimental single-dye equilibrium isotherms fitted the Langmuir–Freundlich model, with maximum biosorption capacities of 0.68 mmol/g for methylene blue and 0.50 mmol/g for rhodamine B. Single-dye dynamic biosorption showed that breakthrough time for methylene blue biosorption was almost four times longer than for rhodamine B and that the alkaline modification of the chips greatly improved the biosorption performance. Competitive dynamic biosorption demonstrated the preference of the modified cone chips for biosorbing methylene blue, confirmed by the exit concentration overshoots obtained in the breakthrough curves of rhodamine.

Liangui Wang (2012) studied the application of activated carbon derived from waste bamboo culms for the adsorption of azo disperse dye. They were performed Kinetic, equilibrium and thermodynamic studies and they were utilized the activated carbon derived

from 'waste' bamboo culms (BAC) for the removal of Disperse Red 167 (DR167), an azo disperse dye, was investigated. They were studied the properties of the adsorbent, and the effect of contact time, the initial pH of the solution, the initial concentration of the dye solution and temperature indicated that a low initial pH or concentration of dye solution favors the adsorption process; temperature exerts a greater effect on the removal of azo disperse red 167 dye from aqueous solution. Kinetic and isotherm data were fitted to five non-linear kinetic and nine non-linear isotherm equations. In addition, the fits were evaluated in terms of the non-linear coefficient, Chi-square test, Marquardt's percent standard deviation error function and small-sample-corrected Akaike Information Criterion (AIC) methodology. The results showed that the AIC analysis was the best statistical tool for analyzing the data, the intra-particle diffusion and the pseudo-first-order models played important roles in the controlling rate step, and the Temkin equation best described the BAC isotherm data. Furthermore, the thermodynamic analysis indicated that the adsorption was a spontaneous, endothermic, entropyincreasing and physical process. Two types of commercial activated carbon, Filtrasorb 400 and Filtrasorb (F400 and F300), were used as contrast adsorbents. The contrast experiments revealed that BAC exhibits similar properties to F400 and F300. The utilization of bamboo wastes as carbon precursors is feasible.

Anna et al. (2011) studied the biosorption of heavy metals from aqueous solutions onto peanut shell as a low-cost biosorbent. They were performed biosorption of Cu(II) and Cr(III) ions from aqueous solutions by peanut shell biomass was investigated as a function of initial pH, initial biomass concentration and temperature. The optimum sorption conditions were studied for each metal separately. The kinetics and equilibrium of biosorption were examined in detail. Four kinetic models (pseudo-first order, pseudo-second order, power function equation, and Elovich model) were used to correlate the experimental data and to determine the kinetic parameters. Four well-known adsorption isotherms were chosen to describe the biosorption equilibrium. The experimental data were analyzed using two two-parameter models (Langmuir and Freundlich) and two three-parameter models (Redlich–Peterson and Sips). The equilibrium biosorption isotherms showed that peanut shells possess high affinity and sorption capacity for Cu (II) and Cr (III) ions, with monolayer sorption capacities of 25.39 mg Cu²⁺ and 27.86 mg Cr³⁺ per 1 g biomass, respectively. All results showed that peanut shells biomass is an attractive, alternative low-cost biosorbent for removal of heavy metal ions from aqueous media.

Zohra et al. (2011) studied the biosorption of basic dye from aqueous solutions by Date Stones and Palm-Trees Waste. They were performed Kinetic, equilibrium and thermodynamic studies-Biosorption potential of Date Stones (DS) and Palm-TreesWaste (PTW) for the removal of a basic dye, Methylene blue from aqueous solution was investigated. The effects of temperature, initial dye concentration and contact time on the biosorption process were studied. Experimental data were modelled by Langmuir, Freundlich and Tempkin isotherms. Langmuir isotherms model fitted well the equilibrium data for the two sorbents (DS and PTW) comparing to the Freundlich and Tempkin isotherms models. The monolayer biosorption capacity of DS and PTW biomass for Methylene blue was found to be 43.47 and 39.47mg/L respectively. The calculated thermodynamic parameters, namely, ΔG° , ΔH° and ΔS° showed that the biosorption of Methylene blue on both agriculture waste biomasses was spontaneous and endothermic under examined conditions. Experimental data were also modelled using the biosorption kinetic models. The results showed that the biosorption processes of Methylene blue on DS and PTW followed well pseudo-second-order kinetics in the temperature range 20–70 °C. Results indicated that DS and PTW could be an alternative for more costly adsorbents used for dye removal.

Niyaz et al. (2011) studied the kinetics, equilibrium and thermodynamics in the adsorption of textile dyes on Pine Cone from colored wastewater. They were investigated the adsorption of Acid Black 26 (AB26), Acid Green 25 (AG25) and Acid Blue 7 (AB7) onto Pine Cone (PC) in aqueous solution. Surface study of PC was investigated using Fourier transform infrared (FTIR) and scanning electron microscopy (SEM). The effect of operational parameters such as adsorbent dosage, dye concentration, inorganic anion (salt), pH and temperature onto dye removal was studied. The intraparticle diffusion model, the pseudo-first order and the pseudo-second order were used to describe the kinetics data. Equilibrium isotherms were analyzed using Langmuir, Freundlich and Tempkin adsorption models. Thermodynamic parameters of dye adsorption were obtained. The experimental data fitted well to the pseudo-second order kinetics model for dyes. The results indicated that isotherm data of AB26 and AG25 followed Langmuir isotherm and isotherm data of AB7 followed Freundlich isotherm models. The thermodynamic data indicated that the adsorption was endothermic process. Dye desorption studies in aqueous solution at pH 12 showed that maximum desorption of 93%, 97% and 94.5% were achieved for AB26,AG25

and AB7, respectively. They concluded that PC could be effectively employed as an effective biosorbent for the removal of dyes.

Safa and Bhatti (2011) studied the kinetic and thermodynamic modeling for the removal of Direct Red-31 and Direct Orange-26 dyes from aqueous solutions by rice husk. They were dealt with the utilization of an inexpensive agro-industrial waste rice husk for the removal of Direct Red-31 and Direct Orange-26 from aqueous solutions in a batch mode. Experiments were carried out as function of pH, biosorbent dose, particle size of biosorbent, initial dyes concentration, contact time and temperature. The equilibrium biosorption data were analyzed by Langmuir, Freundlich, Temkin, Dubinin–Radushevich (D–R) and Harkins–Jura isotherm models. The results indicated that the Langmuir model provided the best correlation of the experimental data for both dyes. The biosorption kinetic data were modeled using the pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetic equations. It was observed that the pseudo-second-order kinetic equation could explain the biosorption kinetics of dyes on rice husk. Thermodynamic parameters such as enthalpy change (ΔH°), entropy change (ΔS°) and free energy change (ΔG°) were also investigated. Free energy change showed that biosorption of Direct Red-31 and Direct Orange-26 was spontaneous at all studied temperatures (30–70 °C). Surface adsorption of both the dyes at specific binding sites was confirmed through and Fourier Transform infrared spectroscopic (FT-IR) analysis. The changes in surface morphology of rice husk before and after adsorption was investigated through scanning electron microscopy (SEM). They were implied that rice husk may be suitable as an adsorbent for removal of direct dyes from aqueous solutions.

Sagnik et al. (2011) studied the adsorption of Crystal Violet from aqueous solution onto NaOH-modified rice husk. They were studied, equilibrium, kinetics and thermodynamics of Crystal Violet (CV) adsorption onto NaOH modified rice husk (NMRH) was investigated. Experiments were carried out as function of contact time, initial solution pH (2–10), adsorbent dose (0.5–5 g) and temperature (293, 303 and 313 K). The adsorption was favoured at higher pH and lower temperatures. Adsorption data were well described by the Freundlich model, although they could be modelled by the Langmuir model as well. The adsorption process followed the pseudo-second order kinetic model. The mass transfer model based on intraparticle diffusion was applied to the experimental data to examine the mechanisms of the rate controlling step. They were found that intraparticle diffusion was

not the sole rate controlling step. The activation energy (E_a) of the system was calculated as 50.51 kJ mol/L. Thermodynamic parameters suggest that the adsorption is a typical chemical process, spontaneous, and exothermic in nature.

Shamik et al. (2011) studied the adsorption thermodynamics, kinetics and isosteric heat of adsorption of malachite green onto chemically modified rice husk. They were treated the rice husk with NaOH and tested it as a low cost adsorbent for the removal of malachite green from aqueous solution in batch adsorption procedure. The adsorption experiments were carried out as a function of solution pH, initial dye concentration, contact time and temperature. The adsorption was found to be strongly dependent on pH of the medium. The Freundlich isotherm model showed good fit to the equilibrium adsorption data. The mean free energy (E) estimated from the Dubinin–Radushkevich model indicated that the main mechanism governing the sorption process was chemical ion-exchange. The kinetics of adsorption followed the pseudo-second-order model and the rate constant increased with increase in temperature indicating endothermic nature of adsorption. The Arrhenius and Eyring equations were used to obtain the activation parameters such as activation energy (E_a), and enthalpy (ΔH°), entropy (ΔS°) and free energy (ΔG°) of activation for the adsorption system. Thermodynamic studies suggested the spontaneous and endothermic nature of adsorption of malachite green by treated rice husk.

Jiyun et al. (2011) studied the adsorption characteristics of methylene blue by peanut husk in batch and column modes. Their study described adsorption of methylene blue by peanut husk in batch and fixed-bed column modes at 293 K. The kinetic and equilibrium of adsorption in batch mode were studied. Nonlinear regressive method was used to obtain relative parameters of adsorption models. The kinetic process was better described by a pseudo-second-order kinetic model. The equilibrium adsorption was effectively described by Temkin adsorption isotherm. The value of q_m from the Langmuir model was 72.13±3.03 mg/L and the diffusion coefficient value was in the order of 10⁻⁸ cm²/s. In fixed-bed column adsorption, the effects of bed height, feed flow rate, and inlet methylene blue concentration were studied by assessing breakthrough curve. The column data were fitted by the Thomas, Clark and modified dose–response models. The modified dose–response model was best to fit the breakthrough curves at experimental conditions. FTIR analysis showed that there were carbonyl and hydroxyl groups on the surface of the adsorbent. The

results implied that peanut husk may be suitable as an adsorbent material for adsorption of methylene blue from an aqueous solution.

Jing et al. (2010) studied the competitive biosorption of Yellow 2G and Reactive Brilliant Red K-2G onto inactive aerobic granules. They were determined the two dyes simultaneously by first-order derivative spectrophotometry and isotherm studies. Their study focused on the competitive biosorption of Yellow 2G (Y2G) and Reactive Brilliant Red K-2G (RBR) by inactive aerobic granules in binary solutions. A first-order derivative spectrophotometric method for the simultaneous determination of Y2G and RBR in binary solutions was developed. Dubinin–Raduskevich (D–R) isotherm successfully predicted the biosorption of Y2G and RBR in both single and binary solutions. However, none of the tested binary adsorption isotherms could realistically represent the biosorption equilibrium data. Maximum biosorption capacity calculated from D–R isotherm for Y2G and RBR in single solution was 58.50 and 66.18 mg /L, respectively; in binary solutions, for Y2G it decreased to 40.38 mg/L, but for RBR it increased to 171.21 mg/L, showing their synergism and antagonistic interactions.

Deniz and Saygideger (2010) studied the equilibrium, kinetic and thermodynamics of Acid Orange 52 dye biosorption by *Paulownia tomentosa* Steud. leaf powder as a low-cost natural biosorbent. They were studied the biosorption of Acid Orange 52 onto the leaf powder of *Paulownia tomentosa* Steud. in a batch adsorption system to estimate the equilibrium, kinetic and thermodynamic parameters as a function of solution pH, biosorbent concentration, dye concentration, biosorbent size, temperature and contact time. The Langmuir, Freundlich and Temkin isotherm models were used for modeling the biosorption equilibrium. The experimental equilibrium data could be well interpreted by the Temkin and Langmuir isotherms with maximum adsorption capacity of 10.5 mg/L. The results revealed that *P.tomentosa* leaf powder could be an efficient biosorbent for the treatment of wastewater containing Acid Orange 52.

Sharma et al. (2010) investigated the potential use of pretreated rice husk (RH) and rice husk ash (RHA) for the removal of methylene blue from wastewater. They carried out a series of batch experiments to determine the influence of different system variables. Neutral pH was optimum for the removal of methylene blue. Adsorption of methylene blue on RH and RHA was favorably influenced by an increase in the temperature of

the operation. The comparative studies of these two adsorbents, RA and RHA with the earlier reported adsorbents obtained from agricultural and industrial waste products, inorganic materials and bioadsorbents, reveals that RH and RHA have maximum adsorption capacity. Adsorption data was fitted to the Langmuir, and Freundlich adsorption model.

Sibel et al. (2009) studied the biosorption of a reactive textile dye from aqueous solutions utilizing an agro-waste, in their study, they tested a low-cost waste biomass derived from canned food plant for its ability to remove reactive textile dye from aqueous solutions. The batch biosorption experiments were carried out at various pH, biosorbent dosage, contact time and temperature. Optimum decolorization was observed at pH 2.0 and 1.6 gdm⁻³ of biomass dosage within 20 min. The first-order and the pseudo-second-order kinetics were investigated for the biosorption system. The applicability of the Langmuir and Freundlich isotherm models was examined. The thermodynamic parameters for the biosorption were also calculated. The experimental results in their study indicated that this low-cost biomaterial was an attractive candidate for the removal of textile dye Reactive Red 198 (RR198) from aqueous solutions.

Gupta and Suhas (2009) provided an overview of the application of low-cost adsorbents comprising natural, industrial as well as synthetic materials/wastes and their application for dyes removal.

Uma et al. (2009) evaluated the adsorptive characteristics of rice husk ash as an effective adsorbent for Indigo Carmine dye. Their study explored the adsorptive characteristics of Indigo Carmine (IC) dye from aqueous solution onto rice husk ash (RHA). Batch experiments were carried out to determine the influence of parameters like initial pH (pH₀), contact time (t), adsorbent dose (m) and initial concentration (C₀) on the removal of IC. The optimum conditions were found to be: pH₀ ¼ 5.4, t ¼ 8 h and m ¼ 10.0 g/l. The pseudo-second-order kinetic model represented the adsorption kinetics of IC on to RHA. Equilibrium isotherms were analyzed by Freundlich, Langmuir, Temkin and Redlich–Peterson models using a non-linear regression technique.

Ayrton et al. (2007) studied the low temperature conversion of rice husks, eucalyptus sawdust and peach stones for the production of carbon-like adsorbent. In their study, the

feasibility of preparing effective adsorbents from unmitigated agroforestry wastes was investigated. Three different kinds of carbon-like materials were produced by low temperature pyrolysis (LTC, <500 °C) of the raw materials rice husks, eucalyptus sawdust and peach stones. They characterized the carbon-like materials by instrumental methods (SEM, X-RDS, BET, MASRMN, and FTIR), physico-chemical adsorption as well as heat value determination.

Venkat S. et al. (2007) studied the kinetics and equilibrium isotherms for the adsorptive removal of Brilliant Green dye from aqueous solution by rice husk ash. Their study dealt with the adsorption of Brilliant Green (BG) on rice husk ash (RHA). Batch studies were performed to evaluate the influences of various experimental parameters like initial pH (pH_0), contact time, adsorbent dose and initial concentration (C_0) on the removal of BG. Optimum conditions for BG removal were found to be $pH_0 = 3.0$, adsorbent dose = 6 g/L of solution and equilibrium time = 5 h for the C_0 range of 50–300 mg/L. Adsorption of BG followed pseudo-second-order kinetics.

Crini (2006) presented a review on the non-conventional low-cost adsorbents for dye removal. Adsorption techniques are widely used to remove certain classes of pollutants from waters, especially those that are not easily biodegradable. Dyes represent one of the problematic groups. Currently, a combination of biological treatment and adsorption on activated carbon is becoming more common for removal of dyes from wastewater. Although commercial activated carbon is a preferred sorbent for color removal, its widespread use is restricted due to high cost. As such, alternative non-conventional sorbents have been investigated. It is well-known that natural materials, waste materials from industry and agriculture and biosorbents can be obtained and employed as inexpensive sorbents.

Maria et al. (2006) studied the characterization of an adsorbent prepared from maize waste and adsorption of three classes of textile dyes. They were investigated and accomplished in order to evaluate both inexpensive and alternative materials as potential adsorbents for pollutants and colored compounds. A novel adsorbent SOMAP, prepared from maize waste, was activated and characterized under the aspect of its reproducible employment using elemental analysis, thermogravimetry, porosimetry and adsorption of different dyes from solution.

Vinod K. et al. (2006) studied the adsorption of a hazardous dye, erythrosine, over hen feathers. They were removed erythrosine dye that is widely used in cosmetics, foodstuffs, medicines, and textiles. It is highly toxic to mankind and can lead to many diseases including carcinogenicity. Removal of erythrosine has been carried out using waste material hen feathers as adsorbent. The effects of pH, concentration of the dye, temperature, and adsorbent dosage have been studied. Adsorption of erythrosine over hen feathers has been correlated with Freundlich and Langmuir isotherms and satisfies both models. The adsorption process has been found endothermic in nature and thermodynamic parameters, Gibb's free energy (ΔG^0), change in enthalpy (ΔH^0), and change in entropy (ΔS^0) have been calculated.

Davila-Jimenez et al. (2005) studied the adsorption interaction between natural adsorbents and textile dyes in aqueous solution. They were used agricultural wastes from maize culture fields were prepared and activated yielding the natural adsorbents designated as SOMAP, SOMAP1, SOMAP2, HELAP, HELAP1, SAGAP, and SAGAP1. The samples were further characterized using microscopy, FTIR spectroscopy, titration, and adsorption from solution. The dry and wet methods of analysis confirmed the presence of functional groups (hydroxyl, carboxylic, phenolic, and lactonic) in the bulk and on the surface, respectively. Each prepared solid sample was tested for adsorption ability using aqueous dye solutions of basic blue 41 (BB41), acid blue 74 (AB74), and reactive black 5 (RB5). The adsorption affinity decreased according to BB41 > AB74 > RB5. For BB41 the relative adsorbent saturation followed the series: SOMAP2 < SOMAP1 < SOMAP, HELAP < HELAP1 and SAGAP < SAGAP1.

Stephen et al. (2005) studied the kinetic modeling of the adsorption of basic dyes by kudzu -The use of kudzu, a rapidly growing. They were used high-climbing perennial leguminous vine, for the adsorption of basic dyes from aqueous solution has been investigated at various initial dye concentrations, masses of kudzu, and agitation rates. The extent and rate of adsorption of the three basic dyes (Basic Red 22, Basic Yellow 21, and Basic Blue 3) were analyzed using a pseudo-first-order and a pseudo-second-order kinetic model. While both rate mechanisms provided an acceptable degree of correlation with the experimental sorption rate data, the pseudo-second-order model gave a much higher degree of correlation, suggesting that this model could be used in design and simulation applications.

Rahman et al. (2005) studied the adsorption characteristics of malachite green on activated carbon derived from rice husks produced by chemical thermal process. They were used Phosphoric acid (H_3PO_4) and sodium hydroxide (NaOH) to treat rice husks, followed by carbonization in a flowing nitrogen were used to study the adsorption of malachite green (MG) in aqueous solution. The effect of adsorption on contact time, concentration of MG and adsorbent dosage of the samples treated or carbonized at different temperatures were investigated. The results reveal that the optimum carbonization temperature is $500\text{ }^{\circ}C$ in order to obtain adsorption capacity that is comparable to the commercial activated carbon for the husks treated by H_3PO_4 . In their study there was interesting to note that MG adsorbed preferably on carbon-rich than on silica rich-sites. They were found that the behaviour of H_3PO_4 treated absorbent followed both the Langmuir and Freundlich models while NaOH treated best fitted to only the Langmuir model.

Bhattacharyya and Sharma (2004) studied the *Azadirachta indica leaf* powder as an effective biosorbent for dyes: a case study with aqueous Congo Red solutions. In their study, the leaves of *Azadirachta indica* (locally known as the Neem tree) in the form of a powder were investigated as a biosorbent of dyes taking aqueous Congo Red solution as a model system. The sorbent was made from mature Neem leaves and was investigated in a batch reactor under variable system parameters such as concentration of the aqueous dye solution, agitation time, adsorbent amount, pH, and temperature. An amount of 0.6 g of the Neem leaf powder (NLP) per liter could remove 52.0–99.0% of the dye from an aqueous solution. The results point to the effectiveness of the Neem leaf powder as a biosorbent for removing dyes like Congo Red from water.

2.2 Literature on the removal of Amido Black and Crystal violet

No work has been investigated for the removal of Amido black by Jackfruit leaf powder (JLP). Only few studies have been reported for the removal of Crystal violet dye using JLP. However, zeolite and other adsorbents such as activated carbon and fly ash have been investigated extensively.

Recently, Sayal et al. (2012) studied undertook investigation to determine whether cheap, commercially available materials (zeolite and bentonite) hold promise in the treatment of wastewater from the textile industry. The initial findings indicate that zeolite synthesized from fly ash has high adsorptive capacity for dyes and it is relatively cheap. The adsorption

of two basic dyes (Amido Black and Thionine) onto granular activated carbon as well as zeolite from fly ash has to be studied as single equilibrium isotherms. The effectiveness of each adsorbent has to be measured in terms of its adsorption capacity towards individual constituents of the effluent. The adsorption isotherm would be described by the Langmuir and Freundlich isotherm equations. The parameters in the adsorption isotherms will be estimated from the experimental equilibrium data using non-linear regression analysis. Using these data, the selection of the best adsorbent can be done for design purposes

Senthilkumar et al. (2011) studied the decolourization potential of white-rot fungus *Phanerochaete chrysosporium*, which is capable of decolourizing synthetic dye bath effluent containing Amido Black 10B. Need of additives such as enzymes and nutrients and inducers such as starch and lignin during the digestion of dye makes the process highly expensive. Although they are capable of removing the dye up to 98% within 7–10 days, it is still a time consuming process.

Ahmad and Kumar (2010) prepared a novel adsorbent polyaniline/iron oxide composite and evaluated its dye adsorption characteristics for aqueous solution of Amido Black 10B. They described the kinetic data successfully in terms of pseudofirst- order and pseudo-second-order kinetic models. The adsorption equilibrium data fitted well with the Freundlich isotherm than the Langmuir isotherm.

Qiu et al. (2009) studied the adsorption of Amido Black 10B and Safranin T dyes onto a natural zeolite *clinoptilolite*. They analyzed the influence of adsorbent concentration, adsorption time, initial dye concentration, and pH on the dye adsorption capacity. They varied the zeolite loading from 0–160 g/L and the dye concentration from 0–40 mg/L. They obtained a maximum removal efficiency of 81.2% for Safranin T and 16.3% for Amido Black. Their observation indicates that clinoptilolite has a limited adsorption capacity for Amido Black dye. They found that these dye–zeolite systems fitted perfectly to the Langmuir isotherm.

Chinniagounder et al. (2011) studied the ability of Cocoa (*Theobroma cacao*) Shell Activated Carbon (CSAC) to adsorb Crystal Violet (CV) dye from aqueous solution was investigated. Activated carbon was prepared from cocoa shell, an agricultural waste and batch mode adsorption experiments were conducted. The influence of various factors such

as initial concentration (20, 40, 60, 80 mg/L), contact time, pH (1.0-10.0) and carbon dosage on the adsorption capacity were investigated and optimal experimental conditions was ascertained. Adsorption data were modeled using Langmuir, Freundlich, Temkin and Dubinin-Raduskevich (DR) adsorption isotherms. Adsorption kinetics was verified by pseudo-first order, pseudo-second order and intraparticle diffusion models. The kinetic adsorption data fitted the pseudo-second order kinetic model well and also followed the intraparticle diffusion model. The results indicated that CSAC could be employed as low cost adsorbent in waste water treatment for the removal of CV.

Patil et al. (2011) studied the adsorption studies of Crystal Violet (CV) on different natural materials were carried out by batch experiments. The parameter they were studied includes initial dye concentration, adsorbent dose, pH, contact time, agitation speed, particle size of adsorbent and temperature. The linear regression coefficient R^2 was used to elucidate the best fitting isotherm model. All isotherm models, Langmuir ($R^2 = 0.982$ to 0.999), Temkin ($R^2 = 0.973$ to 0.998) and Freundlich ($R^2 = 0.98$ to 0.998 and $n = 1.886$ to 2.294) were found to be best fitting models. The monolayer (maximum) adsorption capacities (q_m) were found to be between 142.857 to 250 mg/g for natural adsorbents under study. Lagergen pseudo second order model best fits the kinetics of adsorption. The correlation coefficient R^2 for second order adsorption model has very high values of R^2 for all adsorbents ($R^2 \approx 0.998$) and q_e (the) values are in good agreement with q_e (exp) showed that adsorption of CV on these natural materials followed second order kinetics and chemisorption playing role in rate determining step. Intra particle diffusion plot showed boundary layer effect and larger intercepts indicates greater contribution of surface sorption in rate determining step. pH was found to be an important factor in controlling the adsorption of cationic dye. Adsorption of CV on adsorbents was found to increase on increasing pH, increasing temperature and decreasing particle size. Thermodynamic analysis showed that adsorption was favourable and spontaneous, endothermic physical adsorption and increased disorder and randomness at the solidsolution interface of CV with biosorbents. Mangrove plant leaf powder was found have excellent adsorption capacity towards CV than other natural materials under study.

Shouman et al. (2012) studied the adsorption behavior of crystal violet, on chitosan has been studied extensively. In their study series of experiments were conducted in a batch system to evaluate the effect of the system variables .i.e. initial pH, initial dye

concentration, contact time and temperature. The adsorption facts were analyzed by using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models. The equilibrium data were best represented by Langmuir isotherm model showing maximum monolayer adsorption capacity 28.5 mg/g. The kinetic data were fitted to pseudo – second order kinetic model which shows that intraparticle diffusion has a significant role in the adsorption process. The thermodynamics of crystal violet onto chitosan indicate its spontaneous and endothermic nature. The adsorbent was analyzed by N₂ adsorption – desorption technique, FTIR, SEM, and TG – DTG. Chitosan was shown to be promising adsorbent for the removal of dyes from aqueous solutions.

Das et al. (2012) studied the continuous (fixed-bed column) biosorption of crystal violet by *Artocarpus heterophyllus* (jackfruit) leaf powder. In their study batch and fixed-bed column experiments were performed to investigate the biosorption potential of *Artocarpus heterophyllus* (jackfruit) leaf powder (JLP) to remove crystal violet (CV) from aqueous solutions. Batch biosorption studies were carried out as a function of solution pH, contact time, initial dye concentration and temperature. The biosorption equilibrium data showed excellent fit to the Langmuir isotherm model with maximum monolayer biosorption capacity of 43.39 mg g/L at pH 7.0, initial dye concentration = 50 mg/L⁻¹, temperature = 293 K and contact time = 120 min. According to Dubinin–Radushkevich (D–R) isotherm model, biosorption of CV by JLP was chemisorption. The biosorption kinetics followed the pseudo-second-order kinetic model. Thermodynamic analysis revealed that biosorption of CV from aqueous solution by JLP was a spontaneous and exothermic process. In order to ascertain the practical applicability of the biosorbent, fixed-bed column studies were also performed. The breakthrough time increased with increasing bed height and decreased with increasing flow rate. The Thomas model as well as the BDST model showed good agreement with the experimental results at all the process parameters studied. It can be concluded that JLP is a promising biosorbent for removal of CV from aqueous solutions.

2.3 Summary of Literatures

Of these literatures, adsorptive removal of Amido Black using zeolite studied by Que et al., (2009) seems to be relevant to the present study. The main drawback of their study is they could not remove Amido Black dye more than 16.3 %, which indicates that a suitable low-cost adsorbent for effective removal of Amido Black dye from its aqueous solution needs to be investigated and one more adsorptive removal of Amido black dye by zeolite

synthesize using fly ash studied by Sayal et al. (2012) seems to be more relevant compared to others and they got 70% removal but the main drawback of their study is that they used commercial low cost adsorbent, the adsorbent is not readily available and they were used fly ash to synthesized the zeolite (this process is time consuming). The main thing in these literatures Amido black dye never removed from aqueous solution by the help of natural adsorbent. That's why we plan to remove the Amido black dye by natural adsorbent (JLP). The main purpose of this study is to treat the dye solution by using natural adsorbent because natural adsorbent are easily available any where and the adsorbent does not have any commercial value. As we know that the natural adsorbents are eco-friendly so we could dispose easily after use.

Among the literatures on crystal violet dye, adsorptive removal of Crystal violet using natural adsorbent studied by Patil et al. (2011) seems to be more relevant compared to other studies. They studies the adsorptive removal of Crystal violet by batch process and they were also studied the kinetic model and adsorption isotherms using experimental data. But the main draw back of their study is they could not remove the Crystal violet more than 80% and the natural adsorbent (Mangrove plant leaf) they were using are not readily available every where. Recently Das et al. (2012) studied adsorptive removal of Crystal violet using JLP. They were got 79.88 % removal efficiency, but the main draw back of their study is they were studied the adsorptive removal of Crystal violet using fixed bed column adsorption. Fixed bed column adsorption is a continuous process that's why they did not study the effect of pH, adsorption time, temperature and agitation speed. As we know these parameters are playing major role in the dye removal process and they were adjusted using batch process, so we planed to remove the crystal violet using batch adsorption method.

3.1 Synthesis of jackfruit leaf powder (JPL)

Jackfruit leaves were collected locally and were thoroughly washed with tap water and after washing with tap water it again washed with distilled water to remove all dirt and earthy materials and dried the jackfruit leaves under sun drying for 8 hrs. After drying under sun the leaves are again dried in a hot air oven at 105°C overnight. The dried leaves were crushed and the crushed powder was boiled to remove lignin and other coloring components. After filtration, the powder was dried at 105°C for 24 hrs and sieved to particle size of about 150 nm and stored in plastic bottle for use as adsorbent. This process is presented in the form of a flow chart as shown in figure 3.1.

3.2 Procedure for adsorption experiments

Procedure for adsorption experiments for the removal of dyes using jackfruit leaf powder (JPL) consist of the following steps.

- A 250 ml of standard dye solution (10 mg/L) is freshly prepared by mixing the required amount of dye powder in distilled water in a 1000 ml beaker.
- The pH of the solution is checked and adjusted by adding a few drops of standard HCl/NaOH solution.
- A 2.5 g of Jackfruit leaf powder (JLP) is then added into the beaker containing the dye solution and it is well mixed.
- Adsorption is carried out for hours at ambient temperature (20°C) under continuous agitation.
- The JLP is allowed for 30 min. to settle down and the solution is carefully separated from the JLP.
- A sample of dye solution is collected by hypodermic syringe and then filtered using ordinary filter paper.
- The collected sample after adsorption is then analyzed by UV-Visible spectrophotometer and the absorbance value is noted down.
- The above procedure is repeated by adding different amounts of Jackfruit leaf powder (JLP) at different pH, different Agitation speed and different amount of dye

concentration.

- These absorbance values are matched with the corresponding calibration curve to obtain the dye concentration in the solution after adsorption with JLP.
- The dye removal efficiency and the adsorption capacity of the Jackfruit leaf powder (JLP) are then calculated.

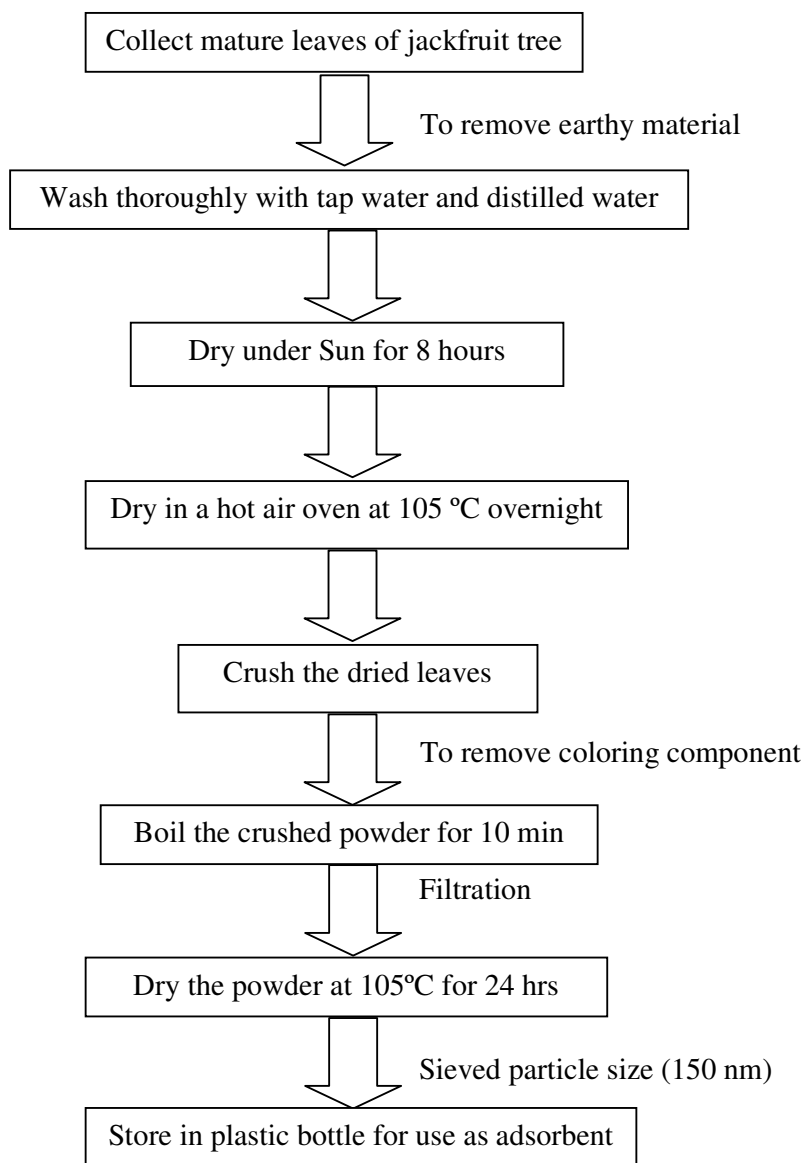


Figure 3.1: Process Diagram for JLP (Jackfruit Leaf Powder) synthesis.

Adsorption analysis was done by the Spectrophotometer: A spectrophotometer is a photometer (a device for measuring light intensity) that can measure intensity as a function of the light source wavelength. Important features of spectrophotometers are spectral bandwidth and linear range of absorption or reflectance measurement. The spectrophotometer is commonly used for the measurement of transmittance or reflectance of solutions, transparent or opaque solids, such as polished glass, or gases. However, they can also be designed to measure the absorbance on any of the listed light ranges that usually cover around 200–2500 nm using different controls and calibration. Within these ranges of light, calibrations are needed on the machine using standards that vary in type depending on the wavelength of the photometric determination. The position of maximum absorbance (λ_{max}) of Amido Black 10B solution was determined to be at 618 nm on a spectrophotometer and the maximum absorbance (λ_{max}) of Crystal Violet solution was determined to be 579 nm on a spectrophotometer.

4.1 JLP Properties

JLP was synthesized from mature Jackfruit leaves using proper grinding and drying. After grinding the JLP was boiled to remove coloring component. Then it was meshed through the sieve having particle sizing capacity of 150 μm .

4.1.1 Morphological analysis by scanning electron Microscope (SEM):

The morphological structure of the JLP (Jackfruit leaf powder) materials was obtained by using scanning electron micrograph (Jeol, JSM 5800) and is shown in Figure 4.1 (a, b, c). The bulk composition was also estimated from SEM/EDXS by indirect method. The elemental composition of the samples was first determined from the SEM/EDXS, then, the percentages of oxides were calculated. The results are shown in Table 4.1(a, b, c).

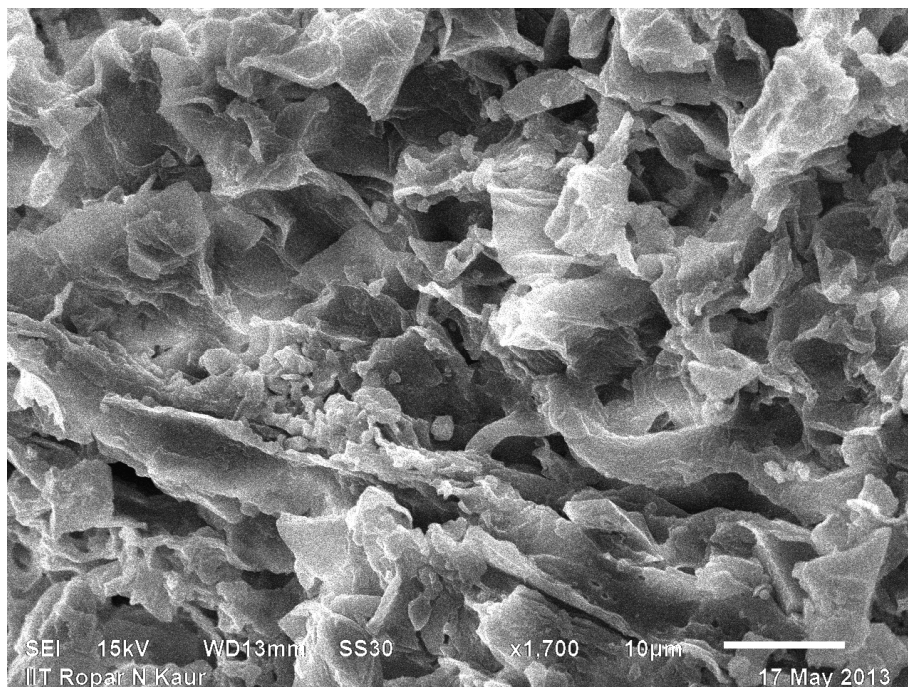


Figure 4.1(a): SEM image JLP adsorbent.

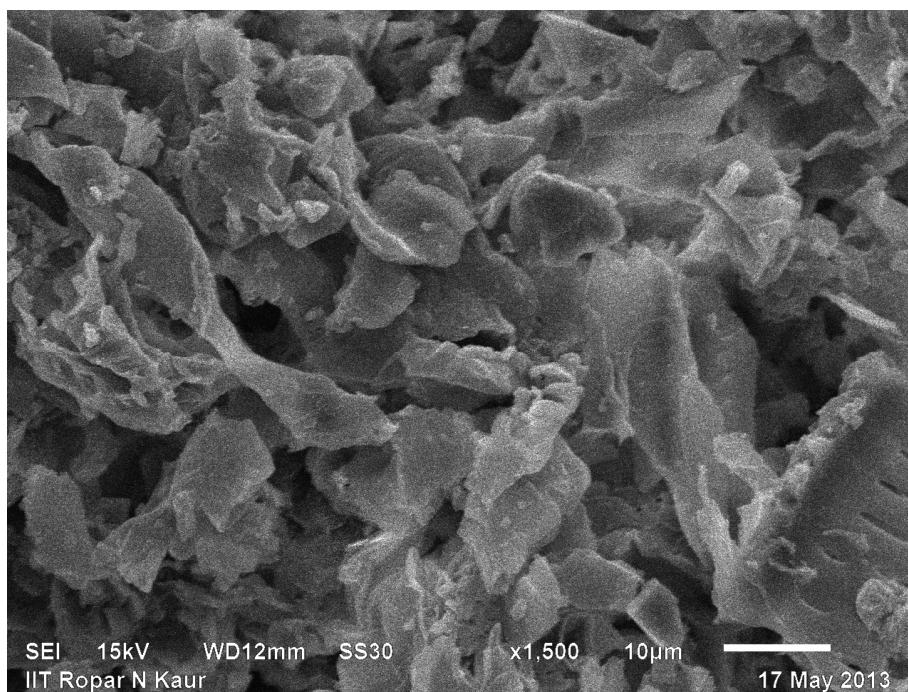


Figure 4.1(b): SEM image JLP adsorbent after adsorption of Amido black dye.

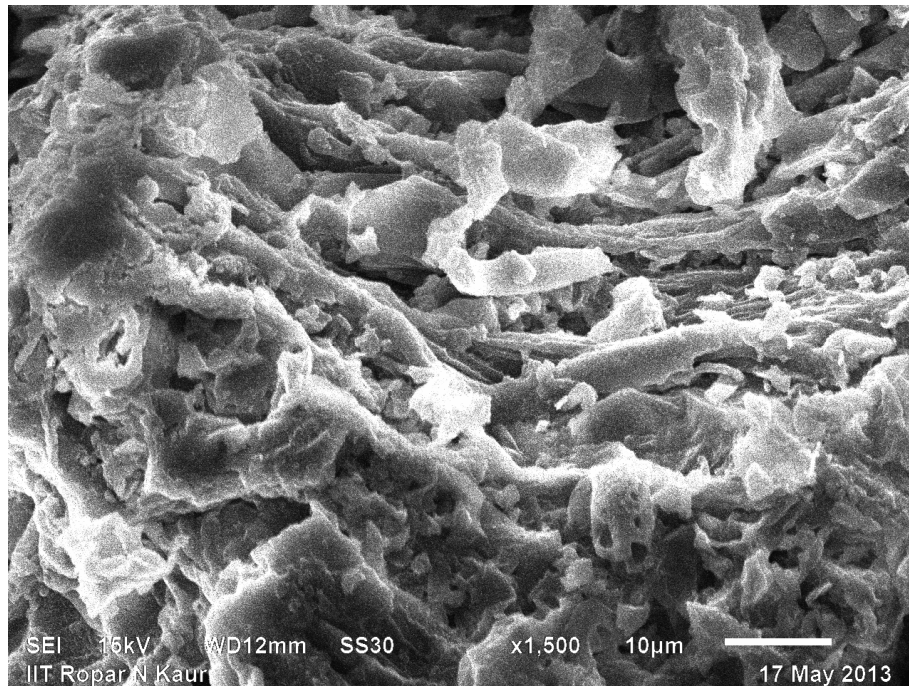


Figure 4.1(c): SEM image JLP adsorbent after adsorption of Crystal violet dye.

Table 4.1(a): EDXS analysis for JLP adsorbent.

Element	Weight (%)	Atomic (%)
C	60.71	68.52
O	36.71	31.10
Zr	2.58	0.38

Table 4.1(b): EDXS analysis for JLP adsorbent after adsorption of Amido black dye.

Element	Weight (%)	Atomic (%)
C	43.21	52.58
O	45.59	41.61
Si	11.17	5.81

Table 4.1(c): EDXS analysis for JLP adsorbent after adsorption of Crystal violet dye.

Element	Weight (%)	Atomic (%)
C	65.79	72.13
O	33.39	27.48
Si	0.82	0.39

4.2 Determination of λ_{\max} for Amido Black and Crystal violet dye solution

To determine the wavelength that corresponds to maximum absorbance (λ_{\max}), a standard solution of Amido Black and Crystal violet (40 mg/L each) in distilled water was scanned through a wavelength range of 200–700 nm using a UV–Visible spectrophotometer. Maximum absorbance value was noticed at a wavelength of 618 nm and 579 nm respectively Figure 4.2(a, b). The same value was also used in several literatures (Qiu et al., 2009) and (Patil et al., 2012) respectively. Therefore, λ_{\max} for amido black and crystal violet was taken as 618 nm and 579 nm respectively.

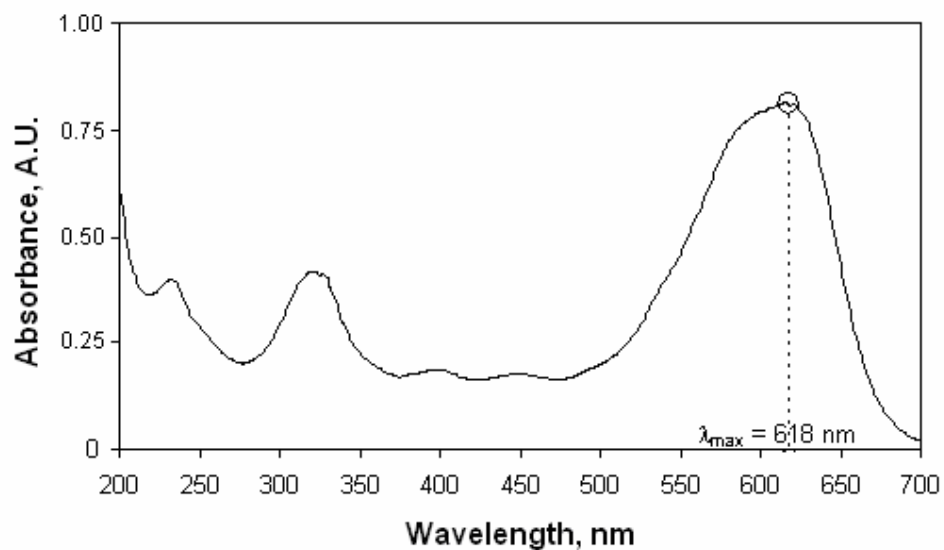


Figure 4.2(a): A plot of absorbance versus wavelength for Amido Black dye solution.

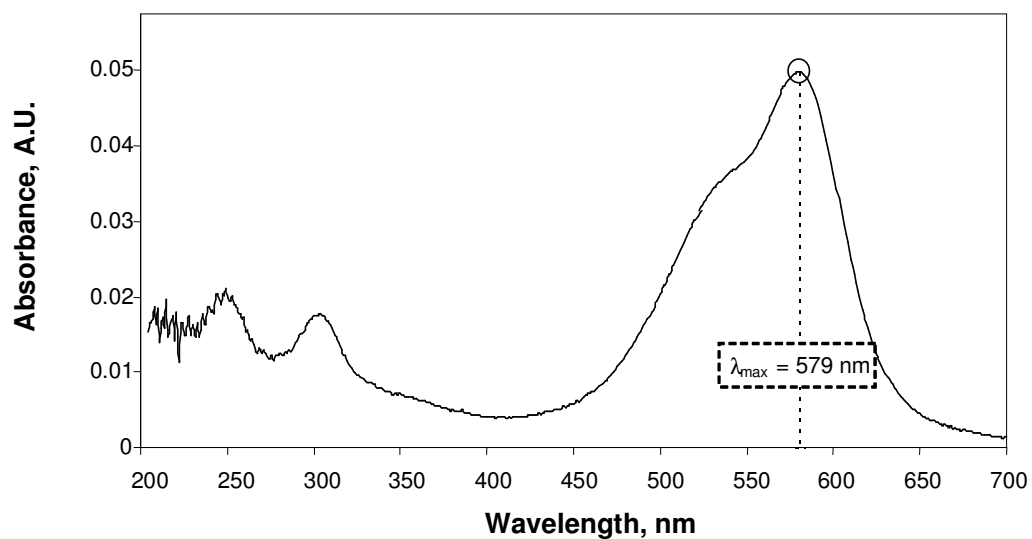


Figure 4.2 (b): A plot of absorbance versus wavelength for Crystal violet dye solution.

4.3 Calibration curve for Amido Black and Crystal violet dye solution

Absorbance values were determined at various known concentrations of the dye solution to obtain a calibration curve for Amido Black and Crystal Violet dye solution. As shown in figure 4.3(a, b) a linear fit to the observed data (absorbance versus dye concentration) yielded a straight line with a slope Amido black and Crystal Violet of 0.0658 and 0.0173 respectively. This calibration curve can be used for the determination of unknown dye concentration in the solution after adsorption with Jackfruit leaf powder (JLP).

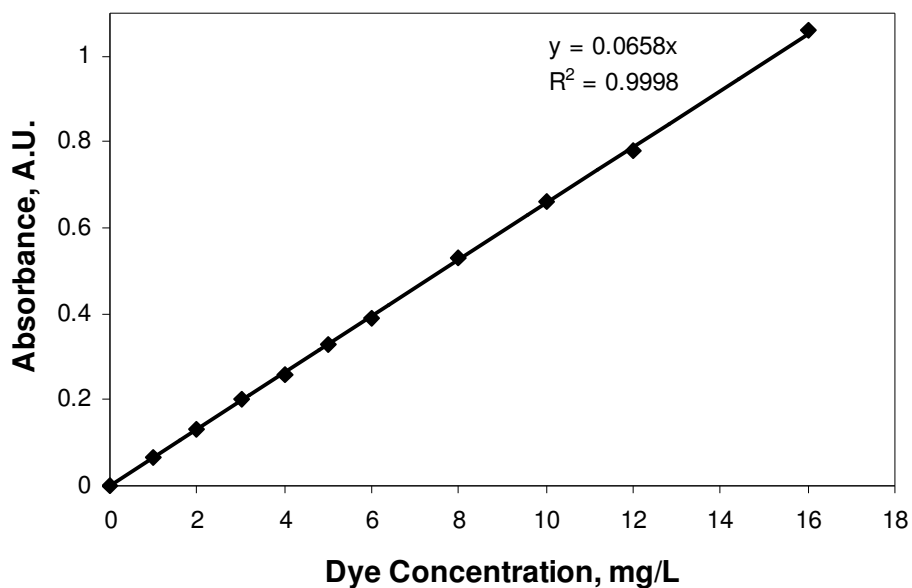


Figure 4.3 (a): Calibration curve for Amido Black dye solution.

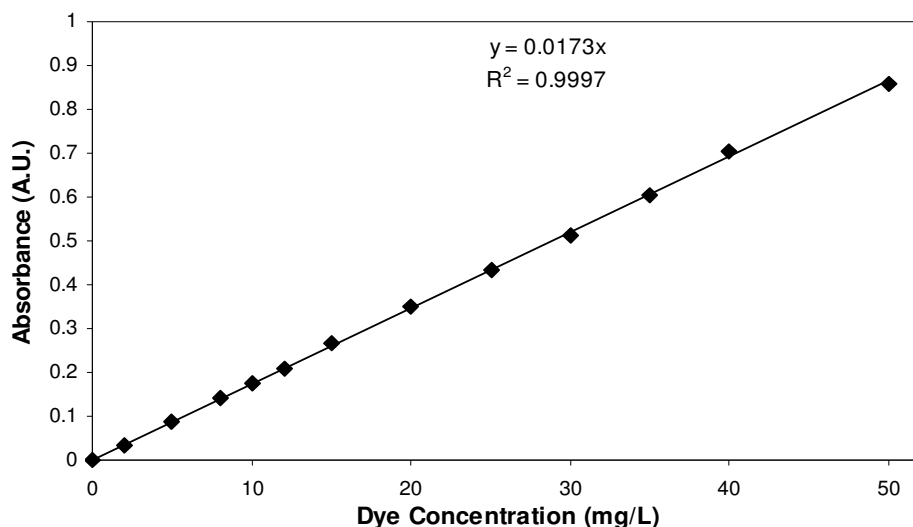


Figure 4.3 (b): Calibration curve for Crystal Violet dye solution.

4.4 Adsorption experiments

The adsorbent used in the experiment was JLP synthesized from Jackfruit Leaves. The adsorption experiments were carried out for 6 hrs and 4 hrs for Amido black and Crystal violet dye solution respectively, under continuous agitation at 275 rpm and 200 rpm to remove Amido black 10B dye and Crystal violet dye from its aqueous solution. Effect of dye concentration on the removal efficiency was studied using different dye concentrations in the range of 0–50 mg/L.

Dye removal efficiency was determined from the dye concentration in the solution before and after adsorption with JLP (Jackfruit leaf powder).

$$\text{Removal efficiency, } R = \left[\frac{C_i - C_f}{C_i} \right] \times 100 \quad (4.1)$$

$$\text{Adsorption capacity, } q_t = \frac{C_i - C_f}{C_j} \quad (4.2)$$

Where,

C_i = initial dye concentration in the solution, mg/L

C_f = dye concentration in the solution after adsorption with JLP, mg/L

C_j = JLP loading (adsorbent dosage), g/L

q_t = amount of dye adsorbed per unit weight of JLP, mg/g

4.4.1 Effect of JLP dosage

The values of dye removal efficiency and adsorption capacity of JLP evaluated using the above formulae (Eq. 4.1–4.2) for various concentration of JLP are listed in Table 4.2 (a, b).

Table 4.2(a): Calculation of Amido black dye removal efficiency from absorbance value at different JLP dosage.

JLP Concentration (g/L)	Adsorption Value (A.U)	Solution concentration (mg/L)	Removal Efficiency (%)	Adsorption capacity (%)
0	0.658	10	0	-
5	0.387	5.88	41.2	0.824
10	0.119	1.81	81.9	0.819
20	0.063	0.96	90.4	0.452
30	0.041	0.62	93.8	0.313

Table 4.2(b): Calculation of Crystal violet dye removal efficiency from absorbance value at different JLP dosage.

JLP Concentration (g/L)	Adsorption Value (A.U)	Solution concentration (mg/L)	Removal Efficiency (%)	Adsorption capacity (%)
0	0.173	10	0	-
5	0.121	5.00	41.2	0.824
10	0.017	1.011	81.9	0.819
20	0.012	0.688	90.4	0.452
30	0.010	0.582	93.8	0.313

A plot of dye removal efficiency versus JLP concentration yielded a non-linear profile as shown in Figure 4.4(a, b). From this figures, it can be observed that the removal efficiency increased with increasing the JLP concentration up to 10 g/L and no significant improvement in the removal efficiency values was observed beyond this value. Hence, the optimal JLP concentration for the removal of dyes was chosen to be 10 g/L. The similar observations were reported for both dye such as Amido black and Crystal violet by Qiu et al. (2009) and Patil et al. (2011) respectively. However, the authors were able to obtain a

dye removal efficiency of 78 % for the removal of Amido Black 10B and 80 % for the removal of Crystal violet dye using a synthetic adsorbent as well as natural adsorbent. Hence, it can be concluded that the JLP synthesized from Jackfruit leaf is far better than other adsorbent.

Initially, rapid increase in the adsorption with the increase in the adsorbent dose can be attributed to a greater surface area and availability of more adsorption sites. After this critical dose (10 g/L) the extent of adsorption is increasingly slowed down due to the fact that although there is increasing number of active sites but there is shortage of adsorbate in the solution.

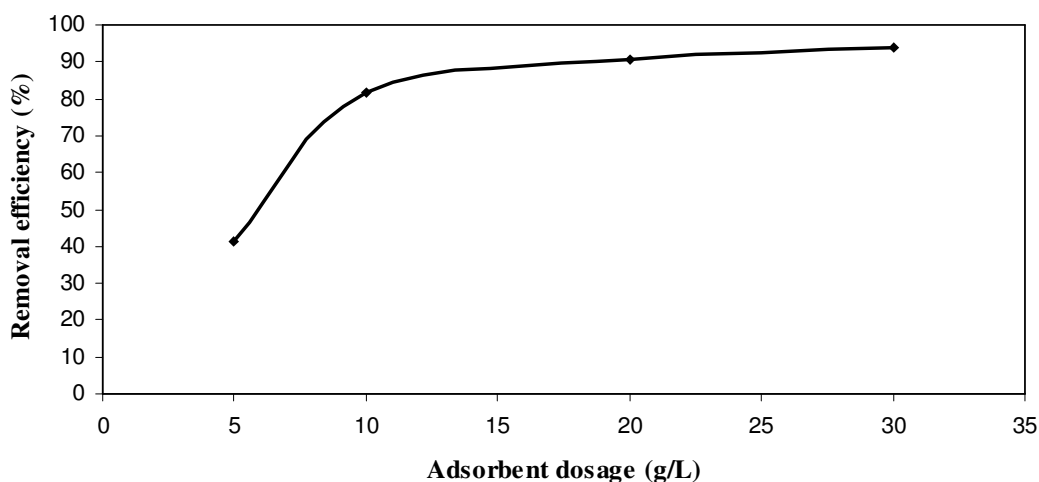


Figure 4.4(a): Variation of Amido black removal efficiency with JLP concentration.

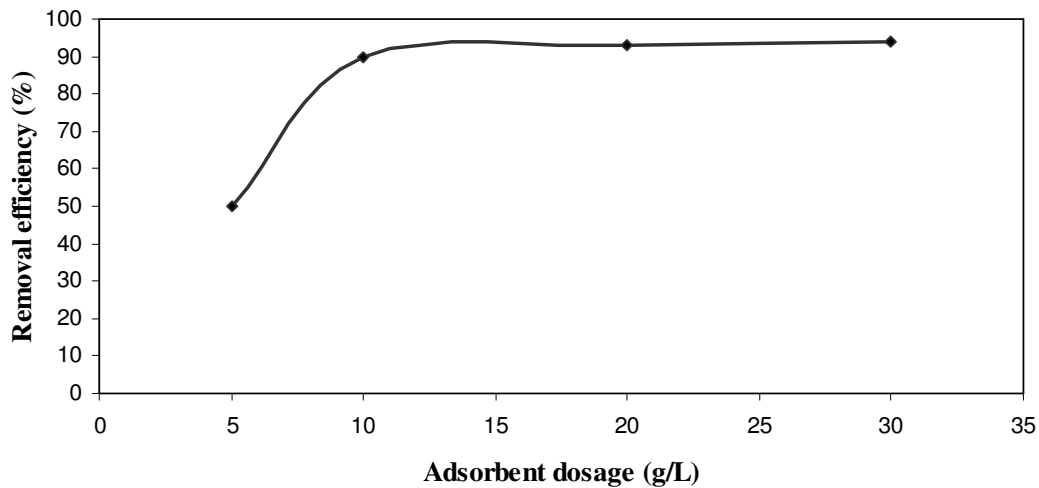


Figure 4.4(b): Variation of Crystal violet removal efficiency with JLP concentration.

As we can see from Figure 4.4(c, d) the adsorption capacity of the JLP (determined by Eq. 4.2) decreased with increasing the JLP concentration. It indicates that the adsorption capacity of a JLP decreases with increasing the JLP dosage. Hence, it can be concluded that too much of JLP concentration in the solution is not effective for adsorption and is also not economical.

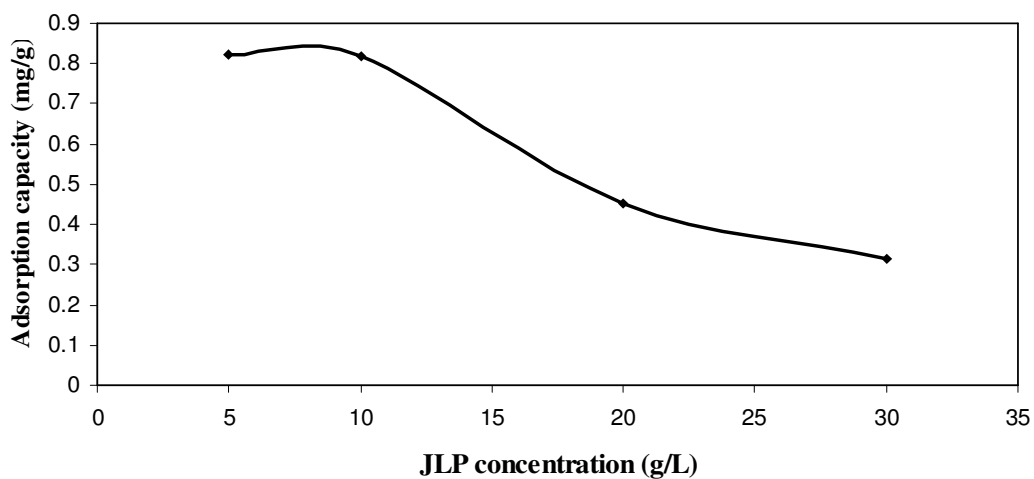


Figure 4.4(c): Variation of adsorption capacity for Amido black dye with JLP concentration.

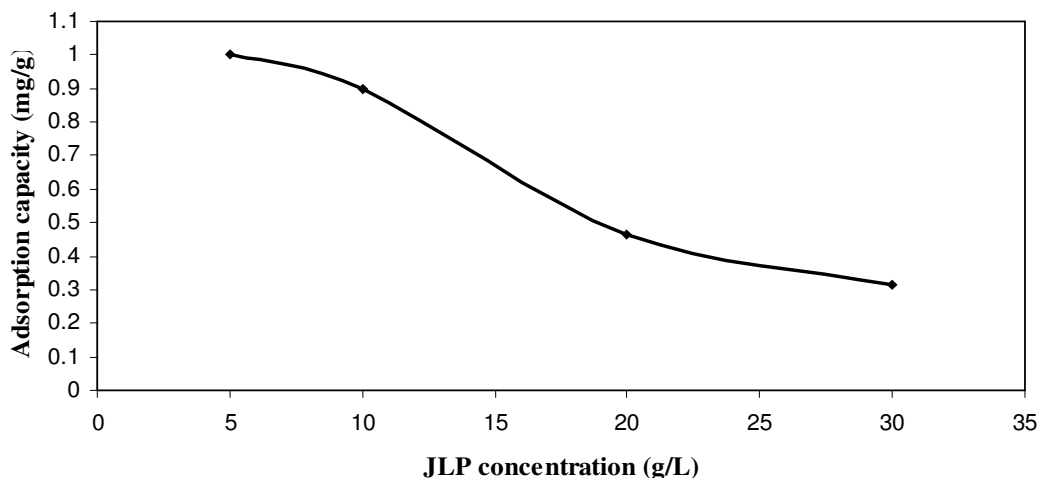


Figure 4.4(d): Variation of adsorption capacity for Crystal violet dye with JLP concentration.

4.4.2 Effect of solution pH

To study the effect of solution pH on the dye removal efficiency, adsorption experiments were conducted at various pH values between 2 and 12. The values of dye removal efficiency for various pH values are presented in Table 4.3 (a, b) and the corresponding plot of dye removal efficiency versus pH is shown in Figure 4.5 (a, b).

Table 4.3(a): Calculation of Amido black dye removal efficiency from absorbance value at different pH values.

pH	Absorbance Value (A.U)	Solution concentration (mg/L)	Removal Efficiency (%)
2	0.086	1.31	86.8
4	0.145	2.20	78.0
6	0.221	3.36	66.40
8	0.431	6.55	34.50
10	0.480	7.29	27.1
12	0.503	7.64	23.6

Table 4.3(b): Calculation of Crystal violet dye removal efficiency from absorbance value at different pH values.

pH	Absorbance Value (A.U)	Solution concentration (mg/L)	Removal Efficiency (%)
2	0.017	0.983	90.17
4	0.034	1.986	80.14
6	0.052	2.987	70.13
8	0.121	6.986	30.14
10	0.129	7.483	25.17
12	0.137	7.917	20.83

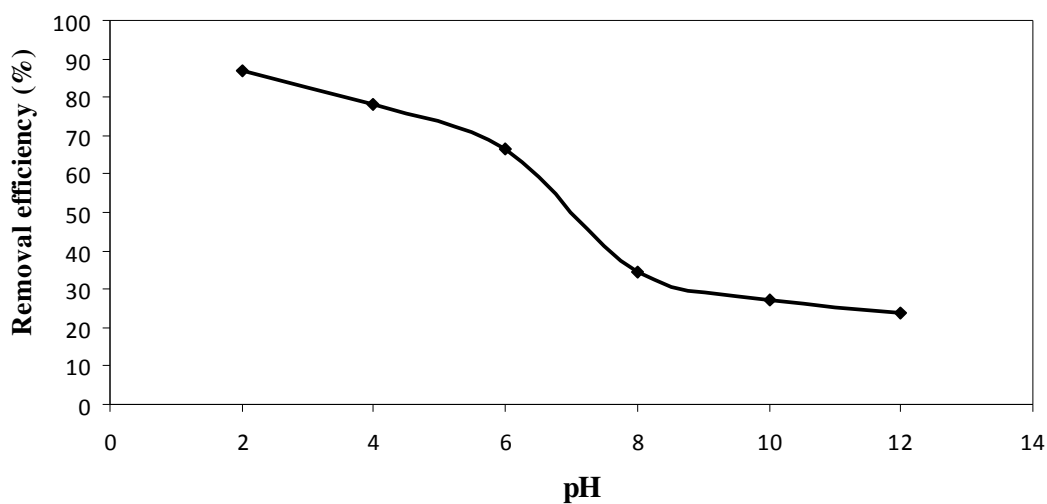


Figure 4.5(a): Variation of Amido black dye removal efficiency with solution pH.

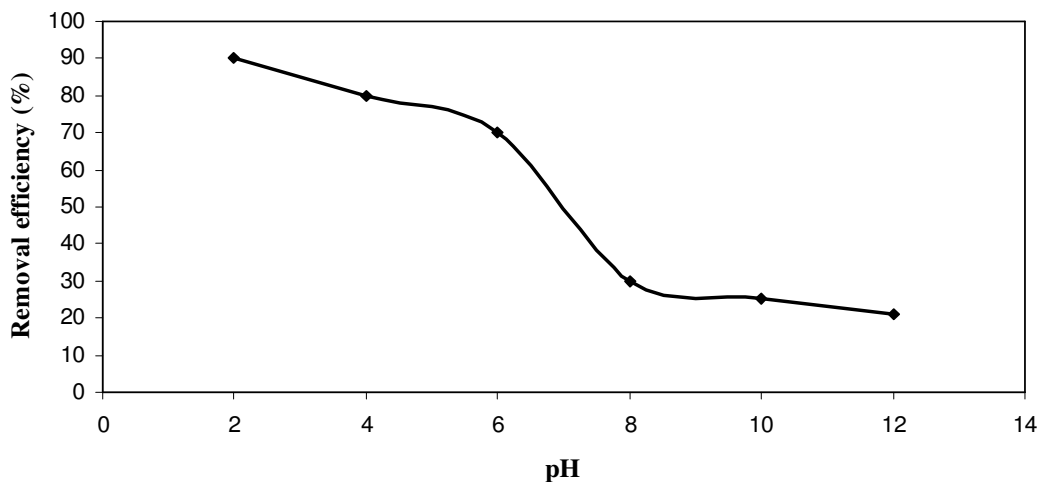


Figure 4.5(b): Variation of Crystal violet dye removal efficiency with solution pH.

It can be observed from the above figure that dye removal efficiency decreases with increase in pH value of the solution as the dye used is an acid dye and the JLP surface is positively charged. There could be fewer attachment sites available at higher pH due to decreased positive charge of the JLP surface. Increasing the pH of the solution could cause the JLP surface to decrease in positive charge, thus limiting its ability to hold onto the negatively charged dye species. The more the pH is raised, the less positive the surface becomes. Therefore, the optimum pH of the dye solution is 2–4. Hence, the pH value is 3 for Amido black and pH 2 for crystal violet that has been used earlier is suitable for all the experiments.

4.4.3 Effect of Stirrer Speed

Stirring is an important parameter in adsorption phenomena, influencing the distribution of the solute in the bulk solution and the formation of the external boundary film. To study the effect of stirrer speed on the dye removal efficiency, adsorption experiments were conducted at various stirrer speeds between 100 and 350 rpm. The values of dye removal efficiency for various stirrer speeds are presented in Table 4.4 (a, b) and the corresponding plot of dye removal efficiency versus stirrer speed is shown in Figure 4.6(a, b).

- Impeller diameter: 2.5 cm
- Impeller type: blade type

Table 4.4(a): Calculation of Amido black dye removal efficiency from absorbance value at different stirrer speed.

Stirrer speed (rpm)	Absorbance Value (A.U)	Solution concentration (mg/L)	Removal Efficiency (%)
100	0.218	3.31	66.90
150	0.197	3.00	70.00
200	0.164	2.49	75.10
250	0.142	2.16	78.40
300	0.118	1.79	82.10
350	0.104	1.58	84.23

Table 4.4(b): Calculation of Crystal violet dye removal efficiency from absorbance value at different stirrer speed.

Stirrer speed (rpm)	Absorbance Value (A.U)	Solution concentration (mg/L)	Removal Efficiency (%)
100	0.018	1.098	89.02
150	0.017	1.013	89.87
200	0.016	0.982	90.18
250	0.016	0.914	90.86
300	0.015	0.898	91.02
350	0.015	0.882	91.18

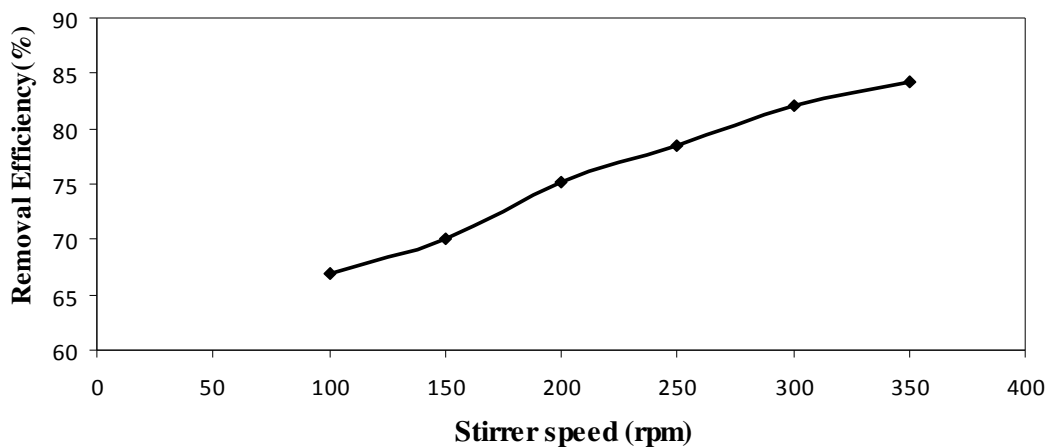


Figure 4.6(a): Variation of Amido black dye removal efficiency with stirrer speed.

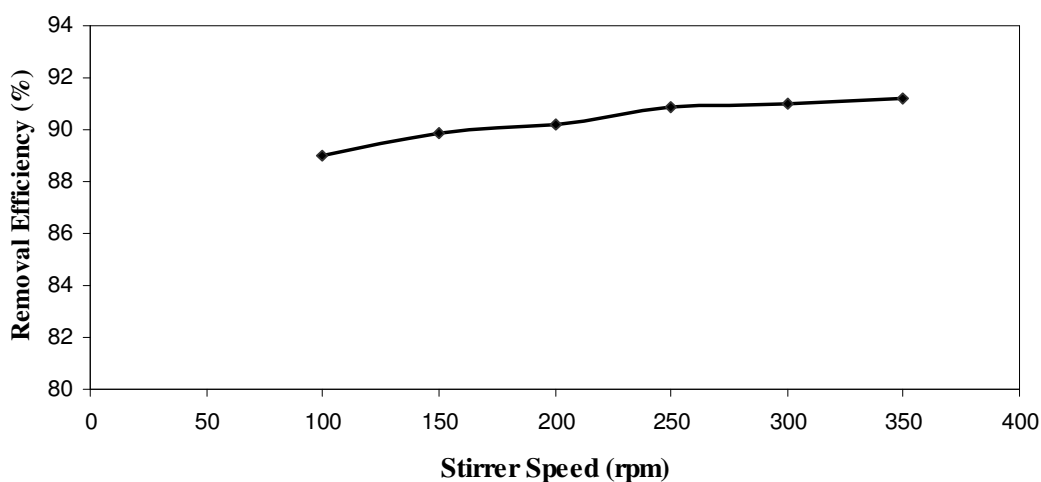


Figure 4.6(b): Variation of Crystal violet dye removal efficiency with stirrer speed.

From this figure 4.6(a, b) it is clear that with increasing agitation speed from 100 to 350 rpm, the removal efficiency increased significantly. This can be explained by the fact that increasing agitation speed reduced the film boundary layer surrounding particles, thus increasing the external film transfer coefficient, and hence the adsorption capacity. The degree of agitation reduces the boundary layer resistance and increases the mobility of the system. With agitation, the external mass transfer coefficient increases resulting in quicker adsorption of the dye molecules. It can be observed from the Figure 4.6(a, b) that agitation could improve the adsorption rate significantly. Very low values of dye removal efficiency

were obtained at low stirrer speeds and the removal efficiency increased with increasing the stirrer speed. There was no significant variation in removal efficiency values at higher stirrer speeds and hence, a stirrer speed of 275 rpm and 200 rpm was chosen for the dyes Amido black and Crystal violet dye respectively.

4.4.4 Effect of dye concentration

To study the effect of initial dye concentration on the removal efficiency, adsorption experiments were conducted at various dye concentration values between 10 and 50 mg/L. The values of dye removal efficiency at various dye concentrations are presented in Table 4.5(a, b). Corresponding plot of dye removal efficiency versus initial dye concentration is shown in Figure 4.7(a, b).

Table 4.5(a): Calculation of Amido black dye removal efficiency from absorbance value at different dye concentration.

Initial dye concentration (mg/L)	Absorbance Value (A.U)	Solution concentration (mg/L)	Removal Efficiency (%)
10	0.104	1.59	84.10
20	0.649	9.86	50.70
30	1.176	17.88	40.40
40	1.743	26.49	33.77
50	2.333	35.45	29.10

Table 4.5(b): Calculation of Crystal violet dye removal efficiency from absorbance value at different dye concentration.

Initial dye concentration (mg/L)	Absorbance Value (A.U)	Solution concentration (mg/L)	Removal Efficiency (%)
10	0.014	0.809	91.91
20	0.172	9.95	50.25
30	0.336	19.40	35.33
40	0.493	28.50	28.75
50	0.657	38.00	24.00

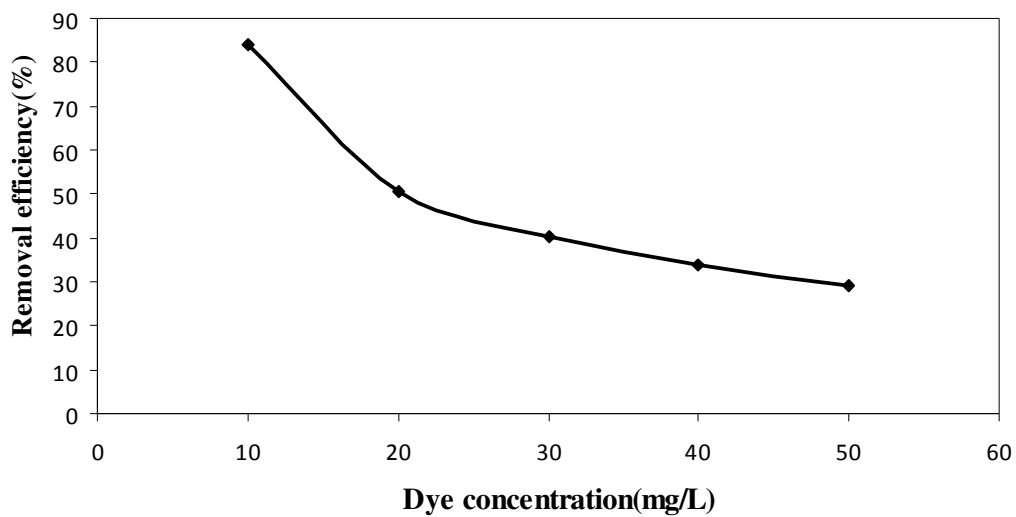


Figure 4.7(a): Variation of Amido black dye removal efficiency with initial dye concentration.

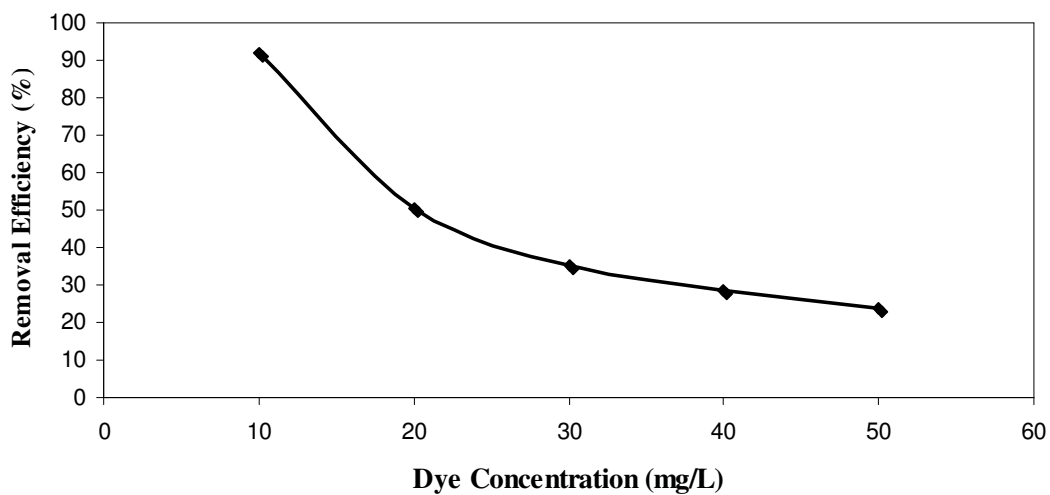


Figure 4.7(b): Variation of Crystal violet dye removal efficiency with initial dye concentration.

From the above figures, it can be observed that the removal efficiency decreases with increasing the initial dye concentration. This indicates that the adsorption process is more effective at low concentrations of the dye solution. Similar observation was reported for Amido black and Crystal violet dyes by Qiu et al. (2009) and Patil et al. (2011).

4.4.5 Effect of adsorption time

To study the effect of adsorption time on the dye removal efficiency, dye concentration values were noted at various time intervals between 0 and 540 min for Amido black and 0 and 420 min for Crystal violet. The values of dye removal efficiency at various time intervals are presented in Table 4.6(a, b) and the corresponding plot of dye removal efficiency versus adsorption time is shown in Figure 4.8(a, b).

From this figures, we can be observed that the removal efficiency increases with increasing the time of adsorption. The slope of the curve in Figure 4.8(a, b) is decreasing with time, indicating that the adsorption rate is faster initially and it decreases with time as more amount of dye is adsorbed on the JLP surface decreasing the availability of active adsorption sites. A similar observation was reported by Qiu et al. (2009) and Patil et al. (2011) for Amido black dye and Crystal violet dye respectively.

Table 4.6(a): Calculation of Amido black dye removal efficiency from absorbance value at different adsorption time.

Adsorption Time (min)	Absorbance Value (A.U)	Solution concentration (mg/L)	Removal Efficiency (%)
0	0.658	10	0
60	0.541	8.22	17.80
120	0.457	6.95	35.50
180	0.393	5.98	40.23
240	0.337	5.13	48.70
300	0.272	4.14	58.60
360	0.208	3.17	68.30
420	0.180	2.74	72.60
480	0.139	2.12	78.80
540	0.104	1.58	84.20

Table 4.6(b): Calculation of Crystal violet dye removal efficiency from absorbance value at different adsorption time.

Adsorption Time (min)	Absorbance Value (A.U)	Solution concentration (mg/L)	Removal Efficiency (%)
0	0.173	10	0
60	0.121	6.98	30.12
120	0.092	5.33	46.70
180	0.072	4.16	58.40
240	0.051	2.94	70.60
300	0.037	2.18	78.16
360	0.028	1.65	83.50
420	0.021	1.25	87.50

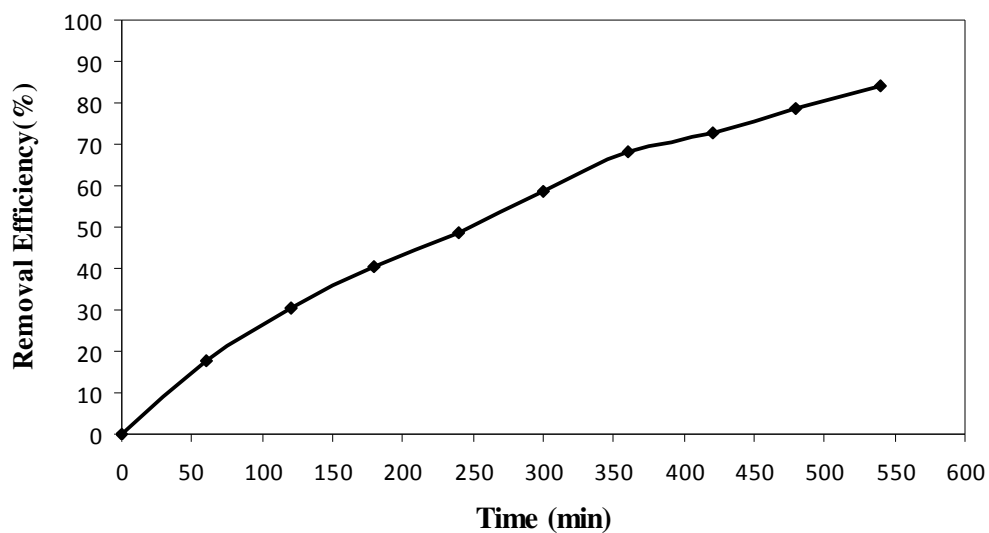


Figure 4.8(a): Variation of Amido black dye removal efficiency with time.

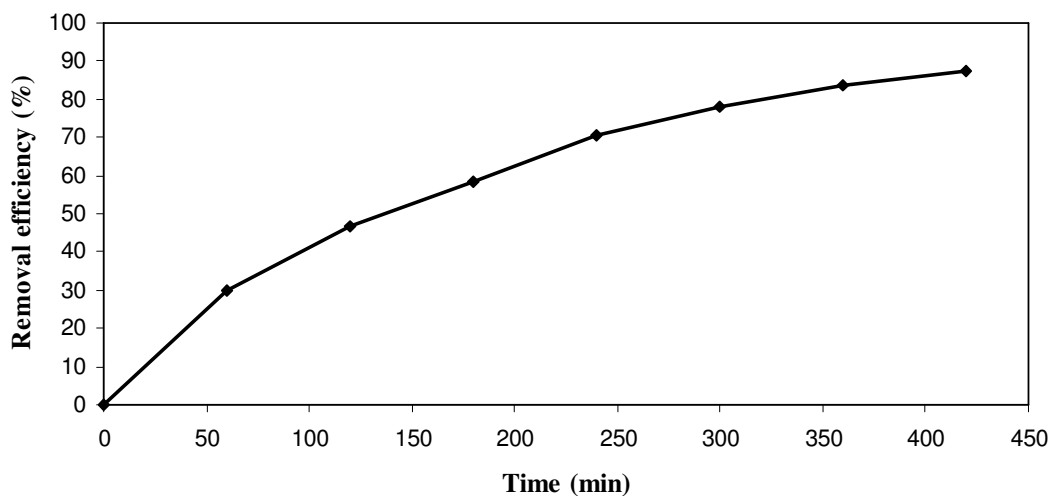


Figure 4.8(b): Variation of Crystal violet dye removal efficiency with time.

4.4.6 Effect of Temperature

To study the effect of temperature on the dye removal efficiency, adsorption experiments were conducted at three different temperatures (20, 40 and 60 °C). The values of dye removal efficiency at different temperatures are presented in Table 4.7 (a, b) and the corresponding plot of dye removal efficiency versus temperature is shown in Figure 4.9 (a, b).

Table 4.7(a): Calculation of Amido black dye removal efficiency from absorbance value at different temperatures.

Temperature (°C)	Absorbance Value (A.U)	Solution concentration (mg/L)	Removal Efficiency (%)
20	0.143	2.17	78.30
40	0.224	3.40	66.00
60	0.325	4.95	50.50

Table 4.7(b): Calculation of Crystal violet dye removal efficiency from absorbance value at different temperatures.

Temperature (°C)	Absorbance Value (A.U)	Solution concentration (mg/L)	Removal Efficiency (%)
20	0.030	1.75	82.50
40	0.072	4.146	58.54
60	0.104	6.017	39.83

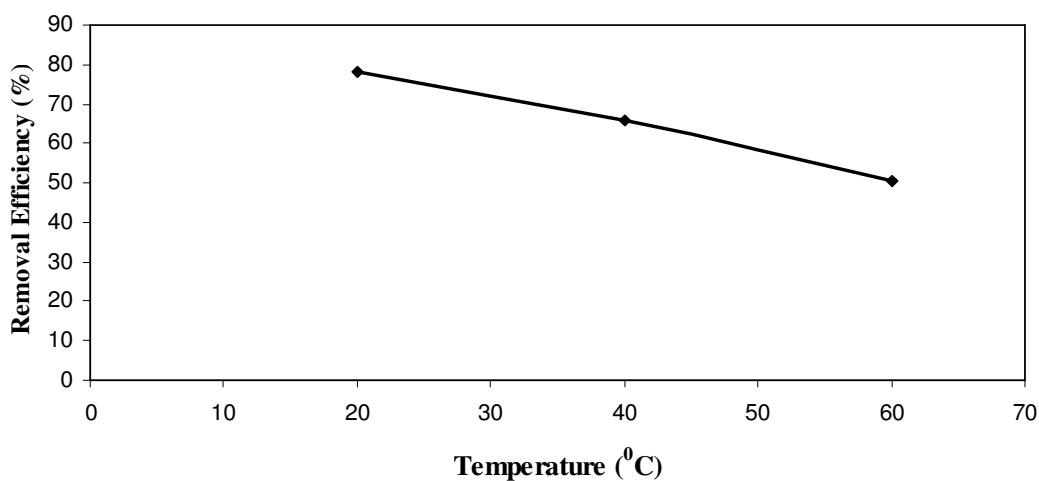


Figure 4.9(a): Variation of Amido black dye removal efficiency with temperature

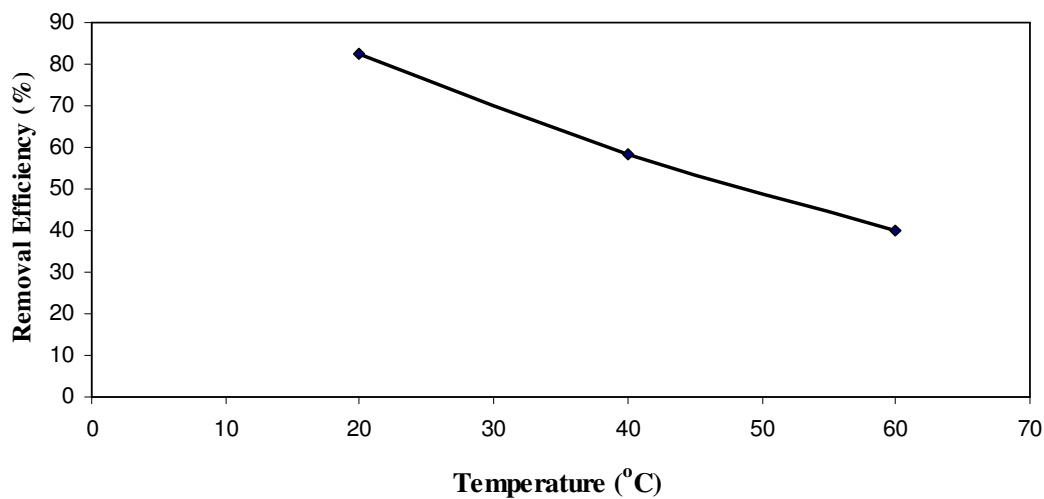


Figure 4.9(b): Variation of Crystal violet dye removal efficiency with temperature

From the above figures, we can be observed that the removal efficiency decreases with increasing the temperature. This indicates that adsorption is favored at lower temperatures and desorption takes place at higher temperatures due to the fact that adsorption is exothermic in nature. Similar observation was reported in several literatures (Nandi et al., 2008; Patil et al., 2012).

4.5 Thermodynamic, Kinetic and Equilibrium studies

4.5.1 Thermodynamics of adsorption

The thermodynamic parameters, such as the changes in the Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of adsorption process are estimated from the following correlations (Eq. (4.3) and (4.4)).

The change in standard free energy (ΔG°) at various temperatures can be estimated as follows.

$$\Delta G^\circ = -RT \ln K_d = -RT \ln \left(\frac{q_e}{C_e} \right) \quad (4.3)$$

Here, R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is the temperature in Kelvin (K). The relation among the thermodynamic parameters mentioned above is given by the following equation.

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (4.4)$$

A plot of ΔG° versus T, (Figure 4.10(a, b)) yields a straight line with the slope of $-\Delta S^\circ$ and intercept of ΔH° .

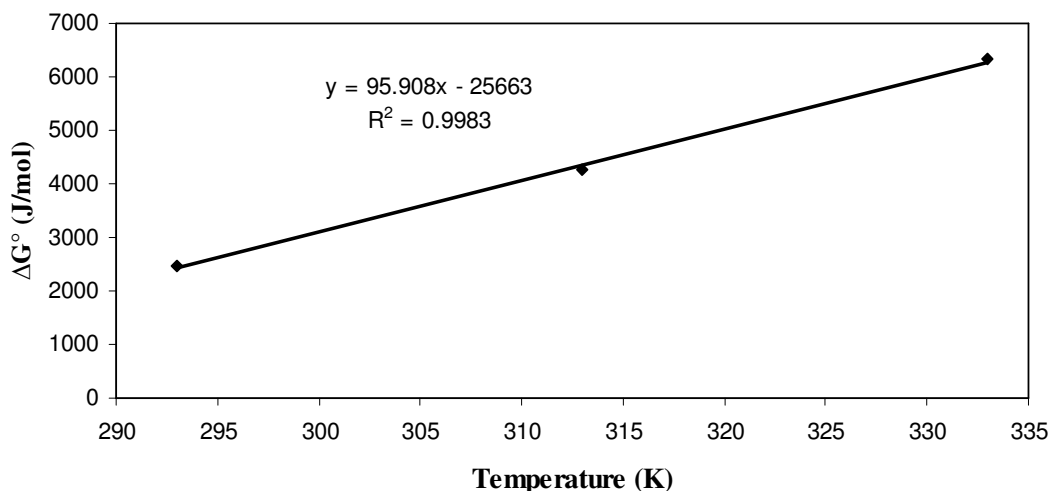


Figure 4.10(a): Plot of Amido black dye change in Gibbs free energy with temperature.

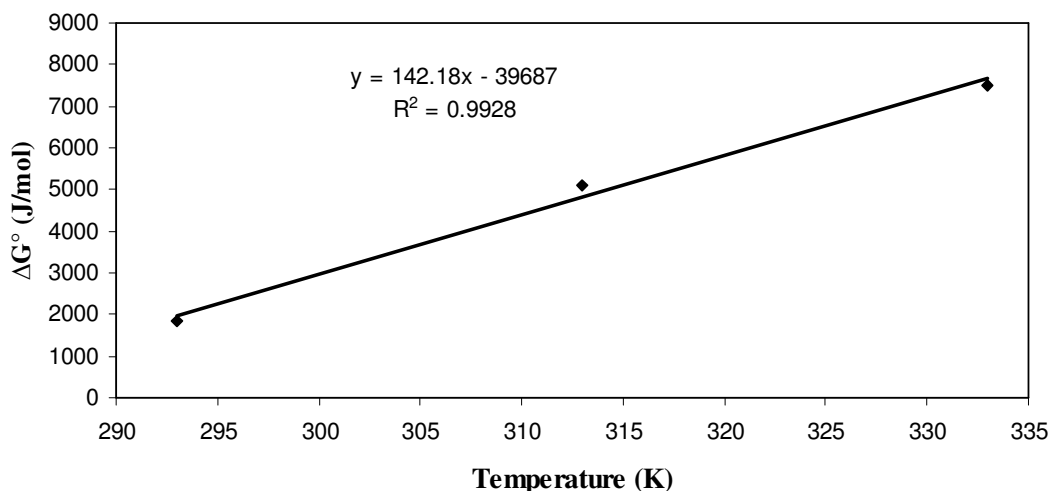


Figure 4.10(b): Plot of Crystal violet dye change in Gibbs free energy with temperature.

The values of ΔG° obtained using Eq. (4.3) at the temperatures 293, 313 and 333 K for Amido black dye are 2.4, 4.2 and 6.3 kJ/mol respectively. The value of ΔG° also calculated for Crystal violet dye as well as it was calculated for Amido black dye and the values are 1.8, 5.0 and 7.5 kJ/mol at the temperatures 293, 313 and 333 k respectively. The values of changes in enthalpy (ΔH°) and entropy (ΔS°) during the adsorption process determined from the slope and intercept of Figure 4.10(a) are -25.66 kJ/mol and -95.90 J/mol K^{-1} and Figure 4.10(b) are -142.18 KJ/mol and -39.68 J/mol K^{-1} . The negative values indicate that the adsorption process considered here is exothermic in nature and hence lower temperatures are favored.

4.5.2 Adsorption kinetics

Various kinetic models proposed to examine the controlling mechanism of adsorption process are a pseudo-first-order kinetic model, a pseudo-second-order kinetic model, and an intra-particle diffusion model. These three models are studied to find the best fitting model for the adsorption of Amido Black dye and Crystal violet dye on JLP surface.

4.5.2.1 Pseudo first order kinetics

This model assumes that the rate of solute uptake is directly proportional to the concentration difference of the solute from the equilibrium saturation concentration on the adsorbent. The form of rate equation for a pseudo first-order kinetic model is as follows.

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \quad (4.5)$$

Here, q_t (mg/g) is the amount of dye adsorbed after time 't' (min), q_e (mg/g) is the equilibrium dye adsorption capacity and k_1 (min^{-1}) is the pseudo first-order rate constant.

The integration of equation (4.5) with the initial condition $q_t = 0$ at $t = 0$ gives the following equation.

$$-\ln\left[1 - \frac{q_t}{q_e}\right] = K_1 t \quad (4.6)$$

The slope of a straight line fit to the data of $-\ln(1 - q_t/q_e)$ versus t (as shown in Figure 4.11(a, b)) passing through origin gives the value of the pseudo first-order rate constant, k_1 . The experimental data was found not to be fitting well with the pseudo first-order model. The regression coefficient value is very close to 1.0 for Crystal violet dye but for Amido black it is not as much closely as Crystal violet. The value of the pseudo first order rate constant, k_1 as obtained from the linear curve fitting is 0.0045 min^{-1} for Amido black and 0.0076 min^{-1} for Crystal violet dye. The value of q_e as obtained from the regression analysis (1.12 mg/g) for Amido black is not much close to the experimental value (0.842 mg/g). By Crystal violet regression plot analysis the value of q_e has obtained (1.04 mg/g) and it is also not close to the experimental value (0.875 mg/g) and this indicates that the pseudo first-order kinetic model can not represent the dye-JLP system under consideration.

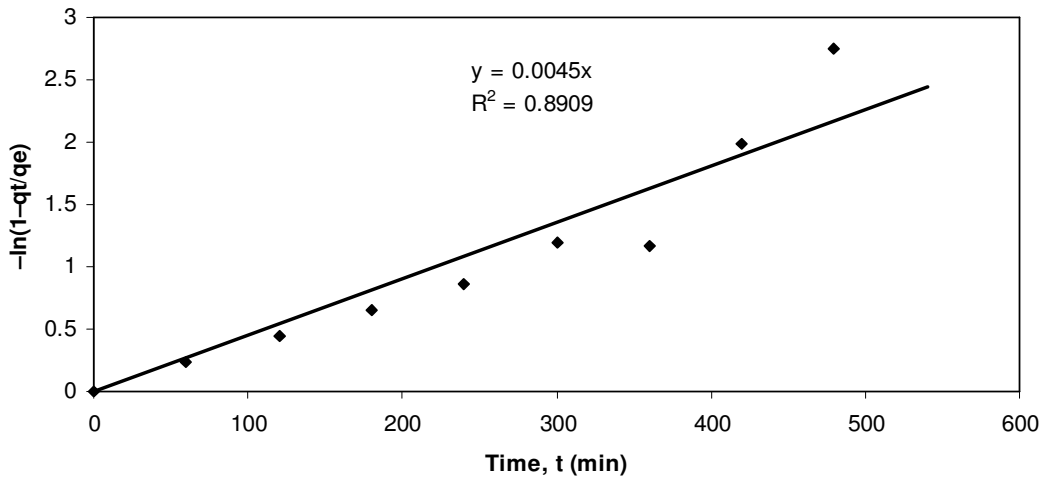


Figure 4.11(a): Pseudo first-order kinetic model for the adsorption of Amido Black 10B dye on JLP surface.

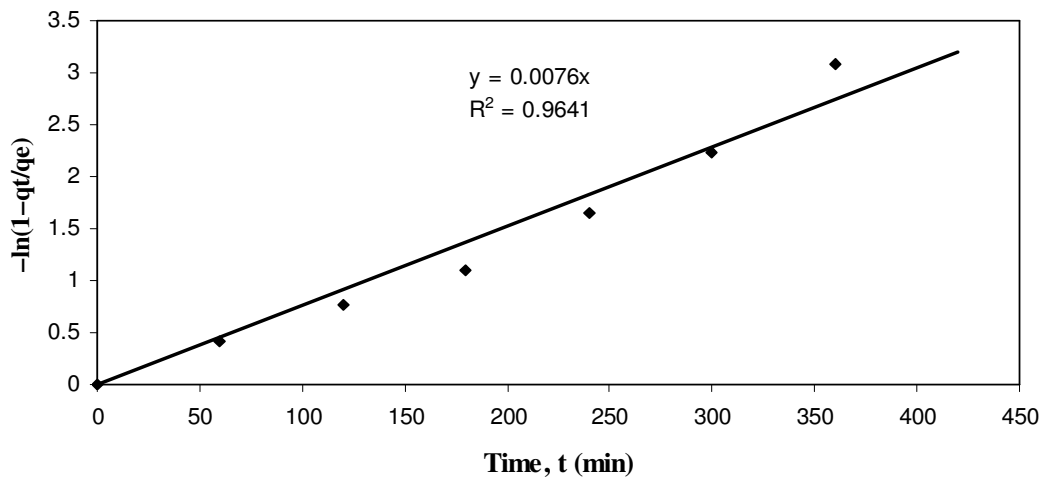


Figure 4.11(b): Pseudo first-order kinetic model for the adsorption of Crystal violet dye on JLP surface.

4.5.2.2 Pseudo second-order kinetics

This model interprets that the rate of solute uptake is directly proportional to the square of the concentration difference of the solute from the equilibrium saturation concentration on the adsorbent. The form of rate equation for a pseudo second-order kinetic model is as follows.

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \quad (4.7)$$

Here, k_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) is the pseudo second-order rate constant.

The integration of equation (4.7) with the initial condition $q_t = 0$ at $t = 0$ gives the following expression.

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (4.8)$$

The values of q_e and k_2 can be obtained from the slope and intercept of a straight line fit to the data of t/q_t versus t (as shown in Figure 4.12(a, b)). The slope and intercept obtained from the graphical analysis of Amido black plot are 1.1876 and 0.0009 and the values of q_e and k_2 thus obtained are 0.842 mg/g and $1567.1 \text{ g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ respectively. Although, the regression coefficient value exactly coming 1.0, the value of q_e (0.842 mg/g) it is exactly matching with experimental value (0.842 mg/g). Again we repeated same procedure for Crystal violet graphical plot analysis. The slope and intercept are 1.1429 and 0.0007 and the value of q_e and k_2 are 0.875 mg/g and $1866 \text{ g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ respectively. The regression coefficient value is exactly coming 1.0, the value of q_e (0.875 mg/g), it is also exactly matching with the experimental value (0.875 mg/g). Therefore, the pseudo second-order kinetic model is appropriate for the dye-JLP system considered in this study.

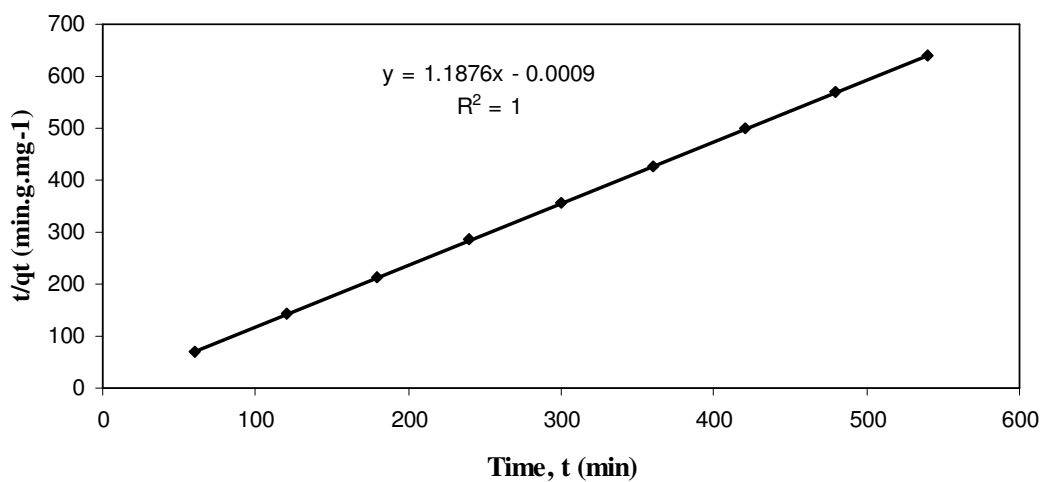


Figure 4.12(a): Pseudo second-order kinetic model for the adsorption of Amido Black 10B dye on JLP surface.

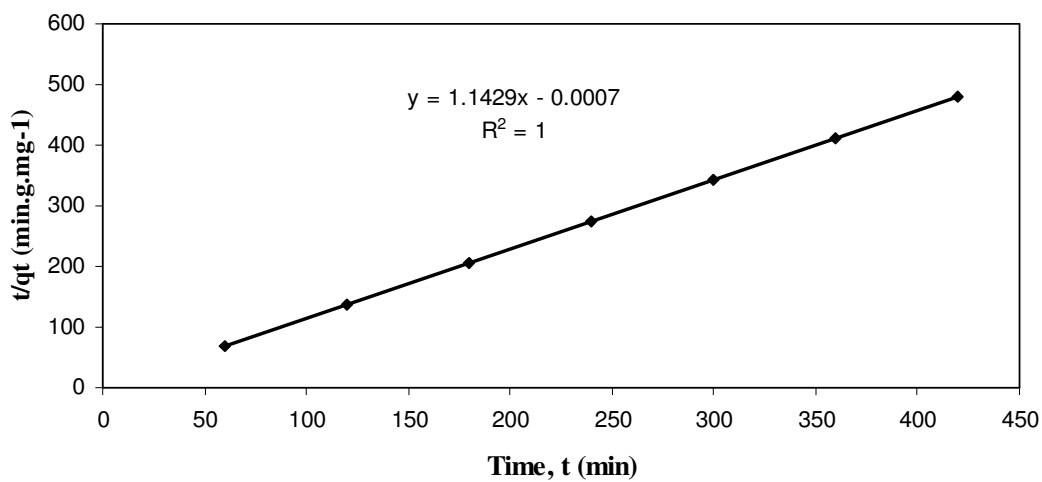


Figure 4.12(a): Pseudo second-order kinetic model for the adsorption of Crystal violet dye on JLP surface.

4.5.2.3 Intra particle diffusion

This model considers the bulk diffusion, film diffusion, pore diffusion in addition to the adsorption phenomenon. The form of rate equation for the intra-particle diffusion model is as follows.

$$q_t = k_i t^{\frac{1}{2}} + C_i \quad (4.9)$$

Here, k_i ($\text{mg/g}\cdot\text{min}^{-0.5}$) is the intra-particle diffusion rate constant and C_i (mg/g) is the intercept, which corresponds to the boundary layer thickness. The values of k_i and C_i can be determined directly as the slope and intercept of the linear plot of q_t versus $t^{0.5}$. The values of k_i and C_i obtained from the graph (Figure 4.13(a, b)) are $0.0383 \text{ mg/g}\cdot\text{min}^{-0.5}$ and 0.0727 mg/g respectively for Amido black. The values of k_i and C_i for Crystal violet are $0.0446 \text{ mg/g}\cdot\text{min}^{-0.5}$ and 0.0128 mg/g respectively.

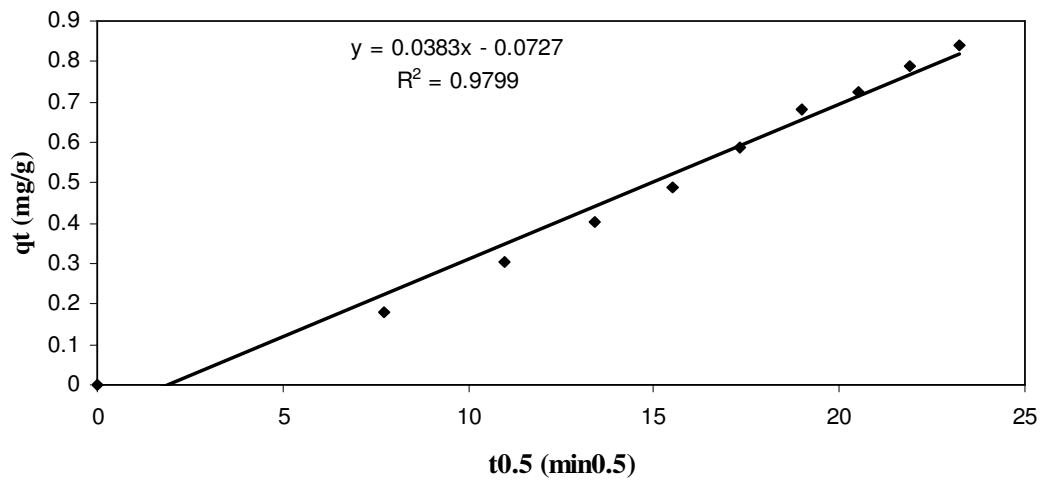


Figure 4.13(a): Intra-particle diffusion model for the adsorption of Amido Black 10 B dye on JLP surface.

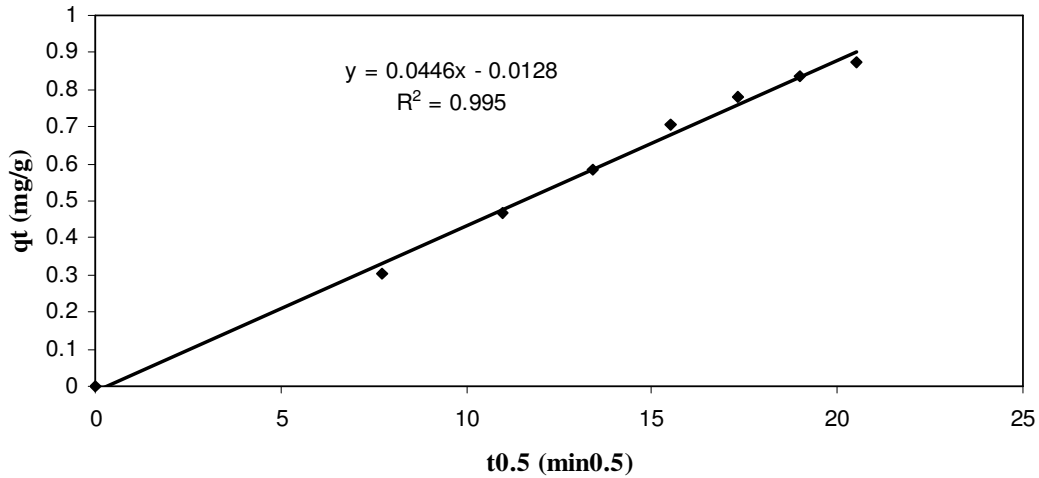


Figure 4.13(b): Intra-particle diffusion model for the adsorption of Crystal violet dye on JLP surface.

Although, the regression coefficient value is close to 1.0, it is still less than that obtained for the pseudo second-order kinetic model.

4.5.3 Equilibrium adsorption isotherm

Adsorption isotherms describe the nature of interaction between the adsorbent and the adsorbate molecules at equilibrium. The two most common types of adsorption isotherms are Langmuir and Freundlich isotherms. The parameters of these equilibrium isotherms are useful in the optimum design of adsorption systems. The Langmuir isotherm simply assumes that there is a homogeneous distribution of active sites (binding sites) on the surface of the adsorbent, which adsorb a single molecular layer of adsorbate molecules with no interaction between the adsorbed molecules. The Langmuir isotherm equation is given by.

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (4.10)$$

Where, C_e (mg/L) and q_e (mg/g) are the liquid phase concentration and solid phase concentration of adsorbate at equilibrium, and Q_m (mg/g) corresponds to the maximum adsorption capacity of the adsorbent where as K_L (L/mg) corresponds to the equilibrium adsorption constant of the Langmuir isotherm.

The linearized form of equation (4.10) is as follows.

$$\frac{C_e}{q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (4.11)$$

The values of Q_m and K_L can be determined from the slope and intercept of a linear curve fit to the plot of C_e/q_e versus C_e (shown in Figure 4.14).

Further, the equilibrium adsorption intensity (R_L), which indicates the type of adsorption, is defined as follows.

$$R_L = \frac{1}{1 + K_L C_i} \quad (4.12)$$

Here, C_i is the initial dye concentration (mg/L) in the solution. For a favorable adsorption, $R_L < 1$; for a linear adsorption, $R_L = 1$; and for an unfavorable adsorption, $R_L > 1$. A plot of R_L versus C_i is shown in Figure 4.15(a, b). From this figure, it can be observed that the adsorption process is more favorable at higher concentrations of dye solution.

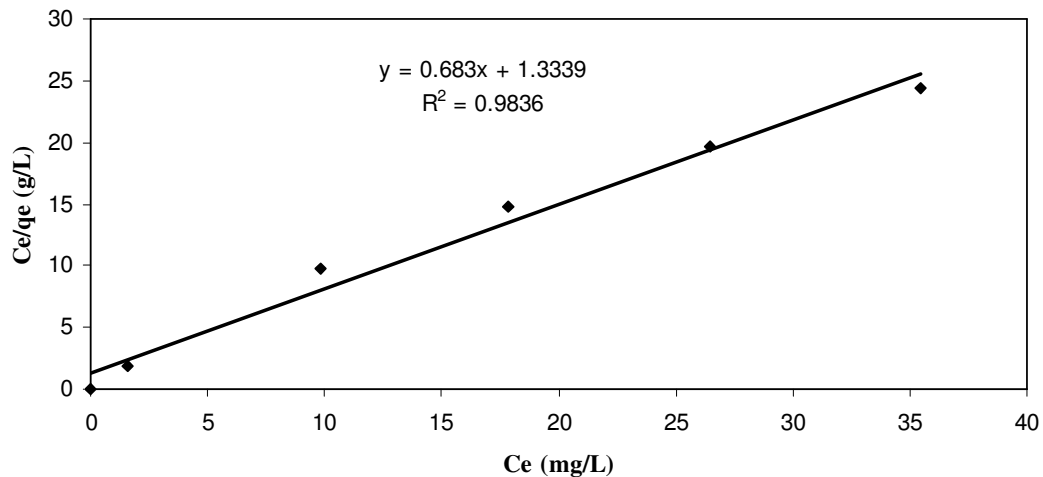


Figure 4.14(a): Plot of C_e/q_e versus C_e for the estimation of Amido black 10B dye Langmuir isotherm constants.

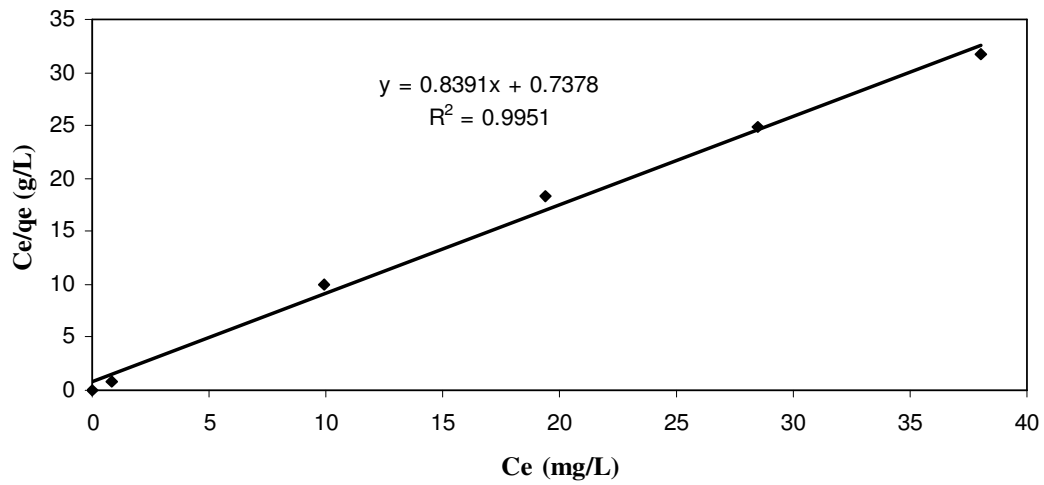


Figure 4.14(b): Plot of C_e/q_e versus C_e for the estimation of Crystal violet dye Langmuir isotherm constants.

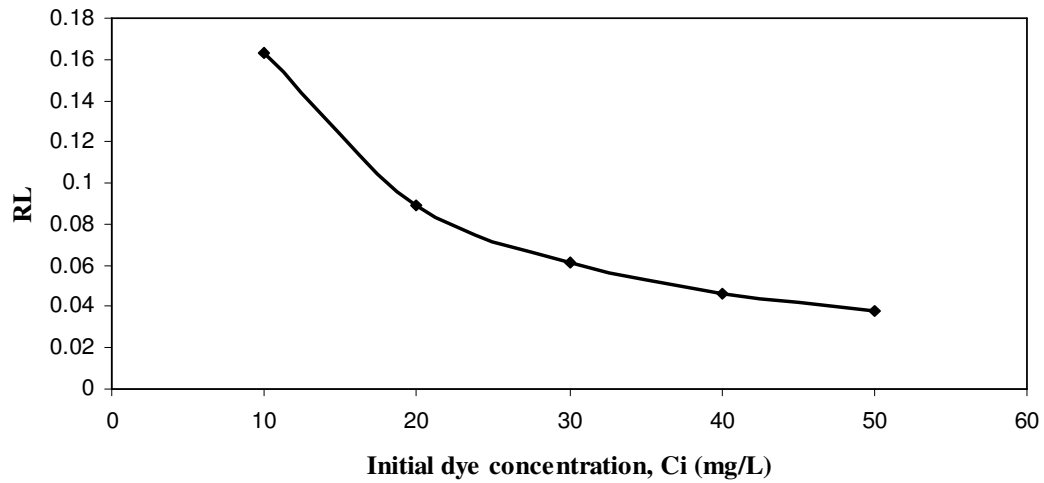


Figure 4.15(a): Variation of equilibrium adsorption intensity (R_L) with initial dye (Amido black 10B) concentration (C_i).

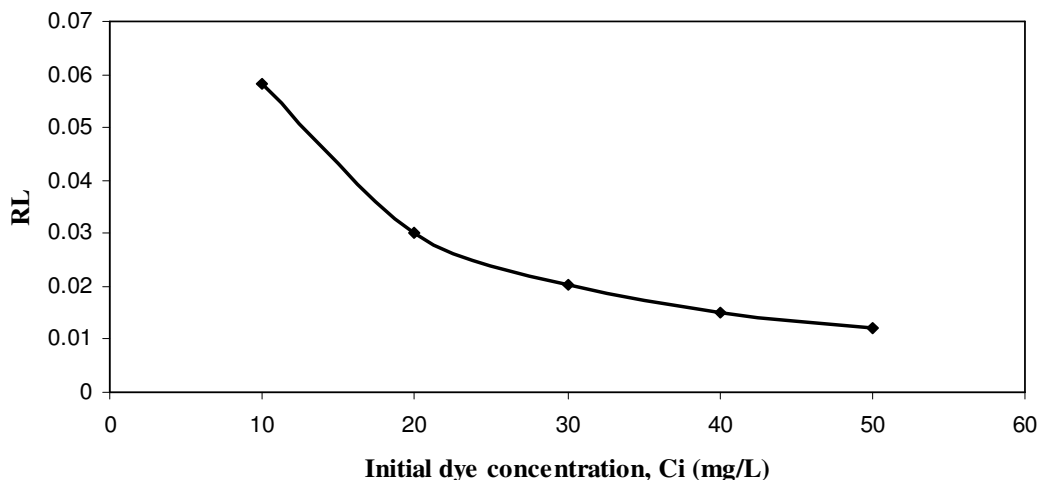


Figure 4.15(b): Variation of equilibrium adsorption intensity (R_L) with initial dye (Crystal violet) concentration (C_i).

The Freundlich isotherm model is an exponential equation, which applies to heterogeneous systems with interaction between adsorbed molecules and is not restricted to the formation of a monolayer. This model assumes that as the adsorbate concentration increases, the concentration of the adsorbate on the adsorbent surface also increases and correspondingly that sorption energy exponentially decreases on completion of the sorption centers of an adsorbent. The well-known expression for the Freundlich model is as follows.

$$q_e = K_F C_e^{\frac{1}{n}} \quad (4.13)$$

Where, ' K_F ' is the Freundlich constant $((\text{mg/g}) \cdot (\text{mg/L})^{-n})$ related to the bonding energy, and n is the heterogeneity factor (exponent). Here, ' n ' is a measure of the deviation from linearity of the adsorption and indicates the degree of non-linearity between the solution concentration and the adsorption rate. A power-law model curve fit to the data of q_e versus C_e could yield the values of K_F and n .

Both the isotherms for the dye–JLP system at 20°C at a pH of 3 and pH of 2 for Amido black 10B and Crystal violet dyes respectively are shown in Figure 4.16(a, b). From this figures, we can be observed that the equilibrium adsorption between Amido Black dye and

Crystal violet dye- JLP can better be represented by Freundlich isotherm than the Langmuir isotherm.

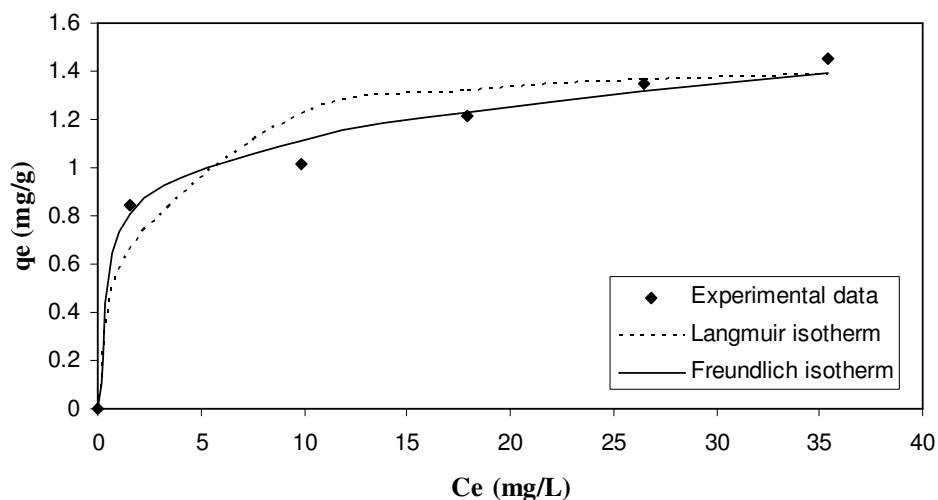


Figure 4.16(a): Equilibrium isotherms for the adsorption of Amido Black on JLP.

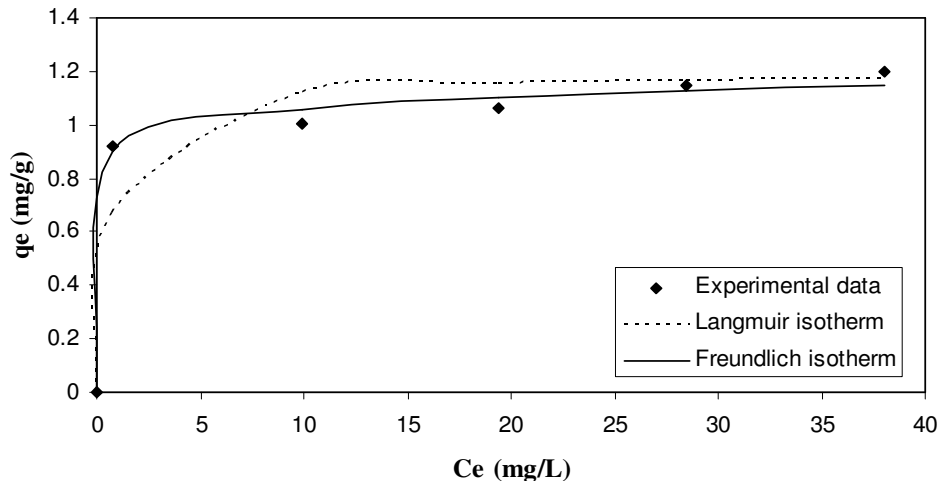


Figure 4.16(b): Equilibrium isotherms for the adsorption of Crystal violet on JLP.

The trend observed in the experimental data is very close to the Freundlich isotherm but it is deviating considerably from the Langmuir isotherm. This indicates that the adsorption process is of multi-layer type with some interaction among the adsorbed molecules. The evaluated model parameters for both Langmuir and Freundlich adsorption isotherms are

presented in Table 4.8(a, b). Corresponding values of correlation coefficients (R^2) are also shown in the table.

Table 4.8(a): Equilibrium parameters for Langmuir and Freundlich adsorption isotherms for Amido black 10B dye.

Langmuir isotherm		Freundlich isotherm	
Parameter	Value	Parameter	Value
Q_m	1.4641	K_F	0.7457
K_L	0.5120	$1/n$	0.1743
R^2	0.9836	R^2	0.9347

Table 4.8(b): Equilibrium parameters for Langmuir and Freundlich adsorption isotherms for Crystal violet dye.

Langmuir isotherm		Freundlich isotherm	
Parameter	Value	Parameter	Value
Q_m	1.1917	K_F	0.9114
K_L	1.6152	$1/n$	0.0635
R^2	0.9951	R^2	0.8557

4.6 Comparison of JLP performance with a commercial adsorbent

The removal efficiency of the JLP is compared with a synthesized zeolite (ZX). It can be observed from the figure (Figure 4.17) that the JLP synthesized from jackfruit leaf performs almost same removal efficiency as synthesized zeolite (ZX). AS the adsorption increases JLP gives better removal efficiency than synthesized Zeolit (ZX) .The maximum dye removal efficiency obtained for the JLP is 84.2% and the removal efficiency for the commercial adsorbent is only 78.4%. However, we can be observed that there is a loss of about 5–10% of the removal efficiency for the synthesized zeolite (ZX).

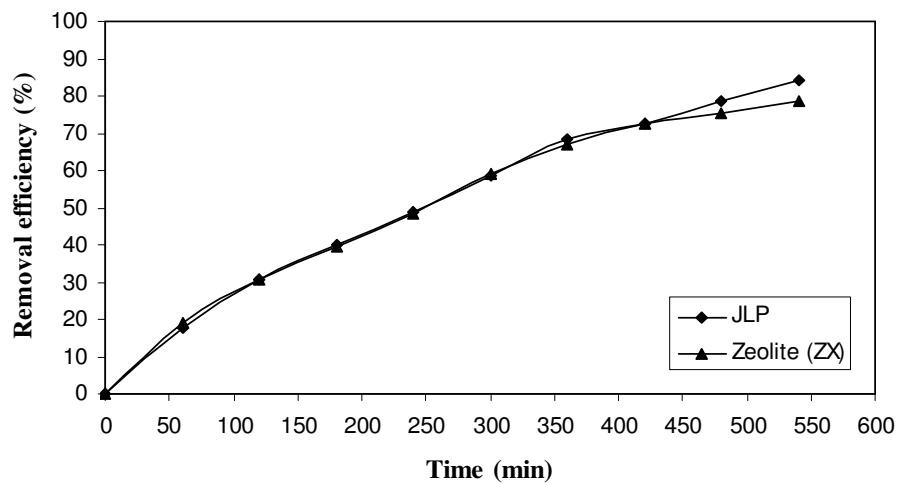


Figure 4.17: Comparison of dye removal efficiency over JLP and synthesized zeolite (ZX).

Jackfruit leaf powder (JLP) has been synthesized from mature Jackfruit leaves. The prepared Jackfruit leaf powder (JLP) has been successfully applied for the adsorptive removal of Amido Black and Crystal violet dyes from their aqueous solutions. The following conclusions have been derived from the experimental analysis carried out so far.

- The prepared Jackfruit leaf powder (JLP) is found to be more effective than the synthetic adsorbent presented in the literatures (Das et al., 2012; Tanez et al., 2008).
- The optimum JLP concentration obtained from the experimental studies for Amido black and Crystal violet is 10g/L.
- λ_{\max} for Amido Black 10B dye and Crystal violet solution was found to be 618 nm and 579 nm respectively. The calibration curve of Amido Black 10B and Crysatal violet is also obtained.
- Optimum adsorption times were 6 hrs and 4 hrs, for Amido black 10B and Crystal violet dyes respectively.
- Optimum pH values were 3 and 2 for Amido black 10B and Crystal violet dyes respectively.
- Optimal stirrer speeds were found to be 275 rpm and 200 rpm using JLP for the removal of Amido black 10B dye and Crystal violet dye respectively.
- Removal efficiency decreases with increasing the initial dye concentration.
- Removal efficiency increases with increasing the adsorption time.
- Adsorption process is exothermic and is favored at low temperatures.
- Experimental data matches well with the pseudo-second-order kinetics.
- Experimental data matches well with the Freundlich isotherm than the Langmuir isotherm.

Most important observation in this work is that the Jackfruit leaf powder (JLP) has been synthesized from mature jackfruit leaves, i.e. JLP could act as a very effective adsorbent for the removal Amido black dye as well as Crystal violet dye. As it was suggested in literature, JLP shows partially cationic in nature (Das et al., 2012), and therefore, it can work against all kinds of anionic dyes.

However, there is a lot of scope for further research in this area. Some of the objectives that can be studied in future are as follows.

- Studying the performance of the JLP for the removal of other industrial dyes.
- Using the JLP for industrial wastewater treatment in continuous mode (Fixed bed or fluidized bed studies).
- Removal of heavy metals from water by adsorption with the JLP.

References

Anna, W., K., Roman, G., Szafran and Szymon, M., (2011), “Biosorption of heavy metals from aqueous solutions onto peanut shell as a low-cost biosorbent”, *Desalination*, 265, 126–134.

Ayrton, F., Martins, Andre, L., Cardoso, Joao, A., Stahl and Diniz, J., (2007), “Low temperature conversion of rice husks, eucalyptus sawdust and peach stones for the production of carbon-like adsorbent” , *Bioresource Technology*, 98, 1095–1100.

Ahmad, and Kumar, R., (2010), “Conducting Polyaniline/Iron Oxide Composite: A Novel Adsorbent for the Removal of Amido Black 10B,”. *J. Chem. Eng. Data*, 55, 3489–3493.

Al-Ghouti, M.A., Khraisheh, M.A., Allen, S.,J., Ahmad, and M.N., (2003), “The removal of dyes from textile wastewater: a study of the physical characteristics and adsorption mechanisms of diatomaceous earth”, *Journal of Environmental Management*, 69 (3), 229–238.

Atun G., Hisarh G., Kurtoglu, A.E., and Ayar N., (2011), “A comparison of basic dye adsorption onto zeolitic materials synthesized from fly ash”, *Journal of Hazardous materials*, 187,562-573.

Bhattacharyya, K.G., and Sharma, A., (2004), “*Azadirachta indica* leaf powder as an effective biosorbent for dyes: a case study with aqueous Congo Red solutions”, *Journal of Environmental Management*, 71,217–229.

Bhatnagar, A., and Minocha, A.K., (2006), “Conventional and non-conventional adsorbents for removal of pollutants from water- a review”; *Indian Journal of Chemical Technology*, 13,203-217.

Chakraborty, S., Purkait, M.K., Das, G., and Basu, J.K., (2003) “Nanofiltration of textile plant effluent for color removal and reduction in COD”,*Journal of Environmental Management*, 71,217–229.

Chang, H.L., and Shih, W.H., (1998), “A general method for the conversion of fly ash into zeolites as ion exchangers for Cesium”, *Ind. Eng. Chem.*, 37: 71-78.

Crini, G., (2006), “Non-conventional low-cost adsorbents for dye removal: A review”, *Bioresource Technology*, 97, 1061–1085.

- Chinniagounder, T., Mysamy, S., and Shivakumar, N., (2011), “ Adsorptive removal of Crystal violet dye using agricultural waste Cocoa shell” *Research Journal of Chemical sciences*, 7, 38-45.
- Chakraborty, S., Chowdhury, S., and Saha, P.D., (2011), “Adsorption of Crystal Violet from aqueous solution onto NaOH-modified rice husk”, *Carbohydrate Polymers*, 86, 1533–1541.
- Chowdhury, S., Mishra, R., Saha, P., and Kushwaha, P., (2011), “Adsorption thermodynamics, kinetics and isosteric heat of adsorption of malachite green onto chemically modified rice husk”, *Desalination*, 265,159–168.
- Deniz, F., and Saadet, D.S., (2010), “Equilibrium, kinetic and thermodynamic studies of Acid Orange 52 dye biosorption by Paulownia tomentosa Steud. leaf powder as a low-cost natural biosorbent”, *Bioresource Technology*, 101, 5137–5143.
- Das, P.S., Chakraborty, S., and Chowdhury, S., (2012), “Continuous (fixed-bed column) biosorption of crystal violet by *Artocarpus heterophyllus* (jackfruit) leaf powder”, *Colloids and Surfaces B: Biointerfaces*, 92, 262– 270.
- Davila-Jimenez, M.M., Elizalde-Gonzalez, M.P., and Pelaez-Cid, A.A., (2005) “Adsorption interaction between natural adsorbents and textile dyes in aqueous solution”, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 254, 107–114.
- Fernandez, M.E., Nunell, G.V., Bonelli, P.R., and Cukierman, A.L., (2012), “Batch and dynamic biosorption of basic dyes from binary solutions by alkaline-treated cypress cone chips”, *Bioresource Technology*, 106 ,55–62.
- Gupta, V.K., and Suhas, (2009), “Application of low-cost adsorbents for dye removal – A review”, *Journal of Environmental Management*, 90, 2313–2342.
- Jing, F.G., Zhang, Q., Su, K., and Wang, J.H., (2010), “Competitive biosorption of Yellow 2G and Reactive Brilliant Red K-2G onto inactive aerobic granules: Simultaneous determination of two dyes by first-order derivative spectrophotometry and isotherm studies”, *Bioresource Technology*, 101, 5793–5801.
- Jiyun, S., Weihua, Z., Yangyang, B., Fengyun, S., and Runping, H., (2011), “Adsorption characteristics of methylene blue by peanut husk in batch and column modes”, *Desalination*, 265, 119–125.

Liangui, W., (2012) “Application of activated carbon derived from ‘waste’ bamboo culms for the adsorption of azo disperse dye: Kinetic, equilibrium and thermodynamic studies”, *Journal of Environmental Management*, 102, 79-87.

Maria, P., Elizalde-Gonzalez, W., Geyer, Maria, R.G., Guevara-Villa, Mattusch, J., Alejandra, A., Pelaez-Cid, and Wennrich R., (2006), “Characterization of an adsorbent prepared from maize waste and adsorption of three classes of textile dyes”, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 278, 89–97.

Mohammad, A., Mohammad A., Yousuf, R., and Ahmad, A., (1998), “Adsorption behaviour of Cadmium, Zinc, Nickel and Lead from aqueous solutions by *Mangifera Indica* seed shell”, *Indian J. Environ. Hlth.*, 40 (1), 15–26.

Mittal, A., Malviya, A., Kaur, D., Mittal, J., and Kurup, L., (2007), “Studies on the adsorption kinetics and isotherms for the removal and recovery of Methyl Orange from wastewaters using waste materials”, *Journal of Hazardous Materials*, 148, (1-2), 229-240.

Niyaz, M., Mahmoodi, Bagher, H., Mokhtar A., and Christopher, L., (2011), “Adsorption of textile dyes on Pine Cone from colored wastewater: Kinetic, equilibrium and thermodynamic studies”, *Desalination*, 268, 117–125.

Patil, S., Deshmukh, V., Rnukdas, S., and Patel, N., (2011), “Kinetics of adsorption of Crysatal violet from aqueous solutions using different natural materials” *International journal of Environmental sciences*, 1-6, 86-85.

Qiu, M., Qian, C., Xu, J., Wu, J., Wang, G., (2009), “Studies on the adsorption of dyes into clinoptilolite”, *Desalination*, 243, 286–292.

Rahman I.A., Saad B., Shaidan, S., and Sya Rizal, E.S., (2005), “Adsorption characteristics of malachite green on activated carbon derived from rice husks produced by chemical–thermal process”, *Bioresource Technology*, 96, 1578–1583.

Stephen, J., Allen, Quan, G., Ronan, M., and Pauline, A., and Johnson, (2005), “Kinetic modeling of the adsorption of basic dyes by kudzu, UK”, *Journal of Colloid and Interface Science*, 286, 101–109.

Sibel, T., Akar, A., Safa, O., Tamer, A., Adnan, O., and Zerrin K., (2009), “Biosorption of a reactive textile dye from aqueous solutions utilizing an agro-waste”, *Desalination*, 249, 757–761.

Safa Y., and Bhatti, H. N., (2011), “Kinetic and thermodynamic modeling for the removal of Direct Red-31 and Direct Orange-26 dyes from aqueous solutions by rice husk”, *Desalination*, 272, 313–322.

Sayal, A., Bulasara, V.K., and Berman, S., (2012), “A study on synthesis of zeolite and removal of Amido Black dye by adsorption with zeolite”, *Chemical and Process Engineering Research*, 2, 54–56.

Senthilkumar, S., Perumalsamy, M., Prabhu, H.J., (2011), “Decolourization potential of whiterot fungus *Phanerochaete chrysosporium* on synthetic dye bath effluent containing Amido black 10B,” *Journal of Saudi Chemical Society*, In Press, doi:10.1016/j.jscs.2011.10.010.

Shouman M.A., Khedr, S.A., and Attia, A.A, (2012), “Basic dye adsorption on low cost biopolymer: kinetic and equilibrium studies”, *Journal of Applied chemistry*, 2 (4), 27–36.

Sharma, P., Kaur, R., Baskar C., and Wook, C., (2010), “Removal of methylene blue from aqueous waste using rice husk and rice husk ash”, *Desalination* ,259, 249–257.

Uma, R. L., Srivastava, V. C., Indra, D. M., and Dilip, H. L., (2009), “Rice husk ash as an effective adsorbent: Evaluation of adsorptive characteristics for Indigo Carmine dye”, *Journal of Environmental Management*, 90, 710-720.

Venkat, S., Mane, Indra, D. M., and Srivastava, V. C., (2007), “Kinetic and equilibrium isotherm studies for the adsorptive removal of Brilliant Green dye from aqueous solution by rice husk ash”, *Journal of Environmental Management*, 84 ,390–400.

Vinod, K. G., Mittal, A., Lisha, K., and Mittal, J., (2006), “Adsorption of a hazardous dye, erythrosine, over hen feathers”, *Journal of Colloid and Interface Science*, 304, 52–57.

Yasmin, K., Mody, K., and Basha, S., (2012), “Efficient removal of Brilliant Blue G (BBG) from aqueous solutions by marine *Aspergillus wentii*, Kinetics, equilibrium and process design”, *Ecological Engineering*, 41, 74– 83.

Zohra, B., Jeguirim, M., Belhachemi, M., Addoun, F., and Trouve, G. (2011), “Biosorption of basic dye from aqueous solutions by Date Stones and Palm-Trees Waste: Kinetic, equilibrium and thermodynamic studies”, *Desalination*, 271, 80–87.