Adsorption Characteristics of Castor Leaf Powder (CLP) for the Removal of Crystal Violet and Brilliant Green Dyes

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Submitted By

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CERTIFICATE

This is to certify that the thesis entitled, "**Adsorption Characteristics of Castor Leaf Powder (CLP) for the Removal of Crystal Violet and Brilliant Green Dyes**" submitted by **Mr. Akshay Mahajan** (Roll No. 601201022) in partial fulfilment of the requirements for the award of the degree of **Master of Technology** in **Environment Science & Technology** at **Thapar University**, **Patiala** is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in this thesis has not been submitted to any other university/ institute for award of any degree or diploma.

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I, the undersigned, hereby declare that the research work presented in the M.Tech project entitled "**Adsorption Characteristics of Castor Leaf Powder (CLP) for the Removal of Crystal Violet and Brilliant Green Dyes**" has been carried out by me under the supervision and guidance of, **Dr. Vijaya Kumar Bulasara,** Department of Chemical Engineering **Thapar University, Patiala**.

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ABSTRACT

Adsorption is a mass transfer process 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 problem is synthetic adsorbent is too costly and is not easily available. So our main focus is on use of natural adsorbent that are readily available and the adsorbent does not have any commercial value. In this work we have used CLP (Castor leaf powder) synthesized from mature Castor leaf, having high adsorption capacity for dye and it is relatively cheap. This work presents the experimental studies on the adsorptive removal of Brilliant green and Crystal violet dye using a natural adsorbent CLP. Preparation methodology for CLP involved grinding, drying (sun drying), boiling and drying in hot air oven at 105 °C. The synthesized CLP was then used to study the effect of various parameters namely pH, temperature, agitation speed, adsorption time, CLP loading initial dye concentration and ultra-sonication time on the dye removal efficiency. Then, the optimal process parameters for the dye–CLP system were determined. 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 CLP dosage, adsorption time and stirrer speed were found to be 10 g/L, 2 h and 200 rpm respectively for Crystal violet and 15g/L, 2h and 300 rpm respectively for Brilliant green. On the other hand, the dye removal efficiency decreased with increasing the initial dye concentration in the solution. The optimum pH observed 8 and 10 for Crystal violet and Brilliant green dyes removal respectively. During comparison analysis CLP 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.

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List of Symbols/Abbreviations

CLP	Castor leaf powder (Adsorbent)
Ci	Initial dye concentration in the solution, mg/L
Cf	Dye concentration in the solution after adsorption with CLP, mg/L
Cj	Castor leaf powder loading (adsorbent dosage), g/L
R	dye removal efficiency, %
qt	Amount of dye adsorbed per unit weight of Castor leaf powder(CLP), mg/g
$\Delta G°$	Change in Gibbs free energy, J
$\Delta H°$	Change in enthalpy, J
$\Delta S°$	Change in entropy, J K-1
R	Universal gas constant, J mol-1K-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

CHAPTER 1

INTRODUCTION

Since the end of the last century a large amount of products, such as medicines, disinfectants, contrast media, laundry detergents, surfactants, pesticides, dyes, paints, preservatives, food additives, and personal care products, have been released by chemical, textile and pharmaceutical industries threatening the environment and human health. Water pollution caused by dye molecules is one of the greatest problems faced by the present society. These dye molecules are due to their high toxicity and poor degradability is undesirable to the aquatic environment. Currently there is a growing awareness of the impact of these contaminants on groundwater, rivers, and lakes. Therefore the removal of emerging contaminants of concern is now as ever important in the production of safe drinking water and the environmentally responsible release of wastewater.

Several research studies showed that, treated wastewater, if appropriately managed, is viewed as a major component of the water resources supply to meet the needs of a growing economy. The greatest challenge in implementing this strategy is the adoption of low cost wastewater treatment technologies that will maximize the efficiency of utilizing limited water resources and ensuring compliance with all health and safety standards regarding reuse of treated wastewater effluents.

Treatment options which are typically considered for the removal of emerging contaminants from drinking water as well as wastewater include adsorption, Advanced Oxidation Processes (AOPs), Nanofiltration (NF), and Reverse Osmosis (RO) membranes. However, the shortcomings of most of these methods are high investment and maintenance costs, secondary pollution (generation of toxic sludge, etc.) and complicated procedure involved in the treatment. On the other hand physicochemical treatments such as coagulation/flocculation processes were generally found to be unable to remove Endocrine Disrupting Compounds (EDCs) and Pharmaceuticals and Personal Care Products (PPCPs). Although AOPs can be effective for the removal of emerging compounds, these processes can lead to the formation of oxidation intermediates that are mostly unknown at this point.

Conversely adsorption processes do not add undesirable by-products and have been found to be superior to other techniques for wastewater treatment in terms of simplicity of design and operation, and insensitivity of toxic substances.

1.1 Adsorption

Adsorption is a mass transfer process which involves the accumulation of substances at the interface of two phases, such as, liquid–liquid, gas–liquid, gas–solid, or liquid–solid interface. The substance being adsorbed is the adsorbate and the adsorbing material is termed the adsorbent. The properties of adsorbates and adsorbents are quite specific and depend upon their constituents. The constituents of adsorbents are mainly responsible for the removal of any particular pollutants from wastewater.

1.2 Benefits of adsorption process over other wastewater treatment processes

- Adsorption has advantages over the other methods because of simple design and can involve low investment in term of both initial cost and land required.
- Materials locally available such as natural materials, agricultural wastes and industrial wastes can be utilized as low-cost adsorbents.
- In recent years, the search for low-cost adsorbents that have pollutant –binding capacities has intensified.
- the shortcomings of most of these methods are high investment and maintenance costs, secondary pollution (generation of toxic sludge, etc.) and complicated procedure involved in the treatment. On the other hand physicochemical treatments such as coagulation/flocculation processes were generally found to be unable to remove Endocrine Disrupting Compounds (EDCs) and Pharmaceuticals and Personal Care Products (PPCPs).
- Conversely adsorption processes do not add undesirable by-products and have been found to be superior to other techniques for wastewater treatment in terms of simplicity of design and operation, and insensitivity of toxic substances.
- Recently natural materials that are available in large quantities from agricultural operations have been evaluated as low cost adsorbents and environmental friendly Moreover the utilization of these waste materials as such directly or after some minor treatment as adsorbents is becoming vital concern because they represent unused resources and cause serious disposal problems.

1.3 Factors affecting adsorption process

- The factors affecting the adsorption process are: (i) surface area, (ii) nature and initial concentration of adsorbate, (iii) solution pH, (iv) temperature, (v) interfering substances, and (vi) nature and dose of adsorbent

1.4 Types of adsorbents used

- The most important property that a good adsorbent, should possess is a porous structure resulting in high surface area. In addition, the time taken for adsorption equilibrium to be established should be as small as possible so that it can be used to remove contaminants in lesser time. Thus, for removal of pollutants, one looks to adsorbents with high surface area and porosity and showing fast adsorption kinetics. Some of the important adsorbents which are generally used in industry and for pollution control are discussed now.

- **Alumina and Bauxite**

Alumina is a synthetic porous crystalline gel, which is available in the form of granules of different sizes. It is found to have a surface area ranging from 200–300 $m^2g^{-1}$and is used in industries requiring the removal of water from gas streams, decolorization, and refining of petroleum oils and waxes. On the other hand, bauxite is a naturally occurring porous crystalline alumina contaminated with kaolinite and iron oxides in varying proportions, depending on the place of origin. It is widely used in place of alumina, and it has been experimentally demonstrated that it removes most aerobic and anaerobic bacteria. Its surface area ranges from 25 to 250 m^2g^{-1}.

- **Silica Gel**

It is prepared by the coagulation of colloidal silicic acid, which results in the formation of porous and noncrystalline granules of different sizes. It shows a higher surface area as compared to alumina, which ranges from 250 to 900 m^2g^{-1}. The gel is considered a good adsorbent and is used in many industries for drying of gases and liquids, purifying of hydrocarbons, etc.

- **Zeolites**

Zeolites are important microporous adsorbents that occur naturally and are also prepared synthetically. They are also considered to be selective adsorbents and show ion exchange property as well as molecular adsorption. Zeolites are crystalline tectosilicates capable of undergoing reversible base-exchange reactions. Earlier zeolites were formed by fusing weighed amounts of feldspar, clay, and soda ash. Later on, synthetic zeolites obtained from mixtures of caustic soda, sodium silicate, and bauxite was also developed. Natural zeolites generally show low surface area; however, the apparent surface area of some synthetic zeolites can be as high as 700 m^2g^{-1}. The textural characterization of zeolites is usually carried out by measuring surface area, pore volume, and pore size distribution by low temperature N_2 adsorption and applying various techniques such as X-ray and neutron diffraction, IR, Raman, NMR, and scanning electron microscopy. A number of zeolites have been used for the removal of pollutants as well.

- **Activated Carbon**

Activated carbon is the oldest adsorbent known and is usually prepared from source material, such as coal, coconut shells, lignite, and wood, using one of two basic activation methods:

- 1) **Physical activation**. This is a process in which the precursor is developed into activated carbons using gases. The precursor is usually subjected to carbonization followed by activation or using either. Carbonization is the first stage where the precursor is pyrolyzed in the temperature range 600–900°C, in an inert atmosphere (nitrogen, argon) resulting in the formation of char, which is normally non-porous. The activation is the process in which the material is exposed to oxidizing atmospheres (carbon dioxide, oxygen, or steam) usually in the temperature range 600–1200°C, which results in the removal of the more disorganized carbon and the formation of a well-developed porous structure, leading to high surface area.
- 2) **Chemical activation**. This is the other method used for the preparation of activated carbons and involves impregnation with chemicals such as H_3PO_4, KOH, or NaOH, followed by heating under a gas (usually nitrogen) flow in the temperature range 450 to 900°C. It is believed that carbonization and activation steps proceed simultaneously in chem- ical activation. Generally, chemical activation is preferred over physical activation owing to the lower temperature and shorter time needed for activating the material.

- The product formed by either of the methods is known as activated carbon and generally has a very porous structure with a large surface area ranging from 500 to 2000 m^2g^{-1}.
- Activated carbon for water treatment is available in two main forms: powdered activated carbon (PAC) and granular activated carbon (GAC). Most of the work on the removal of pollutants from water has been on GAC, due to the fact that the granular form is more adaptable to continuous contacting, and there is no need to separate the carbon from the bulk fluid. On the other hand, the use of PAC presents some practical problems because of the requirement to separate the adsorbent from the fluid after use. However, in spite of these problems, PAC is also used for wastewater treatment due to low capital cost and lesser contact time requirement. Activated carbon is used for wastewater treatment because of its ability to adsorb different types of pollutants such as metal ions, phenols, dyes, pesticide, chlorinated hydrocarbons, humic substances, PCBs, detergents, organic compounds that cause taste and odor, and many other chemicals and organisms., Activated carbons are not low-cost materials; hence, in spite of their good efficiency and applicability for adsorbing a wide variety of materials, their use can sometimes be restricted due to economic considerations.
- **Clay**: It is widely known that there are three basic species of clay: smectites (such as montmorillonite), kaolinite, and micas; out of which montmorillonite has the highest cation exchange capacity and its current market price is considered to be 20 times cheaper than that of activated carbon. Although the removal efficiency of clays for heavy metals may not be as good as that of zeolites, their easy availability and low cost may compensate for the associated drawbacks.

- **Peat Moss**: Peat moss, a complex soil material containing lignin and cellulose as major constituents, is a natural substance widely available and abundant, not only in Europe (British and Ireland), but also in the US. Peat moss has a large surface area (>200m^2/g) and is highly porous so that it can be used to bind heavy metals.

- **Chitosan**: Among various biosorbents, chitin is the second most abundant natural biopolymers after cellulose. However, more important than chitin is chitosan, which has a molecular structure similar to cellulose. Presently, chitosan is attracting an

increasing amount of research interest, as it is an effective scavenger for heavy metals. Chitosan is produced by alkaline N-deacetylation of chitin, which is widely found in the exoskeleton of shellfish and crustaceans. It was estimated that chitosan could be produced from fish and crustaceans.

CHAPTER 2

LITERATURE REVIEW

2.1 REMOVAL OF DYES BY NATURAL ADSORBENT

Ouasif et al. [1] had studied the effect of adsorption for removal of a cationic dye from wastewater by natural adsorbent. They removed methylene blue from waste water by adsorption on clays and oil shale's. They decarbonated these natural materials with hydrochloric acid and characterized by X-ray diffraction, X-ray fluorescence and infrared spectroscopy. They had taken various factors such as quantity and granulometry of adsorbents, initial MB concentration and temperature. Factors affecting adsorption were evaluated. They found amount of dye removed increased with increasing weight, initial dye concentration and temperature and decreased with increase in granulometry. They found that clays composite adsorbent was effective adsorbent for MB and the decarbonated clays adsorbent exhibited excellent adsorption selectivity for MB. They showed kinetic parameters calculated from the experimental data well fitted to a pseudo-second described by the Langmuir model. They finally conclude that clays absorb more methylene blue than oil shale's.

Salleh et al. [2] used agricultural solid wastes as an adsorbent for the removal of anionic and cationic dyes. They reviewed the use of agricultural solid wastes to remove two classes of dye, cationic and anionic dyes and made a simple comparison among cationic and anionic dye adsorption by the same adsorbent, which possibly opening the door for a better understanding of the dye-classified adsorption process. Both classes of dyes are toxic and cause severe problems to aquatic environment. They found some agricultural solid wastes can remove both dye classes, although they need activation. They observed dye adsorption capacities of agricultural waste adsorbents vary, depending on the pH of solution, initial dye concentration, adsorbent dosage and process temperature. The pH of solution was directly related to the dye-classified adsorption, where it affects the surface charge of the adsorbent and the degree of ionization of the adsorbate.

Bhattacharyya et al. [3] had done work on Azadirachta indica leaf powder, used as an effective biosorbent for removal of Congo red dye from aqueous solutions. They made sorbent 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. They observed an amount of 0.6 g of the Neem leaf powder (NLP)/l could remove 52.0–99.0% of the dye from an aqueous solution of concentration 2.87×10^{-2}mmol l^{-1} with the agitation time increasing from 60 to 300 min. They found pseudo-second-order reaction kinetics be more suitable. They observed Langmuir monolayer capacity (q_m) was high and well fitted for the adsorption kinetics. Thermodynamically, the sorption process was exothermic. The spontaneity of the sorption process was also confirmed by the favorable values of Gibbs energy (mean values: -1.09 to -1.81 kJ mol^{-1}) and entropy of adsorption (range: -18.97 to -56.32 J $mol^{-1}K^{-1}$). They showed a small amount (1 g/l) of the adsorbent could decolorize as much as 95% of the dye from an aqueous solution (40 mg/1) if agitated for 5 h. The adsorption of the dye was maximum around the natural pH of the aqueous solution of Congo Red. This shows that adsorption of the dye could be carried out on Neem leaf powder without adjusting the pH of the medium. The results showed the effectiveness of the Neem leaf powder as a biosorbent for removing dyes like Congo red from water.

Singh et al. [4] had studied the Electroplating Industry Wastewater which had heavy metal causes various environmental problem. For the removal of heavy metals from effluent waste streams, they used adsorption process with various commercial adsorbent was being widely used. They showed such adsorbent remains an expensive material, so the use of alternative and perhaps cheaper adsorbents is attractive. This review described a brief description of adsorption process and then the comparative analysis of conventional and non-conventional adsorbents for the removal of emerging compounds. They had given the details of different adsorbents such as Natural adsorbent: Zeolites, clay, peat moss, chitosan and commercial adsorbents such as: Silica gel, activated carbon, activated alumina, activated charcoal, polymeric adsorbents and low cost adsorbents. They also studied the characteristics of different adsorbents and compared them on the basis of different factors.

Crini et al. [5] studied low-cost non conventional adsorbents for dye removal. They studied the adsorption techniques that 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. As the commercial activated carbon is a preferred sorbent for color removal but due to high cost its use is restricted. So, alternative non-conventional sorbents have been investigated. They had given an extensive list of sorbent literature which had been compiled into following sections (i) presented a critical analysis of these materials; (ii) described their characteristics, advantages and limitations; and (iii) discussed various mechanisms involved. It was evident from a literature survey of about 210 recent papers that low-cost sorbents had demonstrated outstanding removal capabilities for certain dyes. Although much had been accomplished in the area of low-cost sorbents, but still need (i) to predict the performance of the adsorption processes for dye removal from real industrial effluents under a range of operating conditions, (ii) to better understand adsorption mechanisms and (iii) to demonstrate the use of inexpensive adsorbents at an industrial scale.

Grassi et al. [6] had studied briefly adsorption mechanism. They had also studied conventional and non-conventional adsorbents for the removal of emerging compounds was reviewed with the comparison between them. They studied conventional wastewater treatment plants (WWTPs) are not always effective for the removal of huge classes of pollutants and so further water treatments are necessary. They had main focus on the adsorption process in the removal of emerging compounds. They had given the brief description of commercial adsorbent such as activated carbon, Clays, Minerals; low cost adsorbents such as agriculture waste, industrial waste and showed that adsorption act as green technology for removal of contaminants from waste water.

Ponnusami et al. [7] had studied Guava (Psidium guajava) leaf powder for removal of methylene blue from aqueous solutions by performed batch experiments. They had considered effect of various parameters such as pH, adsorbent dosage; concentration, particle size and temperature. Temperature–concentration interaction effect on dye uptake was studied and a quadratic model was proposed to predict dye uptake in terms of concentration, time and temperature. This model was used to find optimum temperature and concentration that result in maximum dye uptake. Langmuir model used to represent the experimental data well. Maximum dye uptake was found to be 295mg/g, indicating that GLP can be used as an excellent low-cost adsorbent. They used pseudo-first-order, pseudo-second order and intraparticle diffusion models for tested. From experimental data they found that adsorption of MB onto GLP follow pseudo second order kinetics. External diffusion and intra particle diffusion play roles in adsorption process. Free

energy of adsorption ($\triangle G^{\circ}$), enthalpy change ($\triangle H^{\circ}$) and entropy change ($\triangle S^{\circ}$) were calculated to predict the nature of adsorption. Adsorption in packed bed was also evaluated by them.

Arami et al. [8] had used orange peel adsorbent for the removal of dyes from colored textile wastewater. They had collected orange peel from the fields of orange trees and converted it into a low cost adsorbent. They used Direct Red 23 (DR23) and Direct Red 80 (DR80) as model compounds. They observed adsorption capacity Q_0 was 10.72 and 21.05 mg/g at initial pH 2. They also studied the effects of initial dye concentration (50, 75, 100, 125 mg/l), pH, mixing rate, contact time, and quantity of orange peel at 25°C. They used Langmuir and Freundlich models and found that Langmuir equation fitted better than the Freundlich equation. They showed that acidic condition supported the adsorption process. They found both dyes followed the pseudo-second-order kinetics with a good correlation ($R \geq 0.998$). They found maximum adsorption at pH 2 i.e. 97.7% for DR23 and 93% for DR80 were achieved in aqueous solution. Finally, they analyzed the effect of adsorbent surface by scanning electron microscope (SEM).

2.2 REMOVAL OF CRYSTAL VIOLET BY NATURAL ADSORBENT

Pavan et al. [9] had done work on the removal of crystal violet from aqueous phase by using Formosa papaya seed powder as an alternative adsorbent which is a solid byproduct from industrial and agricultural activities. They characterized FSPS by various techniques such as specific surface area (BET), scanning electron microscopy (SEM), infrared spectroscopy (FT-IR), thermal analysis (TGA) and Boehm titration techniques. They had studied various parameters such as pH, adsorbent dosage, contact time, initial dye concentration and their effect on CV adsorption. Kinetic data were evaluated by pseudo-first order, pseudo-second order and Elovich models. They analyzed equilibrium isotherm by Langmuir, Freundlich and Redlich–Peterson isotherms. Desorption studies were also performed. The adsorption of CV onto FPSP was well fitted using Langmuir isotherm. The maximum adsorption capacity obtained by the Langmuir model was 85.99 mg g^{-1}. Regeneration of FPSP adsorbent was obtained satisfactory using 1.00 mol L^{-1} CH_3COOH

as eluent. Results demonstrated that FPSP is a promising adsorbent to remove CV from aqueous solutions.

Aljeboree et al. [10] had studied the Adsorption isotherm, kinetic modeling and thermodynamics of crystal violet dye on coconut husk-based activated carbon. They showed that the H_2SO_4-modified coconut husk derived activated carbon powder (CHACP) can be used as a potential adsorbent for the removal of crystal violet (CV, basic dye) from aqueous solutions. They carried out experiment as a function of contact time, concentration, pH, mass dosage, and temperature, the equilibrium was attained in 60 min. The amount of dye uptake (mg/g) was found to increase with increase in dye concentration, pH, temperature, and contact time. The kinetics of CV on to the adsorbent can be described well by pseudo-second order > Elovich > pseudo-first order > intra-particle diffusion equation. The applicability of the isotherm's model for the present data follows the order: Freundlich > Temkin > Langmuir. Based on the calculated thermodynamic parameters, it was noticeable that the sorption of CV dye onto CHACP was a spontaneous and endothermic process. The morphological and chemical characteristics of the adsorbent were established by scanning electron microscopy and Fourier transform infrared spectroscopy.

Satish et al. [11] had studied adsorption of crystal violet from aqueous solutions using different natural materials. Adsorption was out carried out by batch experiments. The parameter studied includes initial dye concentration, adsorbent dose, pH, contact time, agitation speed, particle size of adsorbent and temperature. 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. They found monolayer (maximum) adsorption capacities (q_m) between 142.857 to 250 mg/g for natural adsorbents under study. They found pseudo second order model best fits the kinetics of adsorption. The correlation coefficient R^2 for second order adsorption model was very high values of R^2 for all absorbents ($R^2 \approx 0.998$) and qe(the) values are in good agreement with qe(exp) showed that adsorption of CV on these natural materials followed second order kinetics and chemosorption playing role 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. Mangrove plant leaf powder was found have excellent adsorption capacity towards CV than other natural materials under study.

Zhang et al. [12] used clay/PNIPAm nanocomposite hydrogels with various clay contents for removal of crystal violet. The clay/poly(N-isopropylacrylamide) (PNIPAm) nanocomposite (CPN) hydrogels, using lithium magnesium silicate hydrate (LMSH) as a clay mineral physical cross-linker, with the mass ratio of NIPAm/LMSH ranging from 5 to 30 wt.% were prepared to remove crystal violet (CV) from aqueous solution. Morphology and temperature-sensitivity of hydrogels were investigated by SEM and DSC. They had studied adsorption capacity and kinetic under different times, pH values and concentrations were evaluated by using UV/vis spectroscopy. The pore sizes of CPN hydrogels range from 30 to 50 μm, and volume phase transition temperature (VPTT) were 33–36 °C. The adsorption capacity (Qt) of CV onto CPN hydrogels at 25°C increased quickly at initial 12 h, with a maximum value of 6.2.31 mg/g. At 37°C, the Qt values are not more than 2 mg/g. The Qt values of CPN hydrogels increase 2–4 times when CV concentration was added from10 to 30 mg/L, and increase 1–1.5 times as pH value increases from 3.0 to 8.9.

Schoonen et al. [13] studied the effect of aqueous solutions using coal for the removal of crystal violet. They carried out the test to check the hypothesis that pyrite-containing coal removes CV through a combination of sorption and a Fenton-like degradation reaction involving pyrite. While pure pyrite does degrade CV slowly through a Fenton- like mechanism, bituminous coals containing pyrite showed far less CV removal than subbituminous coals without pyrite. Hence, the presence of pyrite in coal does not lead to an enhanced removal of CV from solution. Instead, the surface charge of coal appears to exert a primary role on the uptake of CV. They studied that subbituminous coals had a negative surface charge between pH 3 and 8, which facilitates the uptake of the cationic dye. Sorption of cationic CV onto subbituminous coal leads to a charge reversal. Modeling of the sorption kinetics suggest that CV diffuses into pore space within the coal after sorbing onto the surface, which is consistent with the fact that CV is not released after uptake by the coal. The results of this study indicate that subbituminous coal might be a useful sorbent for CV contained in waste streams generated in dye processes. Coal is a cheap bulk commodity, CV does not desorb easily, and the resulting CV-containing coal could be burned to incinerate the contaminant while producing energy.

Jayaram et al. [14] used wood apple shell (WAS) for the removal of basic dyes, methylene blue (MB) and crystal violet (CV) by using a batch adsorption experiment. They considered various parameters such as solution pH, dye concentration and temperature. Removal of dyes was observed to be most effective at higher pH. They used Freundlich and Langmuir isotherm models for equilibrium data and found that Langmuir model fitted better than Freundlich model. They observed that the WAS adsorbent showed higher adsorption capacity for crystal violet (130 mg/g) than methylene blue (95.2 mg/g). FTIR studies showed that the interaction of dye and WAS surface is via the nitrogen atoms of the adsorbate and oxygen groups of the adsorbent. The adsorption of dyes onto WAS according to a pseudo-second-order model. They showed that WAS, a lignocellulosic inexpensive material, can be an alternative inexpensive adsorbents used for dye removal in wastewater treatment.

Kumar et al. [15] studied crystal violet dye removal from aqueous solution onto treated ginger waste (TGW). They studied various parameters such as the effect of initial dye concentration, contact time, solution pH and temperature. They also studied kinetic data using pseudo-first order, pseudo-second order and intra-particle diffusion models at different concentrations. The equilibrium data fitted better with the Freundlich isotherm equation compared to the Langmuir model. Dynamic biosorption of Crystal violet is well fitted for the pseudo-second order. They also evaluated thermodynamic parameters which showed that positive value of ΔH^0 indicated endothermic nature of biosorption. The maximum breakthrough capacity for the crystal violet dye was found to be 72.6 mg for 0.3g TGW.

El-Sayed [16] studied the palm kernel fiber for the removal of crystal violet and methylene blue dyes from aqueous solutions. They considered various factors which affect the removal of dyes such as initial dye concentration, contact time, pH, adsorbent dosages, stirring rate, ionic strength and temperature of the initial dye solution. They studied Freundlich, Langmuir and Temkin adsorption isotherms for the equilibrium data and found that Freundlich model fitted well into it. They also found that dye adsorption was endothermic for two dyes. They verified adsorption kinetic by pseudo-first-order and pseudo second-order models and found that pseudo-second order fitted well into it.

Mittal et al. [17] used the waste materials such as bottom ash and de-oiled soya (DOS) for the removal of Crystal violet dye through batch and column experiments. During batch studies they considered various parameters such as pH, amount of adsorbent, dye concentration, temperature, and contact time for the removal of dyes. They used different models such as Langmuir, Freundlich, Tempkin, and Dubinin–Radushkevich (D–R) isotherms for the equilibrium data. Thermodynamic parameters revealed that adsorption process is endothermic in nature. Pseudo-first and second-order kinetic models also applied and found that pseudo second-order kinetic model is well fitted on the removal of crystal violet dye by the adsorbent. For bulk removal of dyes, they made column operations. They Recovered dyes by eluting HCL solutions and 95% and 98% of the dye was recovered from BA and DOS columns, respectively.

Chakraborty et al. [18] had studied the adsorption capacity of NaOH-modified rice husk to remove crystal violet and also studied its equilibrium, kinetics and thermodynamics nature. They carried out experiments by using various functions such as contact time, initial solution pH (2-10), adsorbent dose (0.5-5g) and temperature (293,303 and 313K). They found maximum occurred at higher pHs and lower temperatures. They described adsorption data by using Langmuir and Freundlich model and found Freundlich model is more fitted. Pseudo-second order kinetic model is fitted well on the data. Thermodynamic parameters showed that adsorption is a typical spontaneous, chemical and exothermic in nature.

2.3 REMOVAL OF BRILLIANT GREEN BY NATURAL ADSORBENT

Mane et al. [19] had studied the adsorption of brilliant green onto low-cost NaOH treated saw dust from aqueous solution. They had done batch studies and considered various parameters like initial pH, contact time, adsorbent dose, initial concentration and temperature for the removal of brilliant green dye. They found most suitable conditions to be to be initial pH=2.9, contact time=3 h and adsorbent dose=4 g/l. pseudo-second order kinetic model well fitted for the brilliant green adsorption. They studied different models such as Freundlich, Langmuir, Redlich–Peterson and Temkin isotherm models for equilibrium isotherms. Adsorption was favorably influenced by decrease in the temperature of the operation. Adsorbent showed surface area=0.3742 m^2/g, pore

volume=0.00836 cm^3/g and average pore diameter=893.6 A^0. Thermodynamics showed that the Brilliant Green adsorption was most favorable onto NaOH treated saw dust.

Tavlieva et al. [20] had done work on the kinetic study of brilliant green adsorption onto white rice husk ash from aqueous solutions. They performed experiment in the temperature interval 290-320 K in steps and concentration range was 3-100 mg/l. The effect of the initial concentration was studied (pH not adjusted), as well as the effect of temperature on brilliant green. Maximum adsorption capacity of the white rice husk ash for the brilliant green was determined 85.56 mg g^{-1}. They used various kinetic models for adsorption kinetic data such as pseudo-first-order equation, pseudo-second-order equation, Elovichequation, Banghman's equation, Diffusion-chemisorption model, and Boyd kinetic expression. It was found that pseudo-second-order kinetic model fitted well for the adsorption. They used Arrhenius and Eyring equations for determined the activation parameters such as the activation energy (50.04 kJ mol^{-1}), the change of entropy (-18.31 J mol^{-1} K^{-1}), enthalpy(-47.50 kJ mol^{-1}), and Gibbs free energy (range 46.2.41–56.16 kJ mol^{-1}) for activated complex.

Mane et al. [21] studied the rice husk ash used as an adsorbent for the removal of brilliant green. Batch studied was done by them to evaluate the influence of various parameters such as 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 gL^{-1} of solution and equilibrium time= 5 h for the C_0 range of 50–300 mgL^{-1}. Adsorption of BG found followed the pseudo-second-order kinetics. Equilibrium isotherms for the adsorption of BG on RHA were analyzed by Freundlich, Langmuir, Redlich–Peterson (R–P), Dubnin–Radushkevich (D–R), and Temkin isotherm models using a non-linear regression technique. Langmuir isotherms were found best fitted to the data for BG adsorption onto RHA. Temperature also greatly affected the adsorption of brilliant green dye on the RHA. They also studied various thermodynamic parameters which influence the adsorption of brilliant green dyes on RHA.

Mane et al. [22] had studied the adsorption of brilliant green on carbon rich bagasse fly ash. They collected it from the bagasse-fired boilers of cane sugar mills. They performed batch studies by considering various parameters such as initial pH (pH_0), contact time,

adsorbent dose and initial concentration (C_0) on the removal of BG. They found optimum conditions for BG removal were found to be pH_0=3.0, adsorbent dose=3 g/l of solution and equilibrium time=5 h. they found adsorption followed pseudo-second-order kinetics. They analyzed Equilibrium isotherms by Freundlich, Langmuir, Redlich-Peterson, Dubnin-Radushkevich, and Temkin isotherm models using non-linear regression technique and found that Redlich-Peterson and Langmuir isotherms fitted best represent the data for BG adsorption onto BFA. They found change in entropy, heat of adsorption and Gibb's free energy also affect the BG adsorption on BFA.

Esan et al. [23] studied the equilibrium, kinetics and thermodynamics of adsorption of brilliant green onto Luffa Cylindrical Sponge via batch mode. They found optimum removal of BGD at pH 8.2 and the equilibrium was attained within 3 hours. They analyzed kinetic data using various models including pseudo-first-order, pseudo-second-order, power function, simple elovich, intraparticle diffusion, and liquid film diffusion. They fitted different kinetics models to the experimental data, tested by error analysis, using the linear correlation coefficient (r^2) and chi-square analysis (χ^2), showed that the mechanism of adsorption process was better described by pseudo-second-order and power function kinetic models. They analyzed equilibrium isotherm data by using Langmuir, Freundlich, and Temkin models and the sorption process was described by the Langmuir isotherm with maximum monolayer adsorption capacity of 18.2mg/g at 303K. They found thermodynamic properties ΔG_0, ΔH_0, and ΔS_0 of adsorption was spontaneous, endothermic, and feasible within the temperature range of 303–313 K.

Calvete et al. [24] used homemade activated carbons prepared from the Brazilian pine-fruit shell (Araucaria angustifolia) by chemically activated carbon (CAC) and chemically and physically activated carbon (CPAC), for the removal of brilliant green dyes from the aqueous solutions. They studied various parameters such as shaking time, adsorbent dosage and pH on the adsorption capacity. They found fractionary-order kinetic model provided the best fit to experimental data compared with other models. CAC and CPAC as adsorbents equilibrium data fitted better onto the Sips and Redlich-Peterson isotherm. They found enthalpy and entropy of adsorption of BG were obtained from adsorption experiments ranging from 298 to 323 K.

Ghaedi et al. [25] had studied the acorn based adsorbent for the removal of brilliant green. They characterized the prepared adsorbent by BET surface area measurement, FTIR, SEM and elemental analysis. They considered various parameters such as initial dye concentration, adsorbent dose, initial pH and temperature to observe their effects on the dye adsorption process. They found more than 90% removal efficiency obtained within 30 min at adsorbent dose of 2 g/100 mL for initial dye concentration of 25 mg/L. they found adsorption of dye followed pseudo-second-order rate equation. Langmuir model fitted well for the adsorption system with an adsorption capacity of 2.11mg/g of adsorbent. They found that this adsorbent act as an alternative adsorbent for the better performance of the brilliant green dye removal from its aqueous medium.

Mittal et al. [26] used Deoiled soya, an agriculture waste material and bottom ash, a waste of power plants, for the removal and recovery of the hazardous water-soluble dye brilliant green from water by batch operation. They followed the various factors such as effects of pH, concentration, amounts of adsorbents, size of adsorbent particles, etc. They monitored the adsorption process through Langmuir, Freundlich, Tempkin, and D-R adsorption isotherm models. They found adsorption process is endothermic and feasible at all temperatures. The kinetics of the adsorption was also recorded and indicates pseudo-second-order kinetics in both cases. They removed Bulk amount of dye through column studies for both adsorbents. They also made attempts to recover the dye from exhausted columns by eluting sulfuric acid of pH 3.

2.4 Summary of literatures

Activated carbon is widely studied in literature however, it is expensive. Natural adsorbents such as Formosa papaya seed powder, Mangrove plant leaf powder, and Teak tree bark powder, Wood apple shell, palm kernel fiber, NaOH-modified rice husk, low cost NaOH treated saw dust, white rice husk ash, bagasse fly ash, agricultural solid wastes etc are less expensive compared with Activated carbon, Zeolites, Nan particles. Among the many available natural adsorbents are widely used for the removal of different dyes. Formosa papaya seed powder, coconut husk based activated carbon, Clay/PNIPAm nanocomposite hydrogels, coal, Wood apple shell, treated ginger waste, palm kernel fiber, NaOH-modified rice husk, waste materials etc are used for the removal of crystal violet. Similarly Brilliant

green dye was removed by the use of low-cost NaOH treated saw dust, white rice husk ash, bagasse fly ash etc natural adsorbent. CLP is rarely studied in literature and is applied for removal of heavy metals. Castor is easily available and it is widespread throughout tropical regions. Due to its abundant availability and low cost castor leaf powder is chosen as the adsorbent.

2.5 Gap Analysis in Literature

- More research is required to remove the textile dyes from the textile industry effluent using adsorption. Adsorbent should be studied in detail to understand the effect and removal efficiency of textile dyes from the effluent.
- The effect of different parameters such as pH, time, temperature, concentration of adsorbent, concentration of dyes, stirring speed etc need to be studied more to improve the efficiency of adsorption processes.
- The selection of inexpensive natural adsorbent for different types of textile dyes was not studied in detail.
- In addition to natural adsorbent, other low cost adsorbent such as Castor leaf powder is not studied in detail for the removal of textile dye from the waste water.

2.6 OBJECTIVES

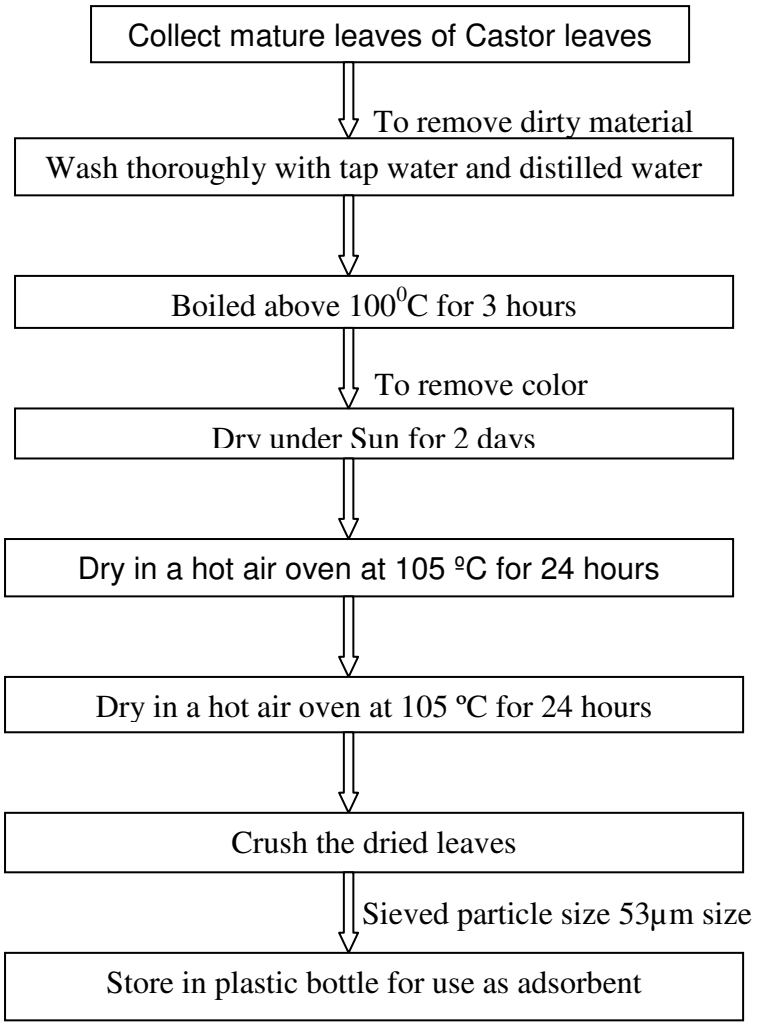
- To study the adsorption characteristics of Castor leaf powder for the removal of Crystal violet and Brilliant green dyes from their aqueous solutions.
- To characterize the adsorbent (CLP) by SEM, EDX, XRD, PSD.
- To study the effect of different parameters (Ph, time, CLP concentration, dye concentration, RPM, Temperature, ultrasound etc) on the % dye removal and adsorption capacity.
- To study the equilibrium and kinetics of adsorption.

CHAPTER 3

EXPERIMENTAL METHODOLOGY

3.1 Preparation of CLP

Castor leaves were collected near from Thapar University 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 after washed with distilled water boiled it at more than 100^0C for 3 hours and after boiling dried it with soaked paper and then castor sun drying for 2 days. After drying under sun the leaves are again dried in a hot air oven at 105ºC overnight. The dried leaves were crushed and the crushed powder was boiled to remove coloring components. After filtration, the powder was dried at 105ºC for 24 hrs and sieved to particle size of about 53 µmm and stored in plastic bottle for use as adsorbent. This process is presented in the form of a flow chart as shown in figure



After preparation of castor leaf powder, it is characterized by using different characterization methods such as SEM (Scanning Electron Microscope), XRD (X-ray Diffraction), PSD (Particle Size Distribution) etc.

3.2 Preparation of dye solution

Crystal violet and Brilliant green dyes are purchased from loba chemicals, Mumbai, India. These are of analytical grade (80% purity) and used without further purification. Stock solution of Crystal violet and Brilliant green dyes was prepared and is diluted to desired concentration for adsorption experiment by using $N_1V_1=N_2V_2$ relationship. λ_{max} and calibration curves are prepared using UV-Vis spectrophotometer.

3.3 Adsorption Experiment

Procedure for the removal of dyes crystal violet and brilliant green using castor leaf powder (CLP) in adsorption experiment consist of the following steps.

- A 500 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 Solutions of (0.1N) HCl/NaOH.
- Then solution is transferred into volumetric flask and 1g of castor leaf powder is then added into it and is mixed well and placed in a shaking incubator at 120 rpm for 2 hrs.
- After the adsorption period, the spent castor leaf powder is separated from the solution using a ordinary filter paper
- The collected sample after adsorption is then analyzed by UV-Visible spectrophotometer and the absorbance value is noted down which will give the dye concentration in the solution by compare with the calibration curve.
- The dye removal efficiency and the adsorption capacity of the castor leaf powder are then calculated by given formula:

$$q = \frac{C_i - C_f}{Cclp} \quad \text{(in mg/g)} \qquad (3.1)$$

$$\%R = \frac{C_i - C_f}{Ci} \times 100 \quad (\%) \qquad (3.2)$$

CHAPTER 4

Characterization of Castor Leaf Powder and dye solutions

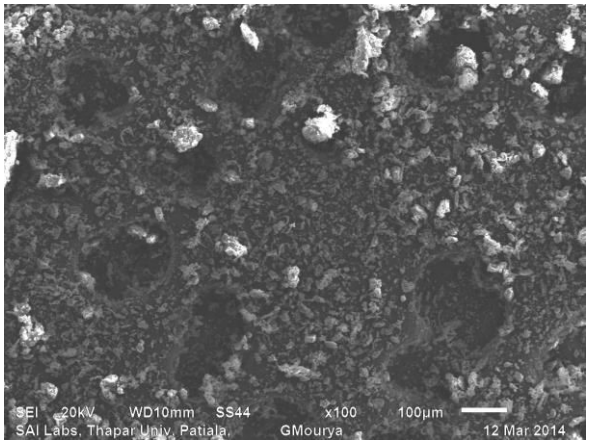
4.1 Castor leaf powder (CLP) characterization

CLP was prepared from mature castor leaves using proper washing, grinding and drying. After grinding the CLP was boiled to remove coloring component. Then it was meshed through the sieve having particle sizing capacity of 53µm. After sieving, Castor leaf powder is further analyzed by using following techniques.

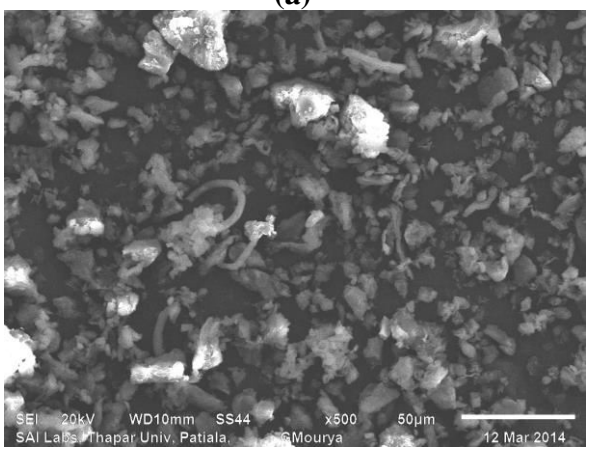
4.1.1 Morphological analysis by scanning electron Microscope (SEM)

The morphological structure of the CLP (Castor 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, and then percentages of oxides were calculated. The results are shown in Table 4.1.

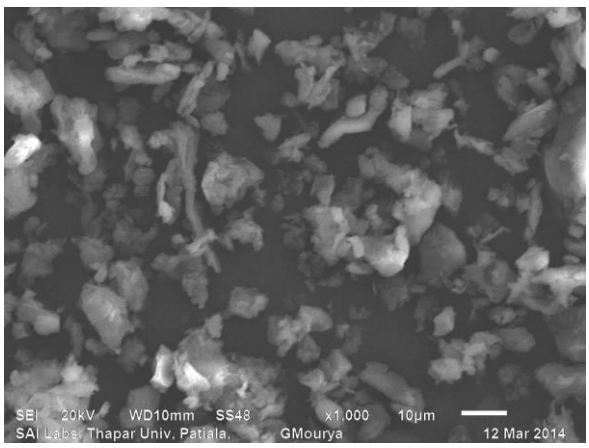
Figure 4.1 SEM images of CLP adsorbent at different magnifications.



(a)



(b)



(c)

Table 4.1: EDXS analysis for CLP adsorbent.

Element	C K	Mg K	Si K	S K	K K	Ca K	Cu K	Zn K	Zr L	Pt M
Weight (%)	75.08	0.52	0.45	1.54	6.21	6.21	3.89	3.70	2.60	1.71
Atomic (%)	92.52	0.32	0.24	0.71	1.67	2.25	0.91	0.84	0.42	0.13

4.1.2 Morphological analysis by X-RAY Diffraction (XRD)

X-ray diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The Castor leaf powder is analyzed by XRD to determine the orientation of a single crystal or grain and also the crystal structure. The given figure describes the crystal structure of castor leaf powder 4.2

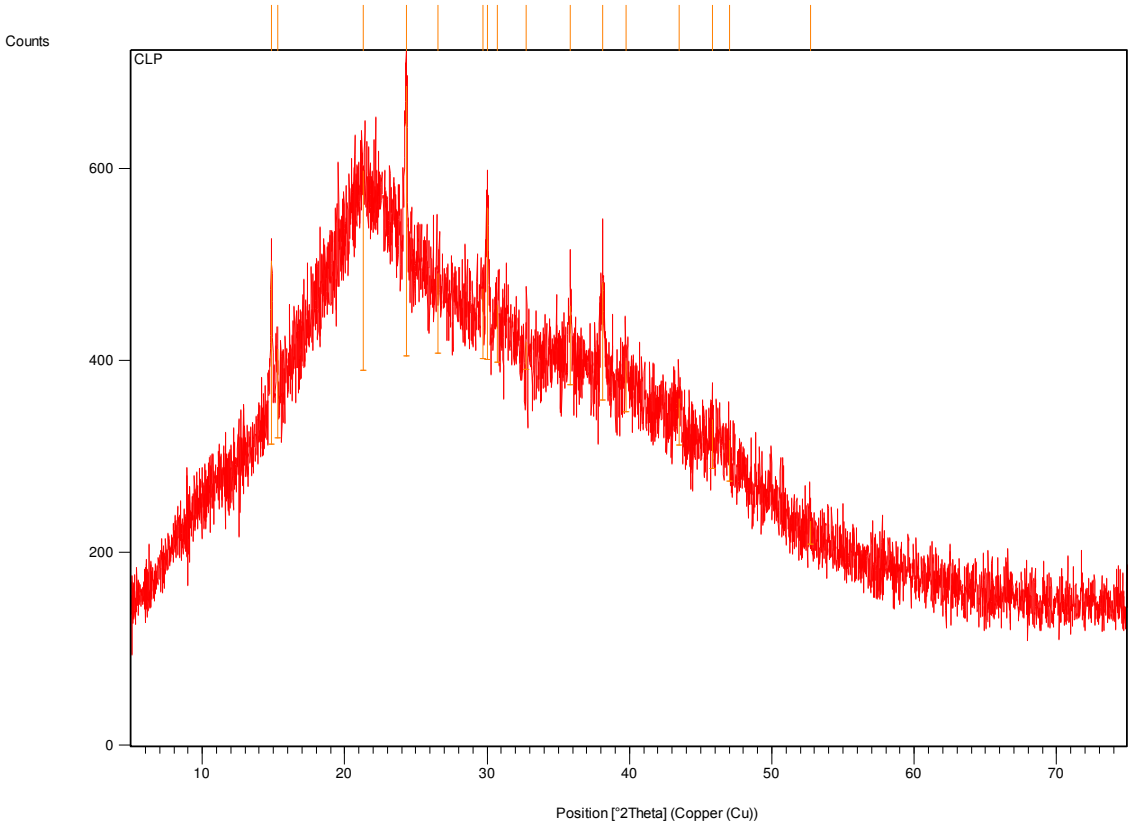


Figure 4.2: XRD of CLP adsorbent

Peak List:

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
16.2.4509	191.06	0.1023	5.96042	68.02
15.2851	93.01	0.1535	5.79206	33.11
21.3228	207.90	0.4093	4.16368	74.01
26.1543	280.90	0.1791	3.65182	100.00
26.5190	83.10	0.2558	3.35845	29.58
29.6976	72.94	0.1791	3.00582	25.97
30.0388	158.64	0.1535	2.97245	56.48
30.7358	59.64	0.3582	2.90661	21.23
32.7533	29.14	0.0768	2.73203	10.37
35.8640	82.48	0.2558	2.50188	29.36
38.1298	122.28	0.2047	2.35826	43.53
39.7388	53.94	0.3070	2.26641	19.20
43.4727	49.28	0.4093	2.08000	17.54
45.8108	51.87	0.1791	1.97913	18.47
47.0029	42.96	0.2558	1.93168	15.30
52.6908	25.13	0.3120	1.73576	8.95

Pattern List:

Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula	SemiQuant [%]
*	00-054-1999	37	Rubia cordifolia L	0.117	1.070		-
*	00-042-0151	23	Sodium Zinc Phosphate	0.062	0.887	Na Zn P Zn O4	-
*	00-023-0922	23	Chromium Arsenate Hydrate	-0.629	0.710	Cr As O4 ·2 H2 O	-
*	00-019-1678	15	Dimethylamine pentabromo triphosphonitrile	0.432	0.472	C2 H6 Br5 N4 P3	-
*	01-073-1136	21	gold(III) telluride	0.053	0.558	Au2 Te3	-
*	00-014-0789	22	Whewellite	0.016	0.564	Ca C2 O4 · H2 O	-
*	00-001-0876	23	Magnesium Hydrogen Phosphite Hydrate	0.100	0.720	Mg (H2 P O2)2 ·6 H2 O	-

4.1.3 Characterization of CLP by Particle size distribution (PSD)

Particle size distribution of a material can be important in understanding its physical and chemical properties. PSD of the Castor Leaf Powder (CLP) has done up to a very fine sieve of 53µm. the analysis of PSD of a CLP is given as:

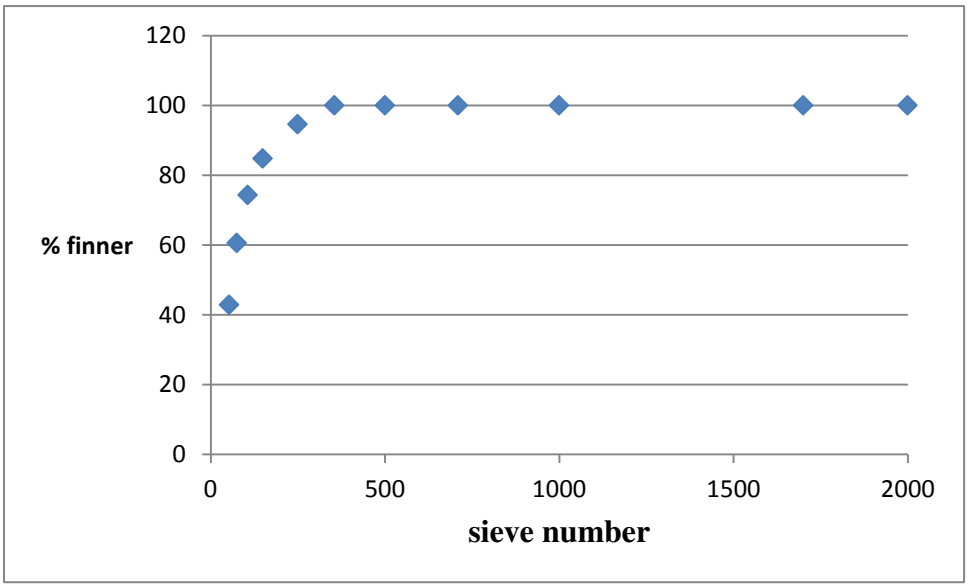


Figure 4.3: PSD of CLP adsorbent

4.2 Characterization of Crystal Violet Dye

4.2.1 Properties of crystal violet

Crystal violet or gentian violet is a triarylmethane dye. Crystal violet has antibacterial, antifungal, and anthelmintic properties and was formerly important as a topical antiseptic.

4.2.2 Structure of CV

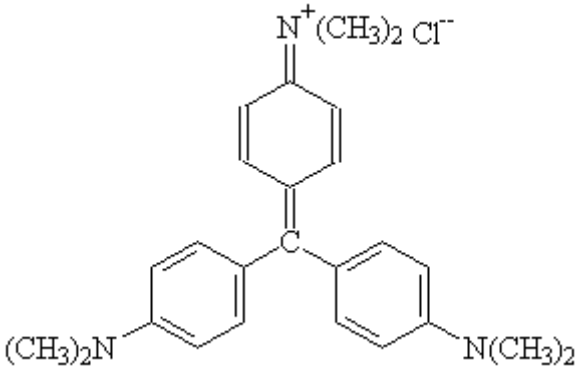


Figure 4.4: Structure of CV

4.2.3 Wavelength graph of CV

To determine the wavelength that corresponds to maximum absorbance (λmax), a standard solution of 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 588 nm respectively Figure 4.5

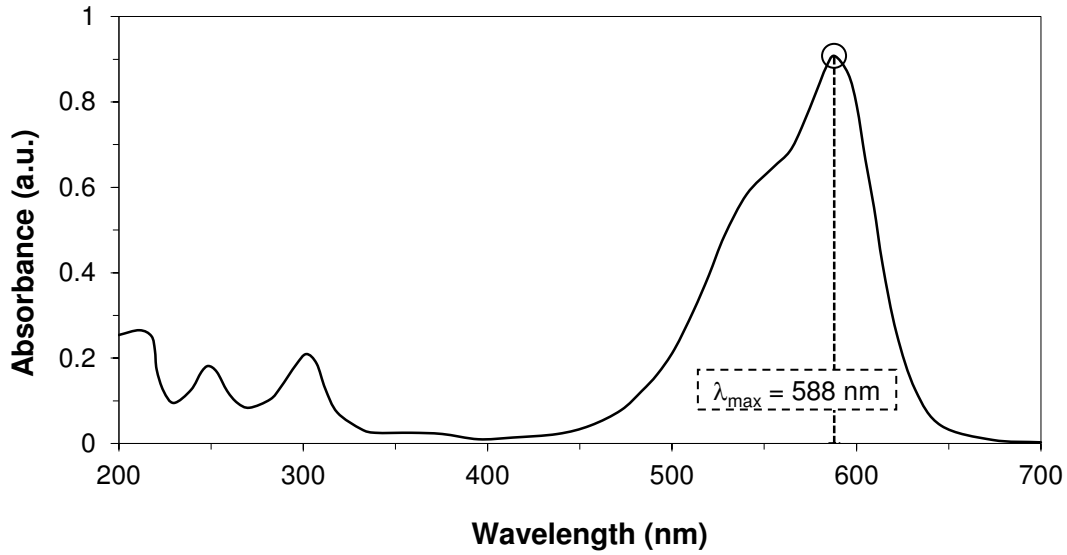


Figure 4.5: A plot of absorbance versus wavelength for Crystal violet dye solution.

4.2.4 Calibration curve of CV

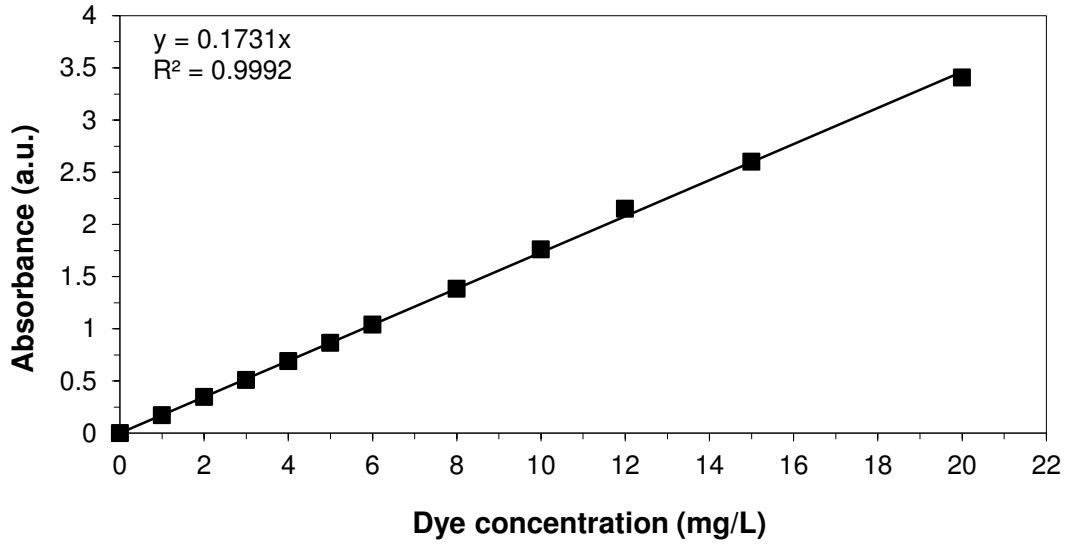


Figure 4.6: Calibration curve of CV

4.3 Characterization of Brilliant green Dye

4.3.1 Properties of Brilliant Green

Brilliant green is one of the triarylmethane dyes which is closely related to malachite green. It has molar mass 482, 64 g/mol. It has melting point 210^0C and solubility in water is 100 g/L at 20^0C. It has sufficient penetrating power. It has Low toxicity in case of absorption.

4.3.2 Structure of BG

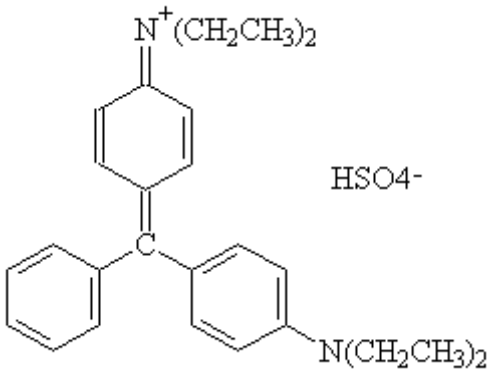


Figure 4.7: Structure of BG

4.3.3 Wavelength graph of BG

To determine the wavelength that corresponds to maximum absorbance (λmax), a standard solution of Brilliant green (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 625 nm in figure 4.8

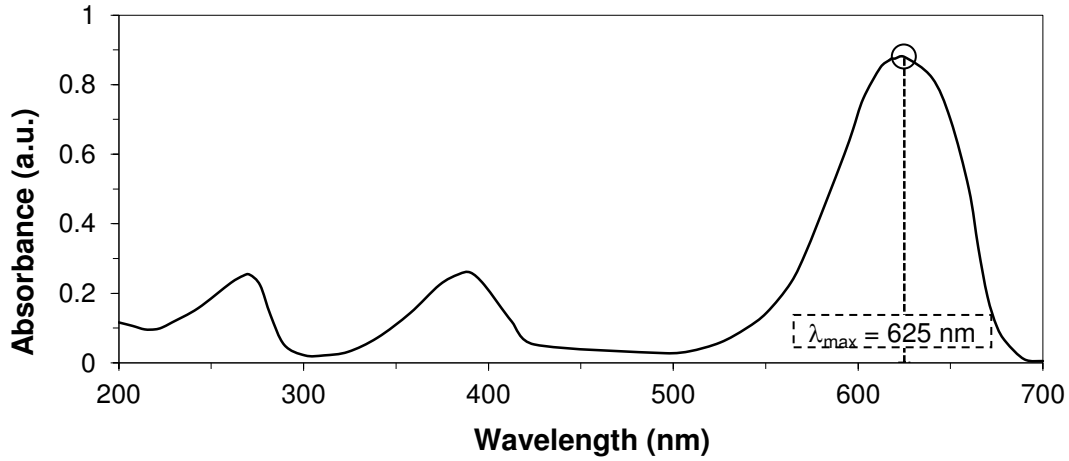


Figure 4.8: A plot of absorbance versus wavelength for Brilliant green dye solution.

4.3.4 Calibration curve of BG

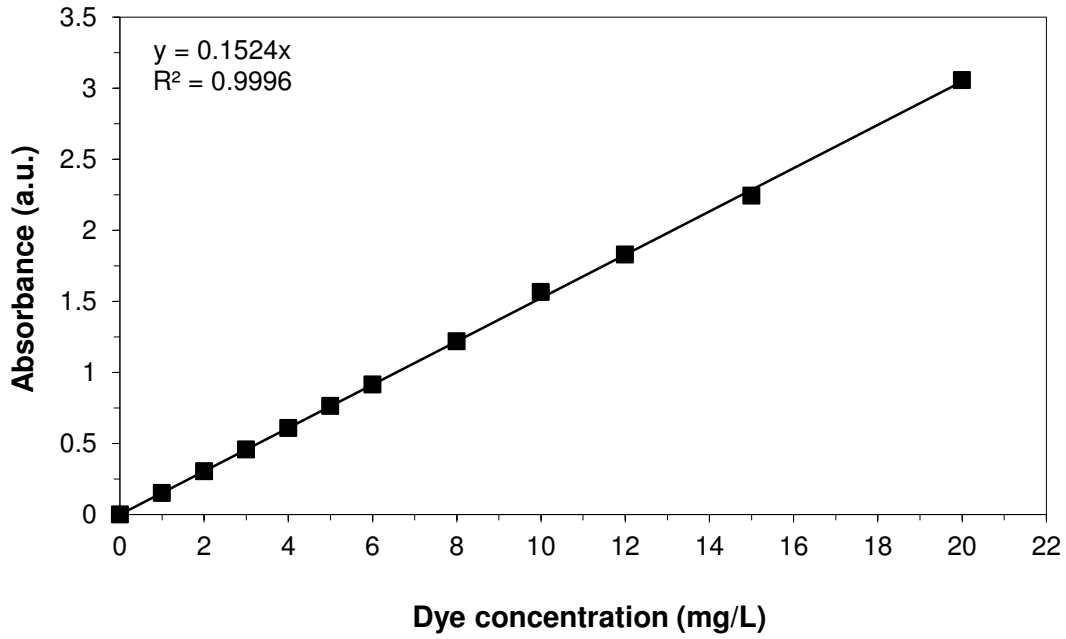


Figure 4.9: Calibration curve of BG

CHAPTER 5

RESULTS

Crystal violet Adsorption experiments

The adsorbent used in the experiment was CLP synthesized from Castor Leaves. The adsorption experiments were carried out for 2 hrs for Brilliant green and Crystal violet dye solution, under continuous agitation at 120 rpm to remove brilliant green 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 CLP (Castor leaf powder).

Removal efficiency,

$$q = \frac{C_i - C_f}{Cclp} \quad \text{(in mg/g)} \qquad (3.1)$$

$$\%R = \frac{C_i - C_f}{Ci} \times 100 \quad (\%) \qquad (3.2)$$

Where,

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

Cf = dye concentration in the solution after adsorption with CLP, mg/L

Cj = CLP loading (adsorbent dosage), g/L

qt = amount of dye adsorbed per unit weight of CLP, mg/g

5.1 Effect of pH solution

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 of crystal violet and brilliant green are presented in Table 5.1 (a, b) and the corresponding plot of dye removal efficiency versus pH is shown in Figure 5.1 (a, b).

Table 5.1 (a): Calculation of Crystal violet dye removal efficiency from absorbance value at different pH values.

pH	Absorption Value	Solution concentration	Removal Efficiency	Adsorption capacity
2	0.302	1.74566474	82.54	0.83
4	0.262	1.514450867	86.2.46	0.85
6	0.206	1.190751445	88.09	0.88
8	0.155	0.895953757	91.04	0.91
10	0.168	0.971098266	90.29	0.90
12	0.207	1.196531792	88.03	0.88

Figure 5.1 (a): Variation of Crystal violet dye removal efficiency with solution pH.

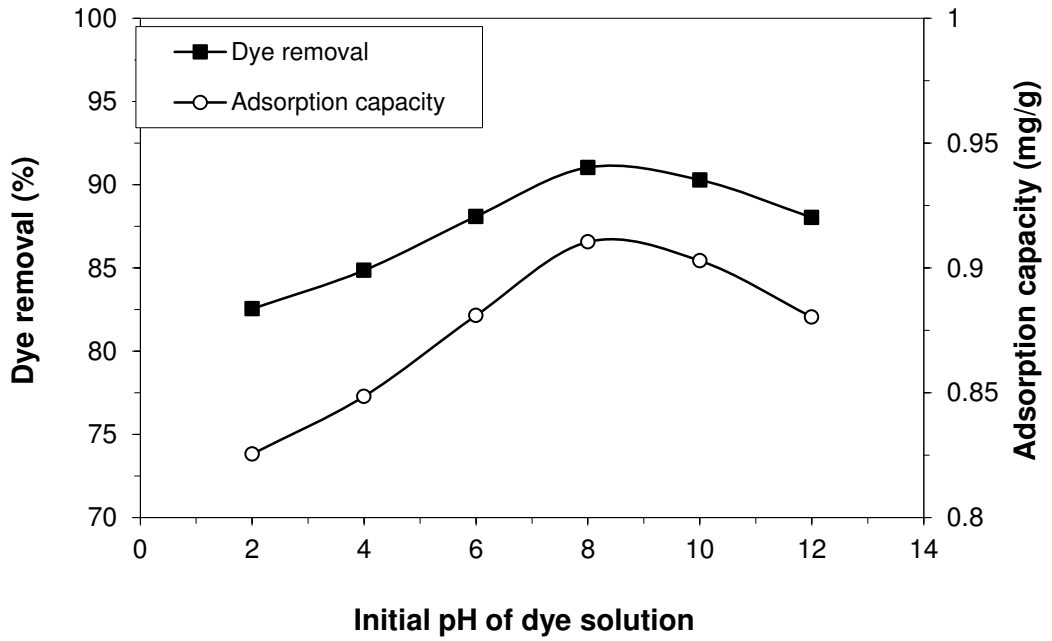
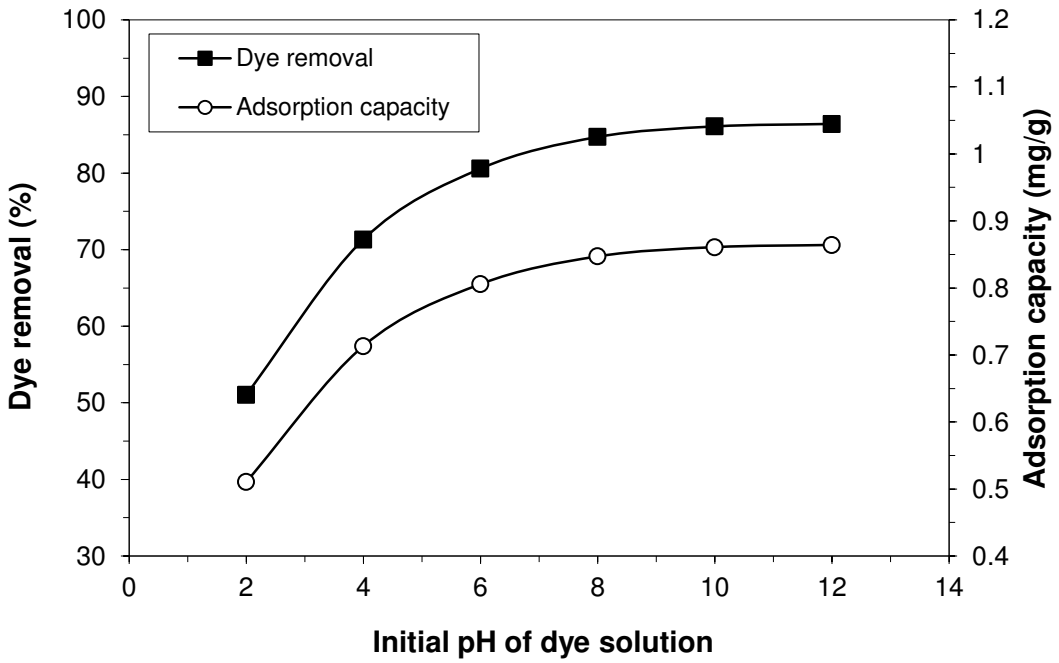


Table 5.1 (b): Calculation of Brilliant green dye removal efficiency from absorbance value at different pH values.

pH	Absorption Value	Solution concentration	Removal Efficiency	Adsorption capacity
2	0.746	6.2.495013123	51.05	0.510
4	0.437	2.867454068	71.33	0.713
6	0.269	1.942257218	80.58	0.806
8	0.233	1.528871391	86.2.31	0.847
10	0.212	1.391076115	86.09	0.861
12	0.207	1.358267717	86.42	0.864

Figure 5.1 (b): Variation of Brilliant green dye removal efficiency with solution pH.



It can be observed from the above figure that Crystal violet dye removal efficiency increases with increase in pH value of the solution as the dye used is an acid dye and the CLP surface is

positively charged. But after ph 8, there could be fewer attachment sites available at higher pH due to decreased positive charge of the CLP surface. The, the optimum pH of the dye solution is 8-10. In case of Brilliant green, dye removal efficiency increases with increase in pH value of the solution and maximum at ph 12. Hence, the pH value is 8 for Crystal violet and pH 12 for Brilliant green that has been used earlier is suitable for all the experiments.

5.2 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 480 min for brilliant green and Crystal violet. The values of dye removal efficiency at various time intervals are presented in Table 5.2 (a, b) and the corresponding plot of dye removal efficiency versus adsorption time is shown in Figure 5.2 (a, b). From this figures, we can be observed that the removal efficiency increases with increasing the time of adsorption.

Table 5.2 (a): Calculation of Crystal violet dye removal efficiency from absorbance value at different adsorption time.

Adsorption Time (min)	Absorption Value (A.U)	Solution Concentration (mg/l)	Removal Efficiency (%)	Adsorption Capacity
0	1.73	10	0	0.00
15	1	5.780346821	42.20	0.42
30	0.4	2.312138728	76.88	0.77
45	0.23	1.329479769	86.71	0.87
60	0.19	1.098265896	89.02	0.89
90	0.165	0.953757225	90.46	0.90
120	0.155	0.895953757	91.04	0.91
180	0.155	0.895953757	91.04	0.91
240	0.154	0.89017341	91.10	0.91
360	0.149	0.861271676	91.39	0.91
480	0.146	0.843930636	91.56	0.92

Figure 5.2 (a): Variation of Crystal violet dye removal efficiency with time

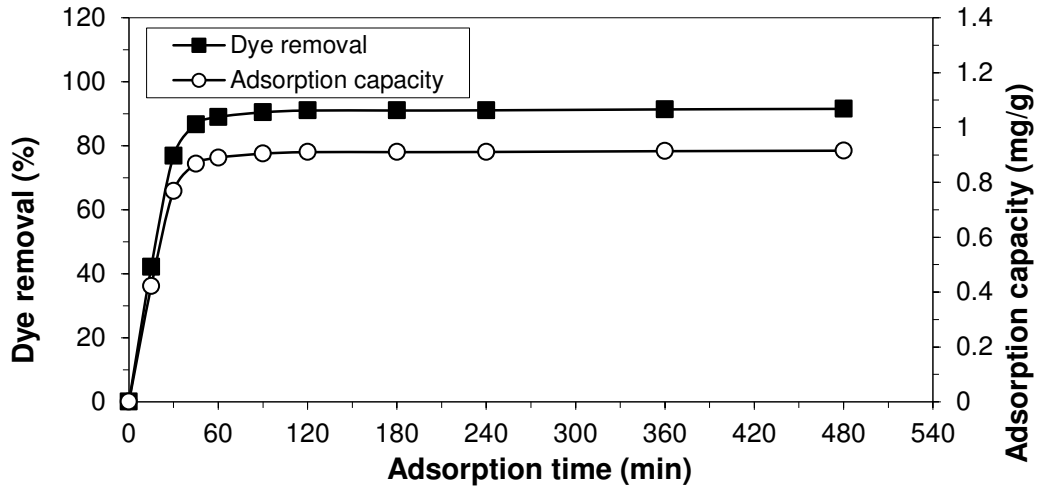
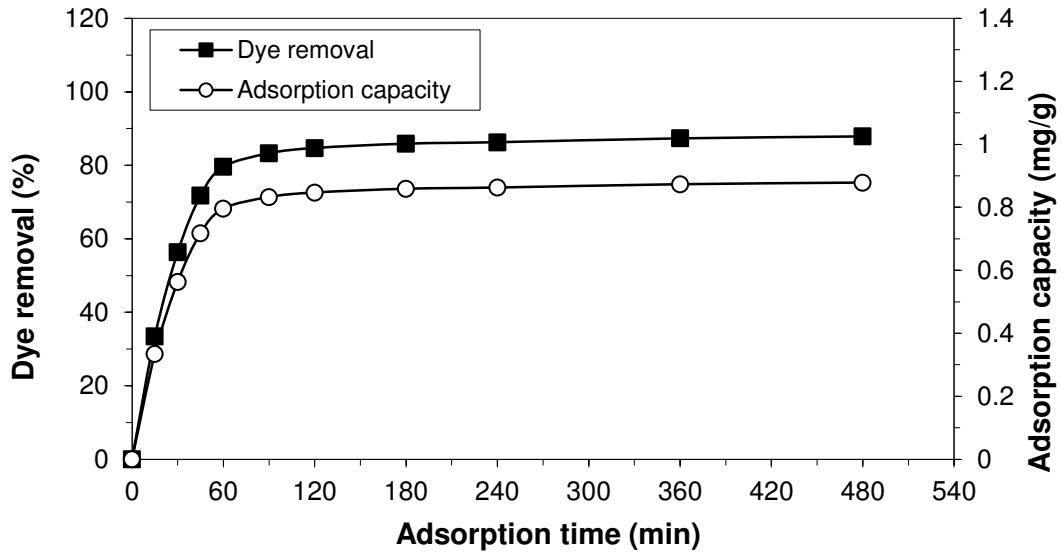


Table 5.2 (b): Calculation of Brilliant green dye removal efficiency from absorbance value at different adsorption time.

Adsorption Time (min)	Absorption Value (A.U)	Solution Concentration (mg/l)	Removal Efficiency (%)	Adsorption Capacity
0	1.524	10	0	0.00
15	1.014	6.653543307	33.46	0.33
30	0.665	6.16351706	56.76	0.56
45	0.43	2.82152231	71.78	0.72
60	0.3111	2.041338583	79.59	0.80
90	0.255	1.673228346	83.27	0.83
120	0.233	1.528871391	86.2.31	0.85
180	0.215	1.410761155	85.89	0.86
240	0.209	1.371391076	86.29	0.86
360	0.193	1.266404199	87.34	0.87
480	0.185	1.213910761	87.86	0.88

Figure 5.2 (b): Variation of Brilliant green dye removal efficiency with time.



5.3 Effect of CLP concentration

The values of dye removal efficiency and adsorption capacity of CLP evaluated using the described formulae for various concentration of CLP are listed in Table 5.3 (a, b)

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Table 5.3 (a): Calculation of Crystal Violet dye removal efficiency from absorbance value at different CLP dosage.

CLP Conc. g/l	Absorption Value (A.U)	Solution Concentration (mg/l)	Removal Efficiency (%)	adsorption capacity
0	1.730	10	0	0.00
1	0.81	6.2.282080925	53.18	5.32
2	0.382	2.208092486	77.92	3.90
5	0.221	1.277456647	87.23	1.74
10	0.155	0.895953757	91.04	0.91
15	0.142	0.820809249	91.79	0.61
20	0.122	0.705202312	92.95	0.46
30	0.155	0.664739884	93.35	0.31

Figure 5.3 (a): Variation of Crystal violet dye removal efficiency with CLP concentration.

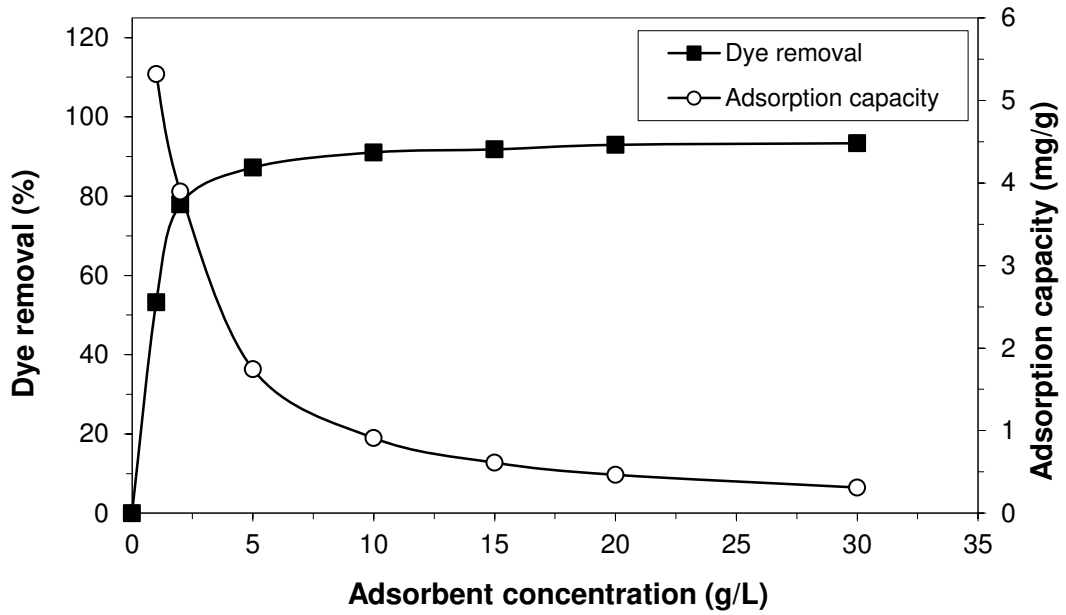
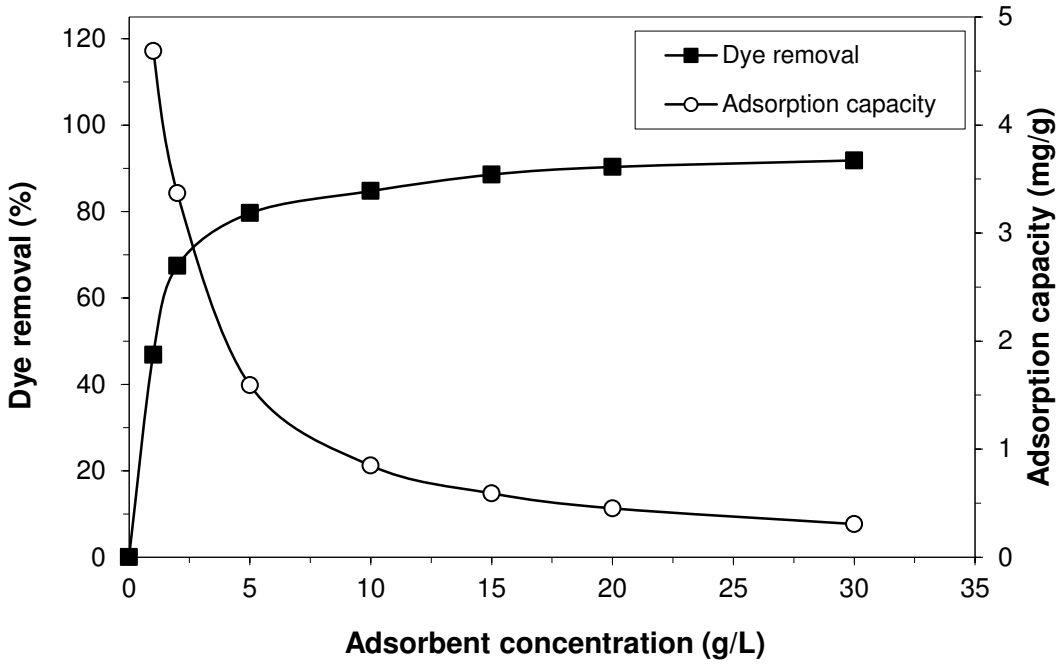


Table 5.3 (b): Calculation of Brilliant green dye removal efficiency from absorbance value at different CLP dosage.

CLP Conc. g/l	Absorption Value (A.U)	Solution Concentration (mg/l)	Removal Efficiency (%)	adsorption capacity
0	1.524	10	0	0.00
1	0.81	5.31496063	46.85	6.2.29
2	0.497	3.261154856	67.39	3.37
5	0.311	2.040682415	79.59	1.59
10	0.233	1.528871391	86.2.31	0.85
15	0.175	1.148293963	88.52	0.59
20	0.148	0.971128609	90.29	0.45
30	0.125	0.820209974	91.80	0.31

Figure 5.3 (b): Variation of Brilliant green dye removal efficiency with JLP concentration.



A plot of dye removal efficiency versus CLP concentration yielded a non-linear profile as shown in Figure 5.3(a, b). From this figures, it can be observed that the removal efficiency increased with increasing the CLP concentration up to 10.00 g/L for crystal violet and 15.00 g/L for Brilliant green and no significant improvement in the removal efficiency values was observed beyond this value. Hence, the optimal CLP concentration for the removal of dyes was chosen to be 30 g/L. 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 the critical dose 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.

5.4. Effect of dye (CV) concentration

To study the effect of initial dye concentration on the removal efficiency, adsorption experiments were conducted at various dye concentration values between 2 and 300 mg/L. The values of dye removal efficiency at various dye concentrations are presented in Table 5.4 (a, b). Corresponding plot of dye removal efficiency versus initial dye concentration is shown in Figure 5.4 (a, b).

Table 5.4 (a): Calculation of Crystal violet dye removal efficiency from absorbance value at different dye concentration.

CV Conc. mg/l	Absorption Value (A.U)	Solution Concentration (mg/l)	Removal Efficiency (%)	adsorption capacity
2	0.001	0.005780347	0	0.00
5	0.043	0.248554913	46.85	6.2.29
10	0.155	0.895953757	67.39	3.37
20	0.396	2.289017341	79.59	1.59
50	1.232	7.121387283	86.2.31	0.85
100	2.821	16.30635838	88.52	0.59
200	9.340	53.98843931	90.29	0.45
300	26.2.81	139.4277457	91.80	0.31

Figure 5.4 (a): Variation of Crystal violet dye removal efficiency with initial dye concentration.

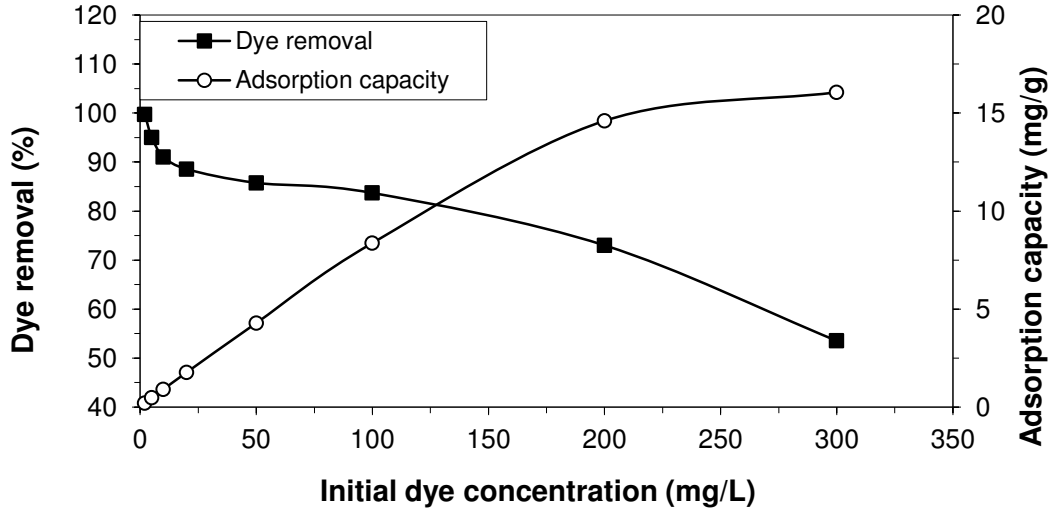
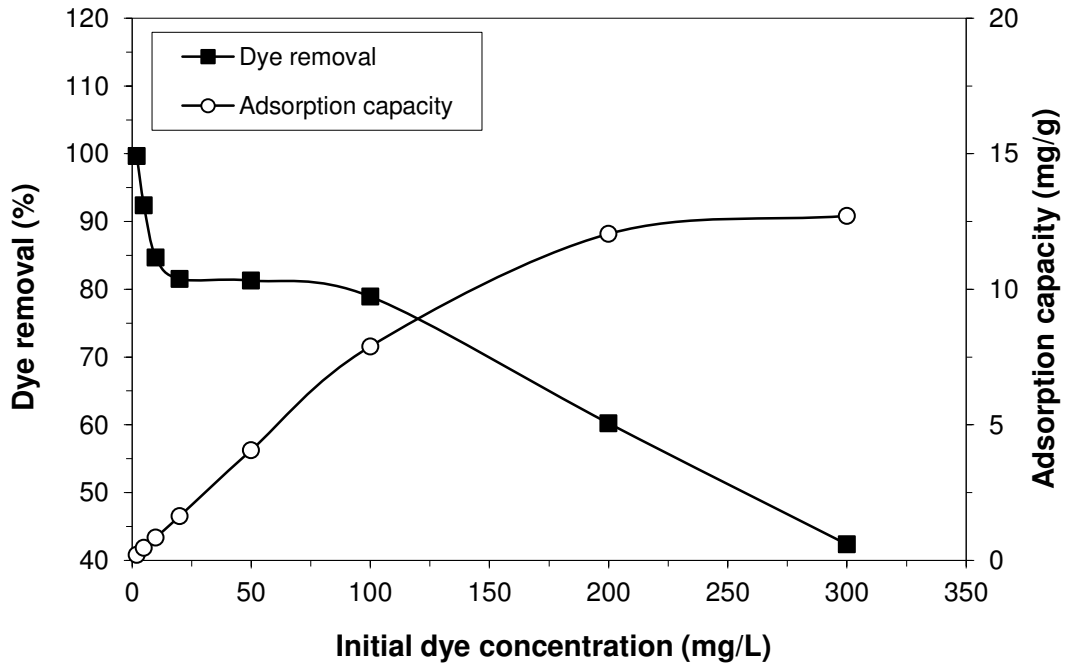


Table 5.4 (b): Calculation of Brilliant green dye removal efficiency from absorbance value at different dye concentration.

CV Conc. mg/l	Absorption Value (A.U)	Solution Concentration (mg/l)	Removal Efficiency (%)	adsorption capacity
2	0.001	0.00656168	99.67	0.20
5	0.058	0.380577428	92.39	0.46
10	0.233	1.528871391	86.2.31	0.85
20	0.563	3.694225722	81.53	1.63
50	1.426	9.356955381	81.29	4.06
100	3.212	21.07611549	78.92	7.89
200	12.124	79.55380577	60.22	12.04
300	26.353	172.9199475	42.36	12.71

Figure 5.4 (b): Variation of Brilliant green 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.

5.5. Effect of ultrasound

To study the effect of ultrasound on the removal efficiency, adsorption experiments were conducted at various ultrasound time values between 0 and 120 minutes. The values of dye removal efficiency at various ultrasound times are presented in Table 5.5(a, b). Corresponding plot of dye removal efficiency versus ultrasound times is shown in Figure 5.5 (a, b).

Table 5.5 (a): Calculation of Crystal violet dye removal efficiency from absorbance value at different adsorption time.

Ultrasound Time (min)	Absorption Value (A.U)	Solution Concentration (mg/l)	Removal Efficiency (%)	adsorption capacity
0	1.730	10	0.00	0.00
1	0.232	1.341040462	86.59	0.87
2	0.184	1.063583815	89.36	0.89
5	0.134	0.774566474	92.25	0.92
10	0.076	0.439306358	95.61	0.96
15	0.042	0.242774566	97.57	0.98
30	0.021	0.121387283	98.79	0.99
60	0.018	0.104046243	98.96	0.99
90	0.015	0.086705202	99.13	0.99
120	0.010	0.057803468	99.42	0.99

Figure 5.5 (a): Variation of Crystal violet dye removal efficiency with ultrasound times.

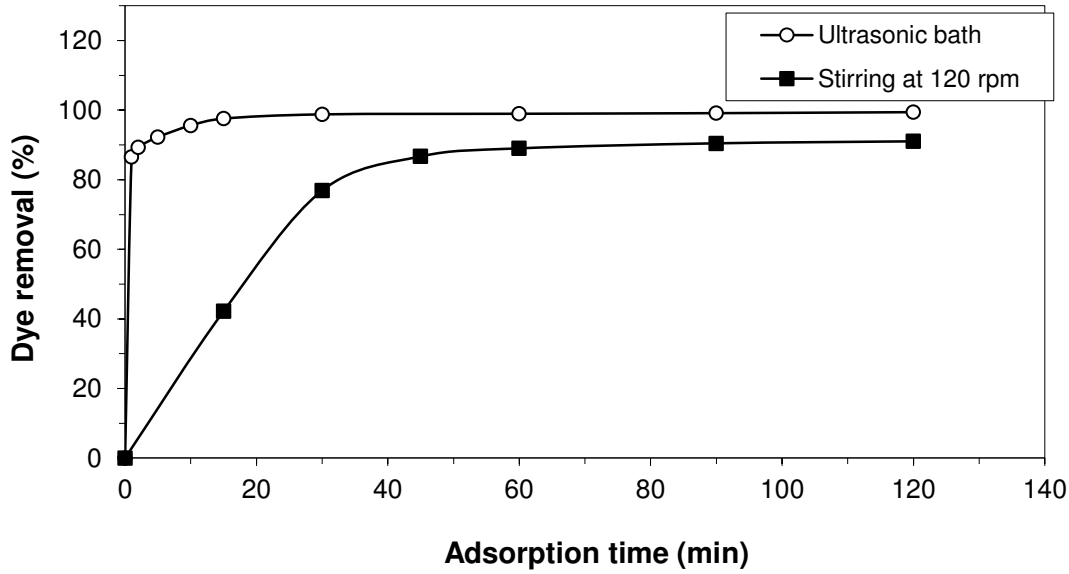


Table 5.5 (b): Calculation of Brilliant green dye removal efficiency from absorbance value at different adsorption time

Ultrasound Time (min)	Absorption Value (A.U)	Solution Concentration (mg/l)	Removal Efficiency (%)	adsorption capacity
0	1.524	10	0.00	0.00
1	0.318	2.086614173	79.13	0.79
2	0.221	1.450131234	85.50	0.85
5	0.162	1.062992126	89.37	0.89
10	0.097	0.63648294	93.64	0.94
15	0.081	0.531496063	96.2.24	0.95
30	0.121	0.793963255	92.06	0.92
60	0.218	1.430446194	85.70	0.86
90	0.315	2.066929134	79.33	0.79
120	0.425	2.788713911	72.11	0.72

Figure 5.5 (b): Variation of Brilliant green dye removal efficiency with ultrasound times

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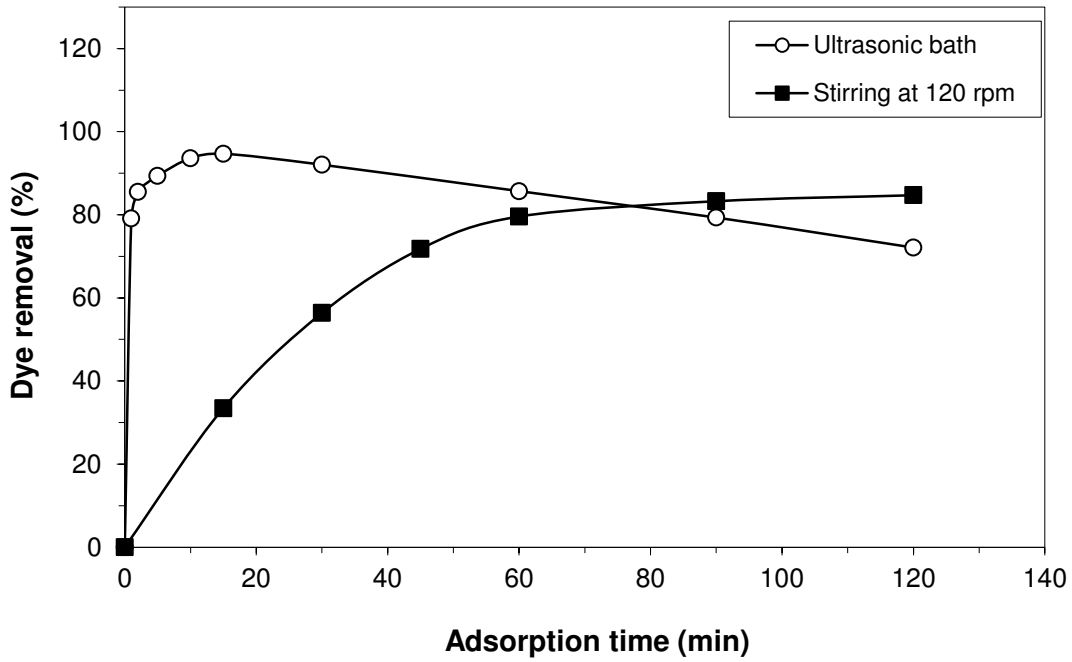


It has been observed from the above figures that dye removal efficiency increase with increase in ultrasound time for the crystal violet dye and for the brilliant green dye removal, initially with increase in time the removal efficiency is also increase but after certain time (80 min) it decreased as there is decrease in adsorption capacity.

5.6. 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 5.6 (a, b) and the corresponding plot of dye removal efficiency versus temperature is shown in Figure 5.6 (a, b).

Table 5.6 (a): Calculation of Crystal Violet dye removal efficiency from absorbance value at different temperatures

Temperature (^{0}C)	Absorption Value (A.U)	Solution Concentration (mg/l)	Removal Efficiency (%)	adsorbent capacity
27	0.155	0.895953757	91.04	0.910
37	0.125	0.722543353	92.77	0.928
47	0.087	0.502890173	96.2.57	0.950
57	0.066	0.38150289	96.18	0.962

Figure 5.6 (a): Variation of Crystal violet dye removal efficiency at different temperatures

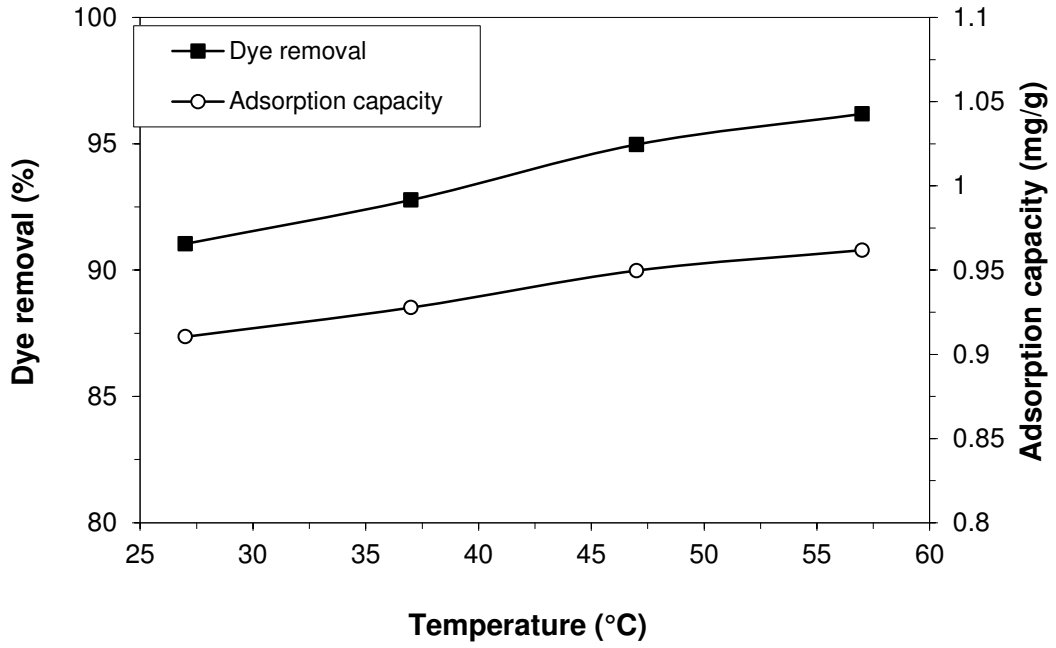
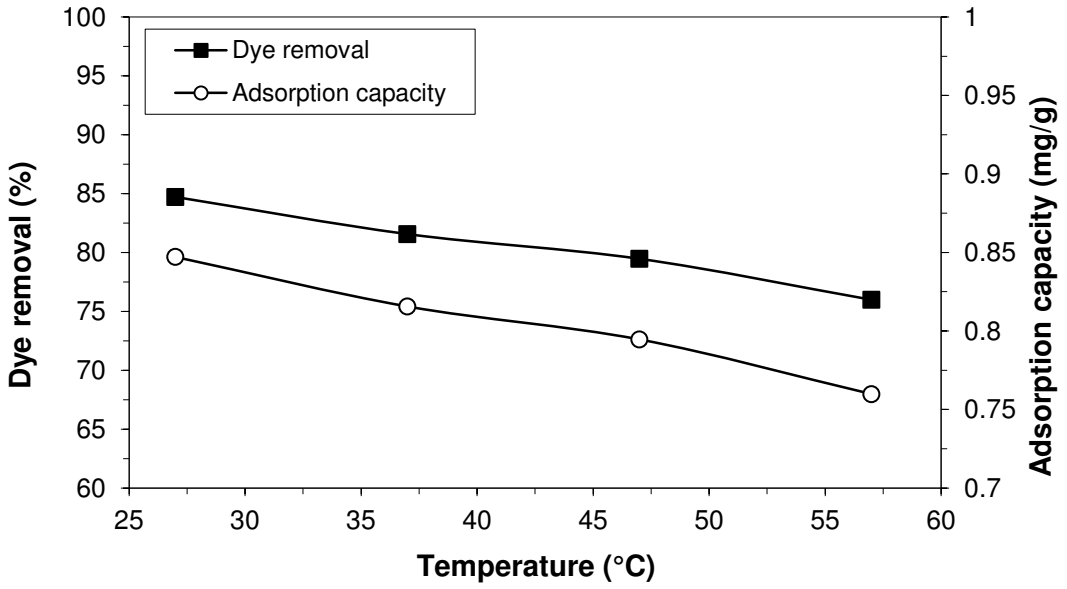


Table 5.6 (b): Calculation of Brilliant green dye removal efficiency from absorbance value at different temperatures.

Temperature (^{0}C)	Absorption Value (A.U)	Solution Concentration (mg/l)	Removal Efficiency (%)	adsorbent capacity
27	0.233	1.528871391	86.2.31	0.847
37	0.281	1.843832021	81.56	0.816
47	0.313	2.053805774	79.46	0.795
57	0.366	2.401574803	75.98	0.760

Figure 5.6 (b): Variation of Brilliant green dye removal efficiency at different temperatures



From the above figures, we can be observed that the removal efficiency increases with increase in temperature for the crystal violet and decrease the removal efficiency with increase in temperature for the Brilliant green. 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 for the Brilliant green.

5.7. Effect of stirring speed

Stirring is an important parameter in adsorption phenomena. To study the effect of stirrer speed on the dye removal efficiency, adsorption experiments were conducted at various stirrer speeds between 0 and 300 rpm. The values of dye removal efficiency for various stirrer speeds are presented in Table 5.7 (a, b) and the corresponding plot of dye removal efficiency versus stirrer speed is shown in Figure 5.7 (a, b).

Table 5.7 (a): Calculation of Crystal violet dye removal efficiency from absorbance value at different stirrer speed.

Stirring speed (rpm)	Absorption Value (A.U)	Solution Concentration (mg/l)	Removal Efficiency (%)	adsorbent capacity
0	1.113	6.433526012	35.66	0.357
50	0.484	2.797687861	72.02	0.720
100	0.155	0.895953757	91.04	0.910
200	0.177	0.676300578	93.24	0.932
300	0.122	0.705202312	92.95	0.929

Figure 5.7 (a): Variation of Crystal violet dye removal efficiency with stirrer speed

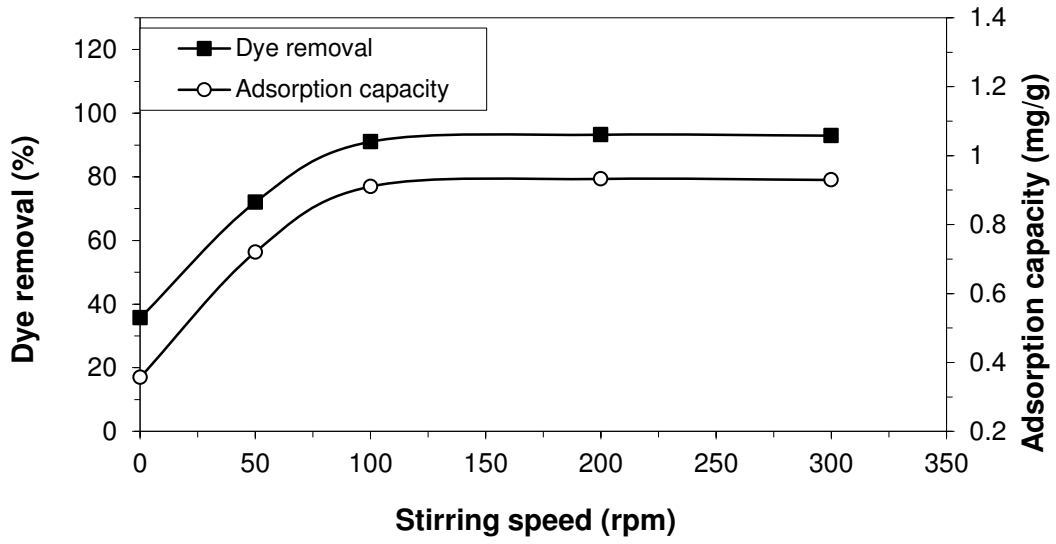
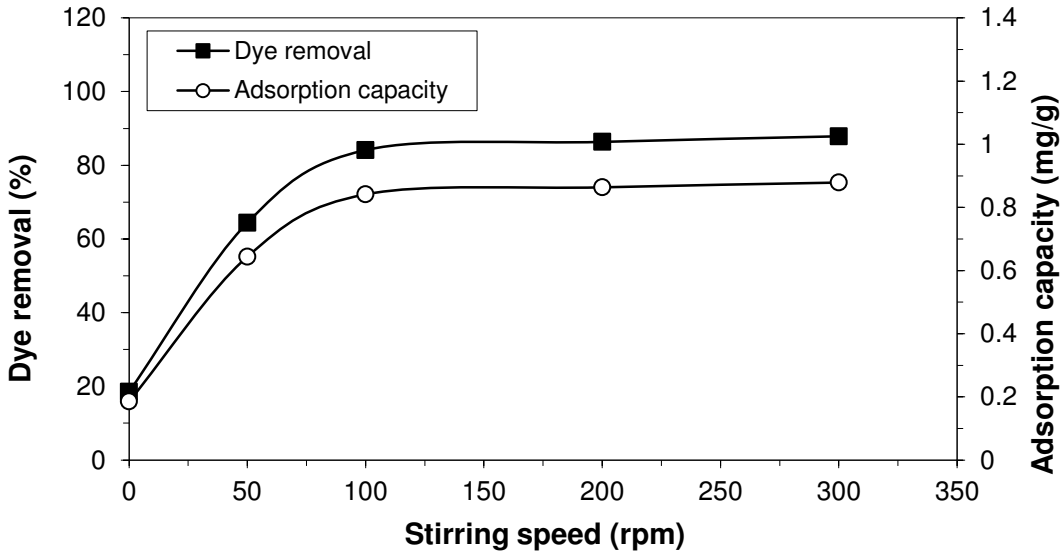


Table 5.7 (b): Calculation of Crystal violet dye removal efficiency from absorbance value at different stirrer speed

Stirring speed (rpm)	Absorption Value (A.U)	Solution Concentration (mg/l)	Removal Efficiency (%)	adsorbent capacity
0	1.242	8.149606299	18.50	0.185
50	0.543	3.562992126	66.17	0.644
100	0.242	1.587926509	86.2.8	0.841
200	0.208	1.364829396	86.35	0.864
300	0.185	1.213910761	87.86	0.879

Figure 5.7 (b): Variation of Brilliant green dye removal efficiency with stirrer speed



From the above figure it is clear that Crystal violet dye removal maximum occurred at 200 rpm and for brilliant green dye maximum removal occurred at 300 rpm.

CHAPTER 6

Thermodynamic, Kinetic and Equilibrium studies

6.1 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. (6.1) and (6.2)).

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

$$\Delta G^\circ = -RT \ln K_d = -RT \ln \left(\frac{q_e}{C_e} \right) \quad (6.1)$$

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

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ \quad (6.2)$$

Table 6.1: Values of Gibbs free energy (ΔG°) at different temperatures

Temperature (K)	ΔG°
300	5783.02
310	6578.83
320	7817.48
330	8856.2.15

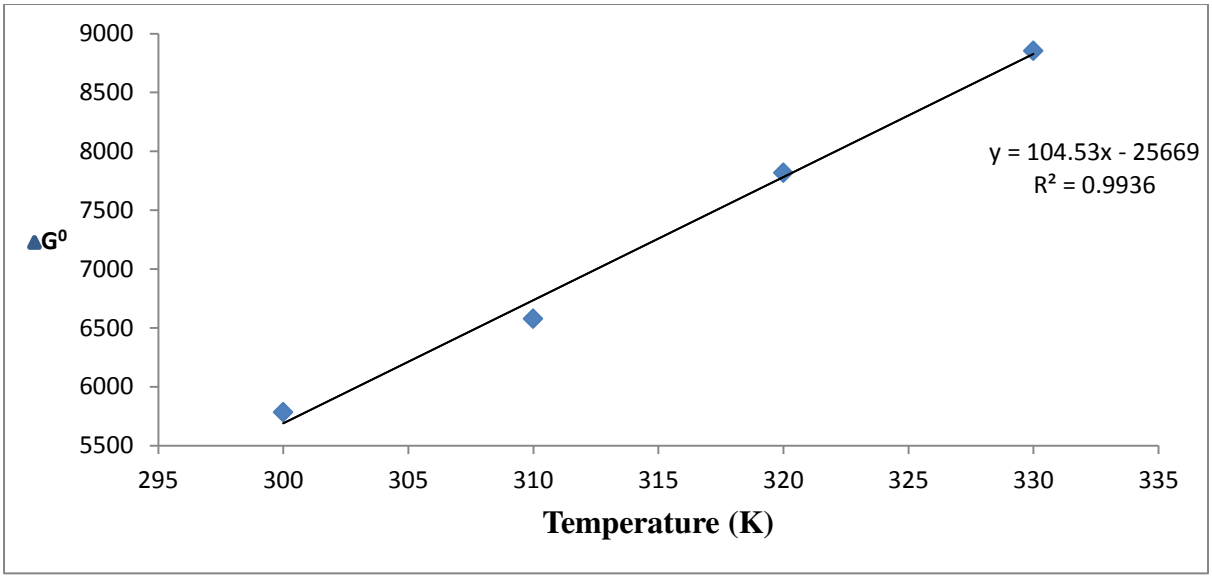


Figure 6.1: A plot of ΔG° versus temperature

A plot of ΔG° versus T, (Figure 6.1) yields a straight line with the slope of –ΔS° and intercept of ΔH°. The values of ΔG° obtained using at the temperatures 300, 310, 320 and 330 K for dye are 5.783, 6.578, 7.817 and 8.856 kJ/mol respectively. The values of changes in enthalpy (ΔH°) and entropy (ΔS°) during the adsorption process determined from the slope and intercept of Figure 6.1 are 104.53 kJ/mol and –25669 J/mol K^{-1} respectively. The negative values indicate that the adsorption process considered here is exothermic in nature and hence lower temperatures are favoured.

6.2 Adsorption kinetics

6.2.1 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.

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \qquad (6.3)$$

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 (6.3) with the initial condition $q_t = 0$ at $t = 0$ gives the following equation.

$$-\ln\left[1-\frac{q_t}{q_e}\right] = K_1 t \qquad (6.4)$$

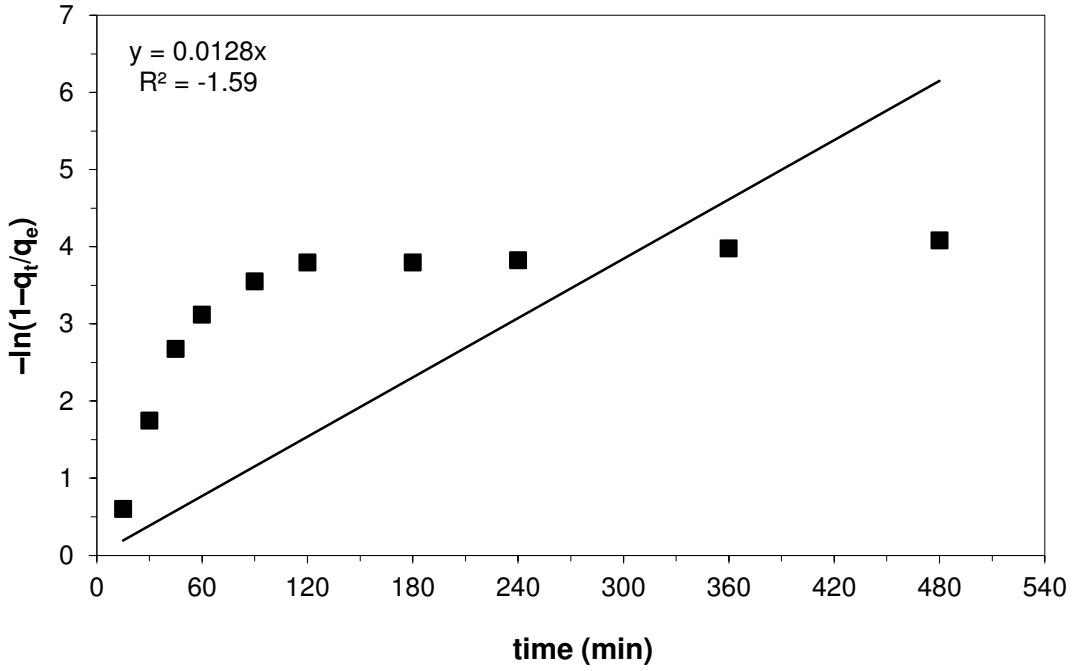


Figure 6.2: Pseudo first-order kinetic model for the adsorption of Crystal violet dye on CLP surface

The slope of a straight line fit to the data of $-\ln(1-q_t/q_e)$ versus t 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 value of the pseudo first order rate constant, k_1 as obtained from the linear curve fitting is 0.0128 min^{-1} for dye. The value of regression coefficient is very far from the experimental value

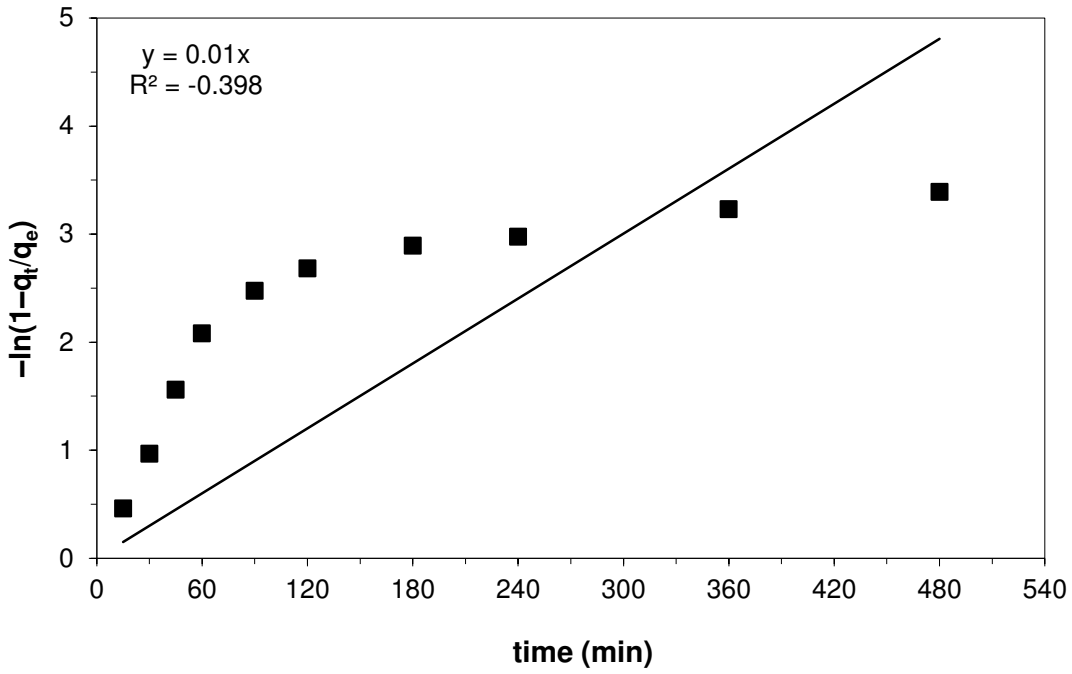


Figure 6.3: Pseudo first-order kinetic model for the adsorption of Brilliant green dye on CLP surface.

The slope of a straight line fit to the data of $-\ln(1-q_t/q_e)$ versus t 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 value of the pseudo first order rate constant, k_1 as obtained from the linear curve fitting is 0.01 min^{-1} for dye.

6.2.1.2 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.

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \qquad (6.5)$$

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

The integration of equation (6.5) with the initial condition $q_t = 0$ at $t = 0$ gives the following expression.

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad (6.6)$$

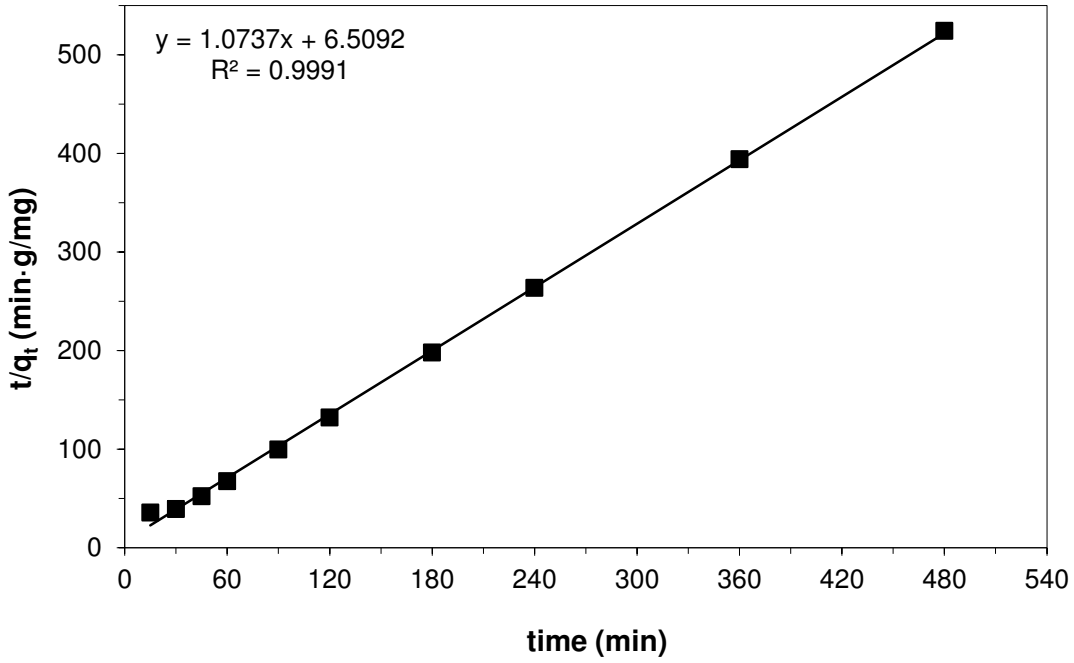


Figure 6.4: Pseudo second-order kinetic model for the adsorption of Crystal violet dye on CLP surface.

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 6.4). The slope and intercept obtained from the graphical analysis of Crystal violet dye plot are 1.0737 and 6.5092. Although, the regression coefficient value exactly near to 1.0 (0.9991), the value of qe (0.842 mg/g) it is exactly matching with experimental value (0.842 mg/g).

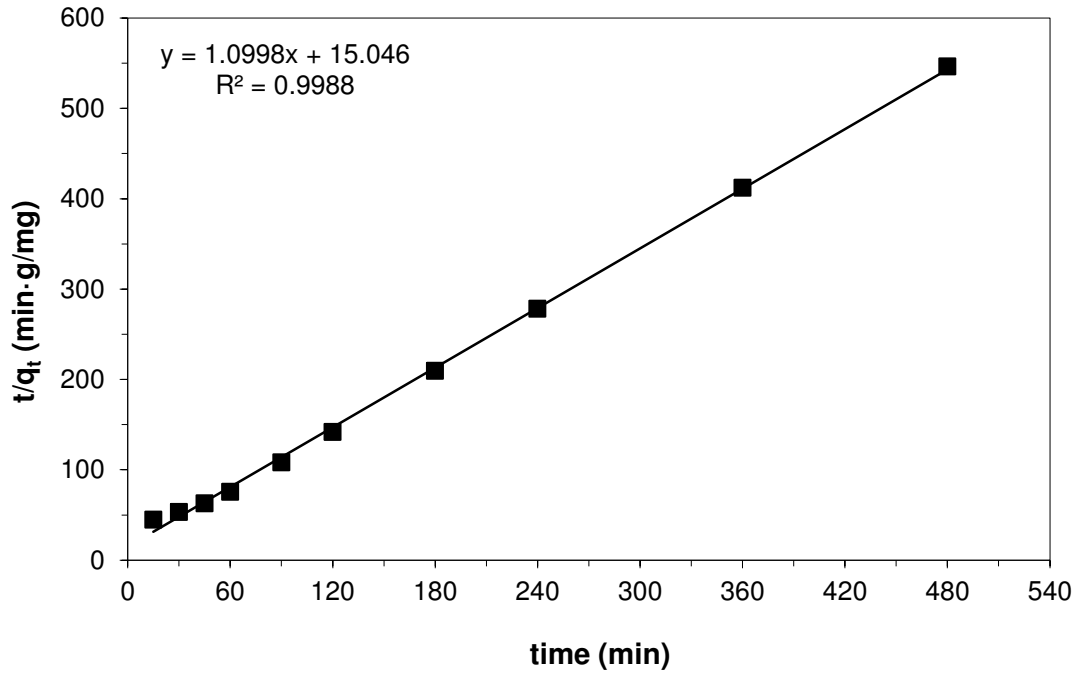


Figure 6.5: Pseudo second-order kinetic model for the adsorption of Brilliant green dye on CLP surface.

The values of qe and k_2 can be obtained from the slope and intercept of a straight line fit to the data of t/qt versus t (as shown in Figure 6.5). The slope and intercept obtained from the graphical analysis of Brilliant green plot are 1.0998 and 15.046. Although, the regression coefficient value exactly coming to near 1.0 (0.9988), the value of qe is exactly matching with experimental value.

6.2.3. 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.

$$q_t = k_i t^{\frac{1}{2}} + C_i \qquad (6.7)$$

Here, k_i (mg/g.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 ki and Ci can be determined directly as the slope and intercept of the linear plot of qt versus t0.5. The values

of k_i and C_i obtained from the graph are 0.0153 mg/g.min^{-1} and 0.6669 mg/g respectively for dye.

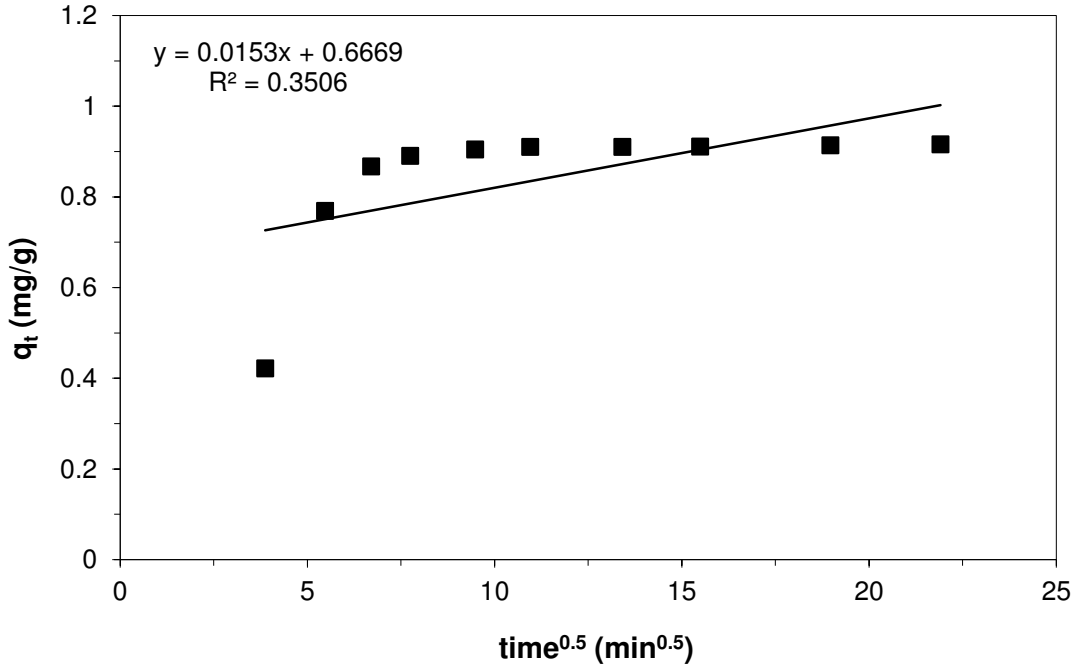


Figure 6.6 Intra-particle diffusion model for the adsorption of Crystal violet dye on CLP surface

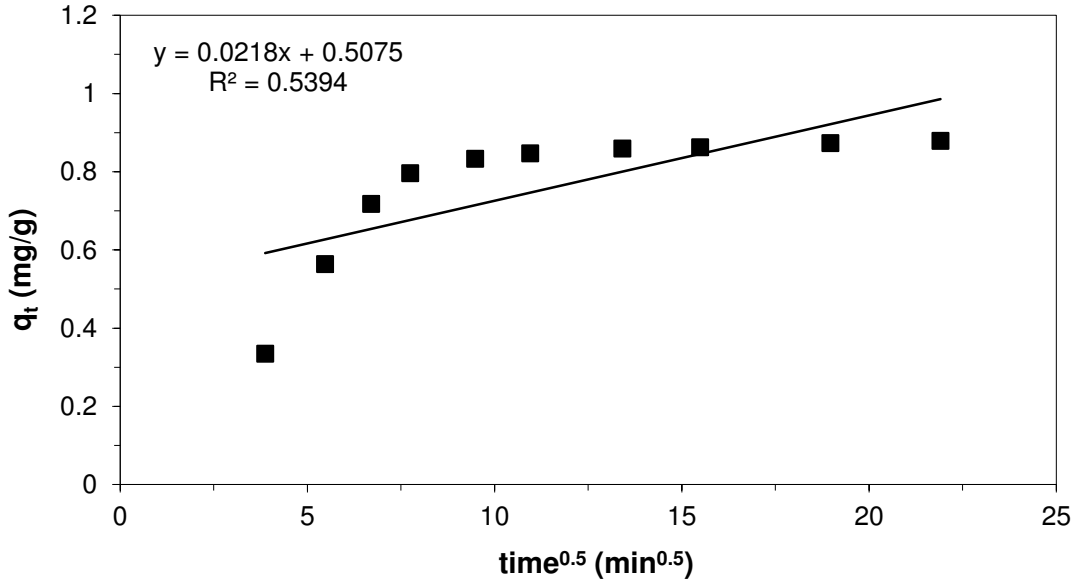


Figure 6.7 Intra-particle diffusion model for the adsorption of Brilliant green dye on CLP surface

The values of k_i and C_i obtained from the graph are .0218 mg/g.min^{-1} and 0.5075 mg/g respectively for dye.

6.2.4 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.

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \tag{6.8}$$

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 (6.8) is as follows.

$$\frac{C_e}{q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \tag{6.9}$$

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 Ce/qe versus Ce.

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

$$R_L = \frac{1}{1 + K_L C_i} \tag{6.10}$$

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, $R_L > 1$.

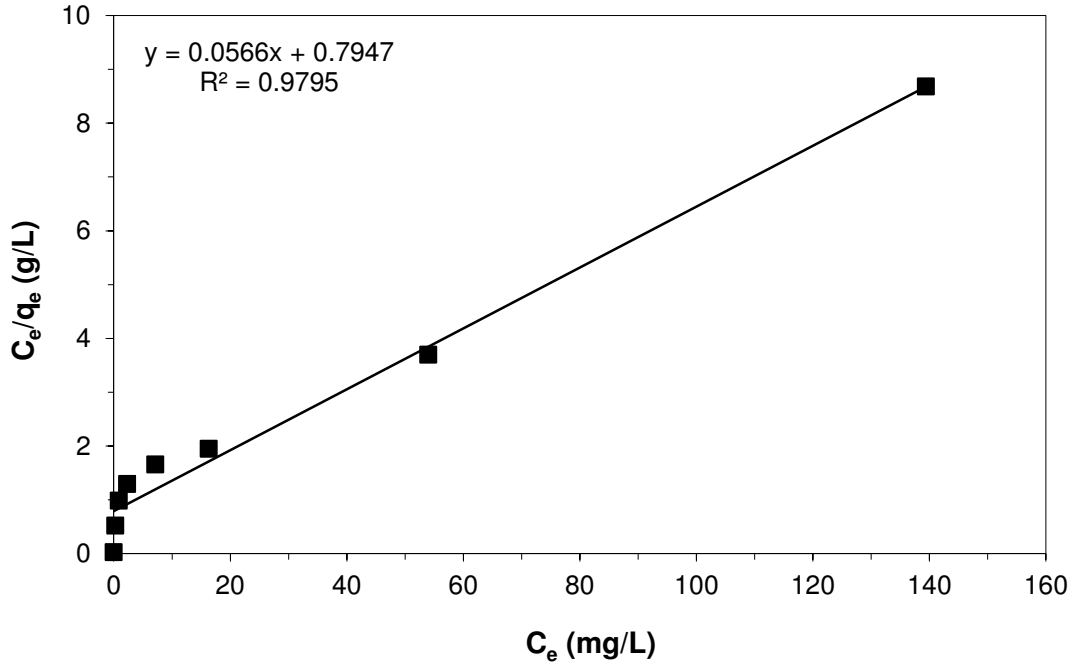


Figure 6.8: Plot of Ce/qe versus Ce for the estimation of Crystal violet dye Langmuir isotherm constants

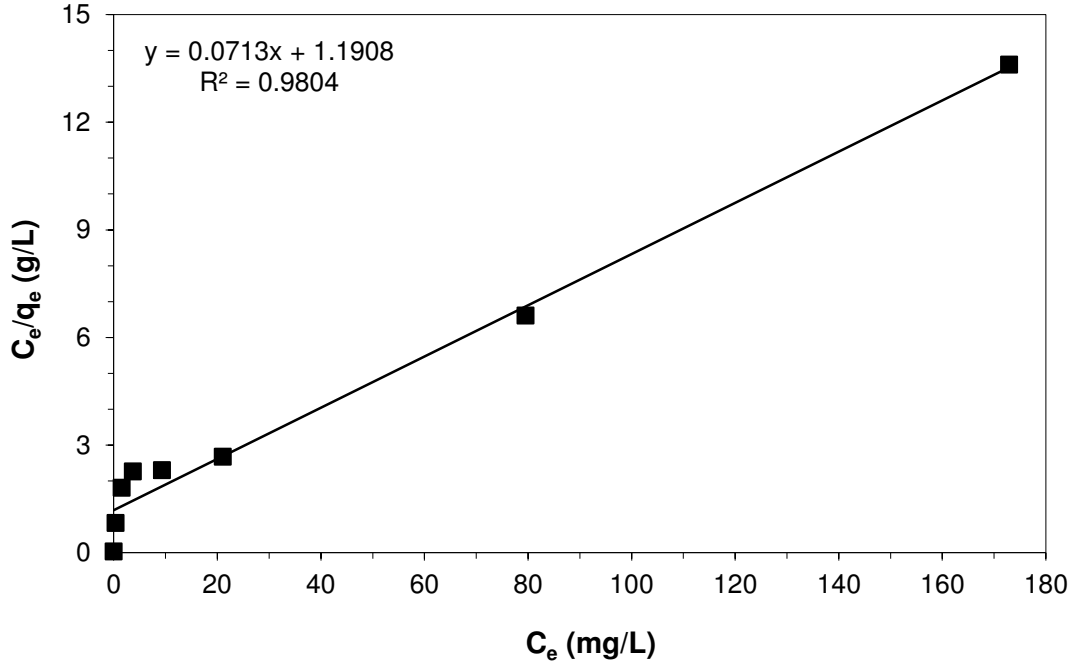


Figure 6.9: Plot of Ce/qe versus Ce for the estimation of Brilliant green violet dye Langmuir isotherm constants

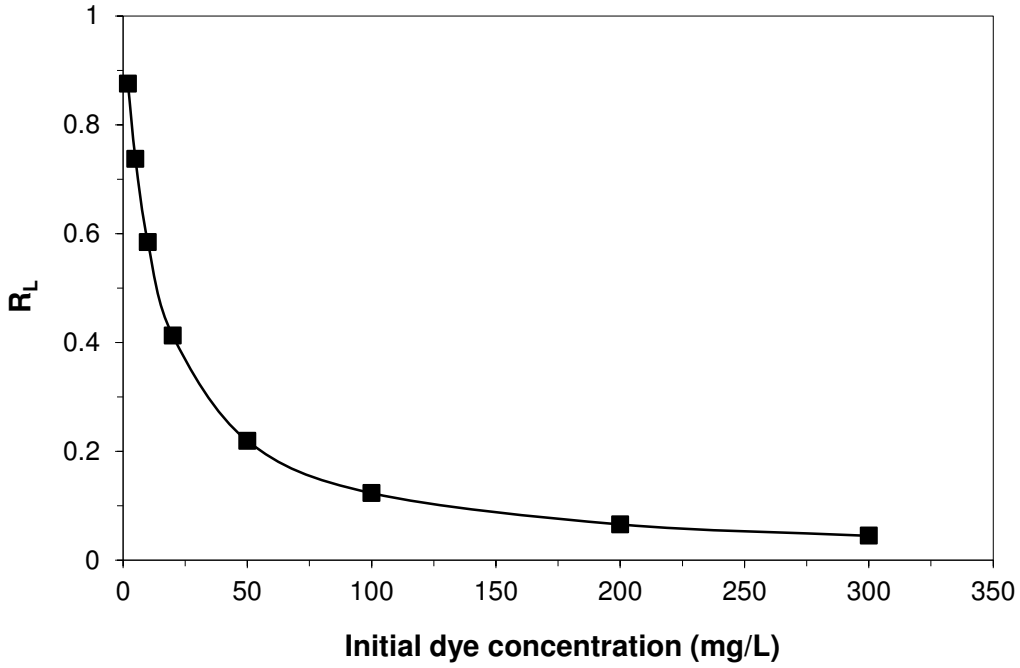


Figure 6.10: Variation of equilibrium adsorption intensity (RL) with initial dye (Crystal violet) concentration (Ci)

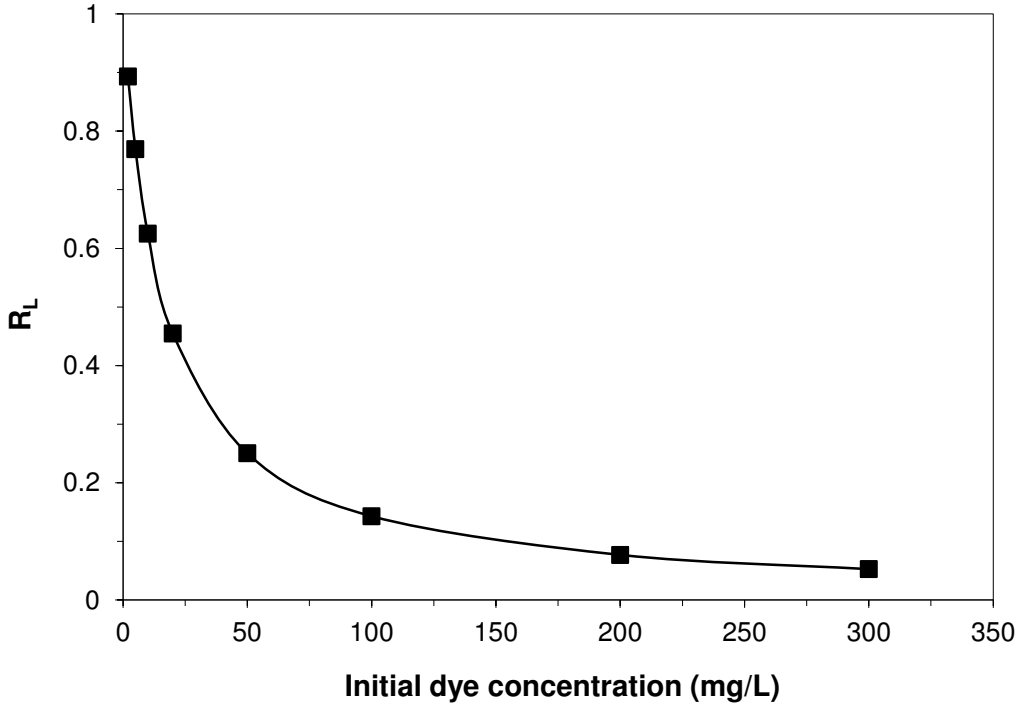


Figure 6.11: Variation of equilibrium adsorption intensity (RL) with initial dye (Crystal violet) concentration (Ci)

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.

$$q_e = K_F C_e^{\frac{1}{n}} \qquad (6.11)$$

Where, 'K_F' is the Freundlich constant ((mg/g). $(mg/L)^{-n}$) 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.

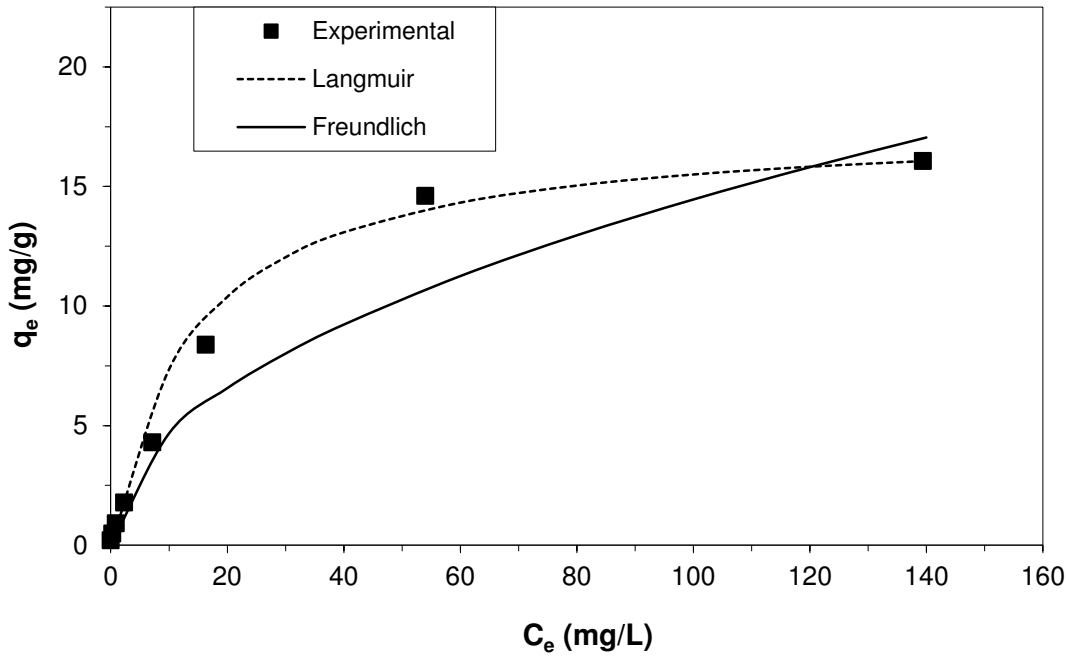


Figure 6.12: Equilibrium isotherms for the adsorption of Crystal violet on CLP.

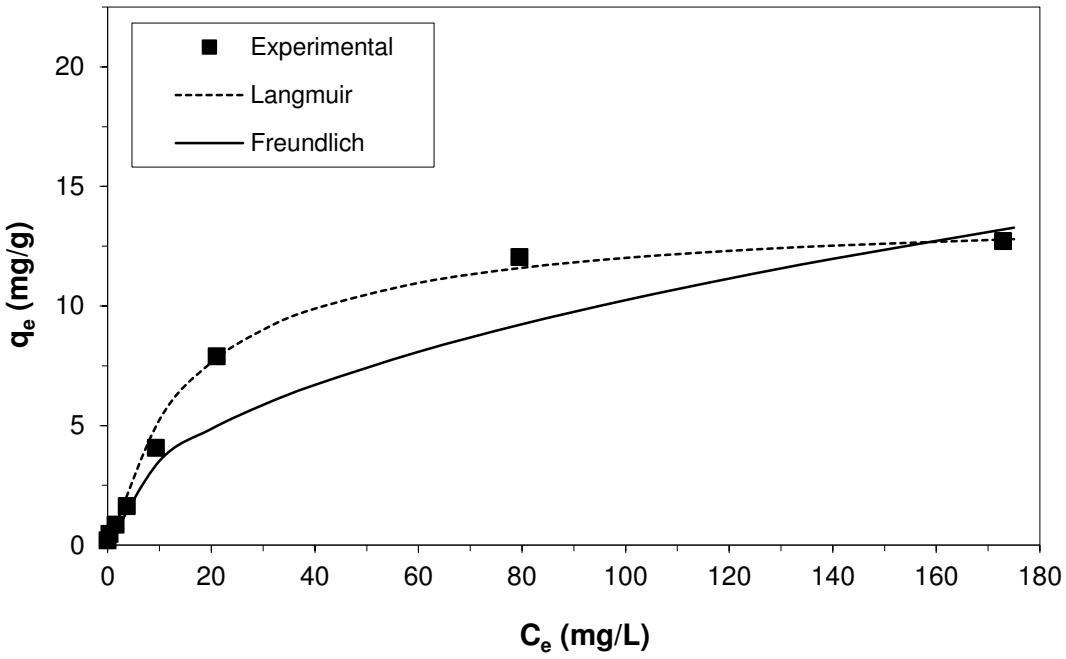


Figure 6.13: Equilibrium isotherms for the adsorption of Brilliant green on CLP.

From this figures (6.12,13) , we can be observed that the equilibrium adsorption between Brilliant green dye and Crystal violet dye- CLP can better be represented by Langmuir isotherm than the Freundlich isotherm.

CHAPTER 7
CONCLUSION AND FUTURE PROSPECTUS

Castor leaf powder (CLP) has been synthesized from mature Castor leaves. The prepared Castor leaf powder (CLP) has been successfully applied for the adsorptive removal of Brilliant green and Crystal violet dyes from their aqueous solutions. The following conclusions have been derived from the experimental analysis carried out so far. The prepared Castor leaf powder (CLP) is found to be more effective than the synthetic adsorbent presented in the literatures.

- The optimum CLP concentration obtained from the experimental studies for Brilliant green and Crystal violet is 15g/L and 10g/L respectively.
- λ_{max} for Crystal violet and Brilliant green solution was found to be 588 nm and 625 nm respectively. The calibration curve of Crystal violet and Brilliant green is also obtained.
- Optimum adsorption times were 2 hrs, for both Crystal violet and Brilliant green dyes.
- Optimum pH values were 8 and 10 for Crystal violet and Brilliant green dyes respectively.
- Optimal stirrer speeds were found to be 200 rpm and 300 rpm using CLP for the removal of Crystal violet and Brilliant green dyes 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 for Brilliant green but for Crystal violet it increased with increase in temperature.
- Experimental data matches well with the pseudo-second-order kinetics.
- Experimental data matches well with the Langmuir than Freundlich isotherm.

Most important observation in this work is that the Castor leaf powder (CLP) has been synthesized from mature castor leaves, i.e. CLP could act as a very effective adsorbent for the removal Brilliant green dye as well as Crystal violet dye. As it was suggested in literature, CLP shows partially cationic in nature 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 CLP for the removal of other industrial dyes.
- Using the CLP for industrial wastewater treatment in continuous mode (Fixed bed or fluidized bed studies).
- Removal of other dyes from water by adsorption with the CLP.

Chapter 8

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