

**The Preparation and Characterization of Phosphoric
Acid modified *Ferula Communis* Biomass and its
Application in the Removal of BR-9 Dye**

Luki Stella Nabukue

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Approval of the Institute of Graduate Studies and Research

Prof. Dr. Elvan Yılmaz
Director

I certify that this thesis satisfies the requirements as a thesis for the degree of Master of Science in Chemistry.

Prof. Dr. Mustafa Halilsoy
Chair, Department of Chemistry

We certify that we have read this thesis and that in our opinion it is fully adequate in scope and quality as a thesis for the degree of Master of Science in Chemistry.

Assoc. Prof.Dr. Mustafa Gazi
Supervisor

Examining Committee

1. Prof. Dr. Elvan Yılmaz
2. Assoc. Prof. Dr. Mustafa Gazi
3. Asst. Prof. Dr. Mehmet Garip

ABSTRACT

In this study, the potential of *Ferula Communis* biomass (FC) was evaluated for removal of cationic dye from aqueous solution. Phosphoric acid modified FC was utilized to remove basic red 9 (BR-9) under varying adsorption parameters such as pH, temperature, contact time, adsorbent dosage, and ionic strength. The adsorption process using modified FC (PFC) was evaluated under isothermal conditions and Langmuir model showed monolayer adsorption of 354.89mg/g with high R^2 value of 0.9997 compared to Freundlich model.

The adsorption process was evaluated under various kinetic models. The experimental results indicated that BR-9 removal fit well with pseudo-second order kinetic and the treatment process is exothermic and spontaneous in nature. The obtained results showed that PFC can be used as an alternative adsorbent for the treatment of dye-containing wastewaters.

Keywords: *Ferulla Communis*, Basic Red 9 (BR9), Biomass, Dye Removal, Adsorption, Water Treatment.

ÖZ

Bu çalışmada, katyonik boyaların sulu çözeltilerden gideriminde, *Ferulla Communis* biyokütlesinin (FC) potansiyeli değerlendirilmiştir. Fosforik asit modifiye FC, pH, sıcaklık, temas süresi, adsorban dozaj ve iyonik kuvveti gibi çeşitli adsorpsiyon parametreleri altında, bazik kırmızı 9 (BR-9)'un giderimi için kullanılmıştır. İzotermik şartlar altındaki Modifiye FC (PFC) kullanılarak yapılan adsorpsiyon işlemleri değerlendirilmiştir ve Langmuir modeli Freundlich modeli ile karşılaştırıldığında yüksek, R^2 , 0.9997, değeri ile Langmuir modeli 354.89mg/g'lık tek tabakalı adsorpsiyon göstermiştir.

Adsorpsiyon süreci çeşitli kinetik modeller altında değerlendirilmiştir. Deneysel sonuçlar, BR-9'un gideriminin yalancı ikinci dereceden kinetik ile iyi uyumlu olduğunu ve iyleştirme sürecinin de ekzotermik olarak doğada kendiliğinden olduğunu göstermiştir. Elde edilen sonuçlar, PFC boya ihtiva eden atık suların iyleştirilmesi için alternatif bir adsorban olarak kullanılabileceğini göstermiştir.

Anahtar Kelimeler: *Ferulla Communis*, Bazik Kırmızı 9 (BR9), Biokütle, Boya Giderimi, Adsorpsiyon, Su İyleştirme.

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TABLE OF CONTENTS

ABSTRACT.....	iii
ÖZ	iv
ACKNOWLEDGEMENT	v
LIST OF TABLES	ix
LIST OF FIGURES	x
ABBREVIATIONS	xi
1 INTRODUCTION	1
1.1 Effect of Contaminated Dye Containing Water	1
1.2 Adsorbent	2
1.2.1 Classification of Adsorbents.....	3
1.3 Dyes.....	5
1.4 Methods of Waste Water Treatments	7
1.4.1 Physical Methods of Waste Water Treatment	7
1.4.2 Chemical Method	8
1.4.3 Biological Method	9
1.5 Activation/Modification of Adsorbent	10
1.5.1 Physical Activation.....	10
1.5.2 Chemical Activation	11
1.6 Literature Review	11
1.7 Terminology	12
1.7.1 Chemisorption	12
1.7.2 Physisorption	12
1.7.3 Langmuir Isotherms.....	12

1.7.4 Freundlich Isotherms	12
1.8 Biosorption Processes.....	12
1.9 Objective	16
2 EXPERIMENTAL.....	17
2.1 Equipment	17
2.2 Chemical Used	18
2.3 Preparation of Stock Solution of Dye.....	19
2.4 Adsorbent Synthesis	19
2.4.1 Effect of Concentration	21
2.4.2 Effect of Dosage	21
2.4.3 Effect of pH	21
2.4.4 Effect of Ionic Strength	22
2.4.5 Effect of Temperature.....	22
3 RESULTS AND DISCUSSION	23
3.1 FT-IR Analysis	23
3.2 Adsorption Calibration	24
3.3 Batch Adsorption Studies	25
3.3.1 Effect of Change in Concentration on Adsorption	26
3.3.2 Effect of Contact Time on Adsorption	27
3.3.3 Effect of Dosage on Basic Red Dye Adsorption	28
3.3.4 Effect of pH on Basic Red Dye Adsorption	29
3.3.5 Effect of Ionic Strength on Dye Adsorption.....	30
3.3.6 Effect of Temperature on the Removal of Basic Red 9 Dye.....	31
3.4 Adsorption Study.....	32
3.4.1 Thermodynamic Study	33

Figure 3.9: Pseudo Second Order Plot.....	36
3.4.2 Adsorption Isotherm Parameters for the Adsorption of Basic Red Dye ...	36
3.4.3 The Adsorption Kinetics of Basic Red Dye	37
4 CONCLUSION.....	41
REFERENCES	42

LIST OF TABLES

Table 1: Classification of Different Adsorbents.....	2
Table2: Types of Dyes.....	2
Table 3: Chemicals and Manufacturers.....	3
Table 4: Thermodynamic Parameters for Adsorption of BR-9 onto PFC at Different Temperatures.....	4
Table 5: Isotherms Parameters for Adsorption of BR-9 onto PFC at Different Temperatures.....	6

LIST OF FIGURES

Figure 2.0: Structure of Basic Red 9 dye.....	19
Figure 2.1: Ferula Communis Plant.....	21
Figure 3.0: FT-IR for the Raw, Modified and Dye Adsorbed Ferula Communis.....	23
Figure 3.1: Calibration Curve of Basic Red Dye Adsorption onto PFC.....	25
Figure 3.2: A, B, and C represent Raw, Phosphoric Acid Modified, and Dye Adsorbed Ferula Communis respectively.....	26
Figure 3.3: Effect of Initial Dye Concentration on Adsorption.....	27
Figure 3.4: Contact Time Effect on Adsorption of PFC.....	28
Figure 3.5: Effect of Dosage on the Adsorption of Basic Red Dye.....	29
Figure 3.6: Effect of pH on the Adsorption of Basic Red Dye from Aqueous Solution.....	30
Figure 3.7: Effect of Ionic Strength on Adsorption of Basic Red Dye.....	31
Figure 3.8: Effect of Temperature on Adsorption of Basic Red Dye.....	32
Figure 3.9: Pseudo Second Order Plot.....	39
Figure 3.10: Basic Red dye stock solution before and after adsorption.....	40

ABBREVIATIONS

MFC: Modified Ferula Communis

RFC: Raw Ferula Communis

AFC: Activated Ferula Communis

FTIR: Fourier Transform Infra- Red Spectroscopy

BR-9: Basic Red-9 Dye

PFC: Phosphoric Acid Modified Ferula Communis

FC: Ferula Communis

MB: Methylene Blue

RB: Rhodamine Blue

RPM: Revolution per minute

Chapter 1

INTRODUCTION

The notion of applying color to fabric has been known to mankind since 3500BC. The process of dyeing of fabrics were usually done using dyes that were extracted from fruits, flowers, some insects, fish, starch producing materials, and vegetables. The dyes that were obtained from these materials had limited color range and could easily degrade during washing or when exposed to sunlight. It is upon this basis that dye production has been the order of the day in the field of research nowadays. The estimated amount of dye that is being produced in the world today is about 10000 tons per year (Zoonoonzi et al, 2008). These dyes possess properties such as stable to light, resistant to aerobic digestion, intractable organic molecules, stable to heat and oxidizing agents, which makes them difficult to be treated (Crini, 2006). The subsequent chapters provide brief information about dyes and their effects in waste water bodies, formal and current treatment technologies, with special emphasis given to adsorption as a method of treatment using low cost adsorbent such as Biomass.

1.1 Effect of Contaminated Dye Containing Water

In 1856, WH Perkins came out with the applications of synthetic dyes. Synthetic dyes are capable of providing a wider range of colors compared with natural dyes. However their toxic nature has become the talk of the day and calls for concern to the environmentalists (Kant, 2012).

Industries such as the textile industries, plastics, leather, and paper amongst others are noted for being heavy consumers of dyes and water; their industrial end products are large amounts of colored waste (Crini, 2006). Studies have revealed that the waste of all these industries are made up of compounds like naphtha, nitrates, arsenic, mercury and acetic acid and when they come in contact with organisms ,they causes adverse effects on all forms of life (Kant, 2012). Also, compounds like formaldehyde, hydrocarbons and other non-biodegradable dyeing chemicals found in these dyes react with other components in wastewater to form products that are carcinogenic to man and aquatic life (Crini, 2006). More so, the presence of colloidal materials tend to produce oily solutions which makes water become turbid, giving it a bad smell, appearance, and even color .The oily residues also prevent direct penetration of sun-rays into the water bodies thus resulting in low levels of oxygen in the water, and aquatic plants and organisms tend to suffer from this effect (Rauf et al, 2011). Also, discharge of these waste waters bodies into farm lands causes soil infertility and also renders rivers, streams amongst others, toxic and unsafe for consumption. Lastly, effluents from wastewater bodies are usually at high temperatures at acidic pH hence causes environmental degradation and illnesses to humans (Nguyen and Ruey-Shin, 2013).

1.2 Adsorbent

An adsorbent is a porous material with a large surface area which is capable of adsorbing other materials unto its surface through the use of intermolecular forces. Examples include activated charcoal; saw dust, natural propylene glycol, and polymeric adsorbents. (Bhatnagar and Minocha, 2006).

Most importantly adsorbents are used in water treatments for the removal of pollutants found in waste-waters. Adsorbents can also be applicable in the process of vulcanization, and for recovering sulphur from natural gas. Adsorbents can be characterized with respect to their porosity, which helps to increase surface area and thus the adsorption kinetics (Bhatnagar and Minocha, 2006).

1.2.1 Classification of Adsorbents

Table 1: Classification of Different Adsorbent Types

Natural Adsorbents	These are adsorbents whose properties can easily be altered to enhance adsorption. They include ores, clays, minerals, charcoal etc. They are readily available and are cheaper.
Synthetic adsorbents	They mostly come from natural origin, waste sewage sludge, and industrial waste.
Based upon the type of element present.	Examples, presence of oxygen makes it hydrophilic and polar. For carbon based compounds is hydrophobic and non-polar.
Inorganic Adsorbents.	Inorganic materials are used effectively as adsorbents and are mostly synthetic in origin. Some examples include; CaO, limestone, MgO, and silicates. They mostly occur in hydrated or anhydrous states, others are commercial products e.g alumina, zeolite, silica etc. (Stojanovic et al, 2012).
Organic	These are adsorbents that are organic of origin. They

Adsorbents	<p>maybe synthetic or natural. Examples are chitin, collagen, starch, polyamide, polysaccharides etc.</p> <p>They may also be of commercial sources e.g. wood, coconut, peat, recycled tires etc. (Stojanovic et al, 2012).</p>
Polymeric Materials	<p>They are made up of spherical beads which are opaque, and possess the ability to change color, with their color changing ability varying with the type of product. They mostly appear white; though some are black, orange, and brownish in color. examples include polystyrene\divinyl benzene copolymers, with high pore volume and circular shape. They also have macro pore that are formed collectively from micro pore. It also has beads with porous gels which facilitate adsorption. They are mostly activated by pyrolysis. Examples are Chloro methylated, vinyl pyridine etc. (Stojanovic et al, 2012).</p>
Biomass	<p>Biomass refers to bio molecules that are effective in the removal of selected ions and other molecules from solution. This process is called Bioadsorption. Some of this biomass includes algae, yeast, plants, and bacterial. The process involves a fast step initially called the metal-blind step and secondly a slow irreversible step. It is advantageous because material is abundant, renewable, cheap, regenerative and</p>

	possibly metal recovery can be achieved (Gregorio, 2006).
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1.3 Dyes

These are coloring compounds with different chemical composition. Its ability to ionize and produce color is due to presence of auxochromes.

Dyes are characterized as follows:

Table 2: Types of Dyes

Dyes type	Description
Reactive dyes	They form covalent bonds with the fibers in which it is in contact.
Solvent dyes	They are non-ionic and have specific substrates on which it can dissolve e.g plastic, ink, waxes.
Pigment dyes	Non-ionic, insoluble salts and can retain their structure e.g phthalocyanines.
Mordant Dyes	They are mostly metals salts and help in the fastness and act as fixing agents. They are used together with wool, silk, amongst others (Shreve et al, 1922).
Basic Dyes	These are water soluble cationic dyes applied to acrylic fibers.
Direct Dyes	They are poly azo compounds which

	<p>have high affinity for cellulose and are water soluble.</p> <p>These dyes use sulphur as a reducing agent.</p>
Cationic (basic dyes).	They are applied to paper, modified polyester, nylons etc. They are soluble in water (Ozfer et al, 2014).
VAT Dyes	They are obtained from alkaline reduction. They are water insoluble non - ionic dyes applied mainly to cellulosic fibers.
Acid dyes	(Water soluble anionic dyes); they are attached to fibers using neutral to acid dye baths.
Classification can also be based upon the type of chromophoric groups, and nuclear structure.	Examples are dyes with azo group, sulfuric group, and cationic or anionic dyes respectively.
Industrially	Can be proteinous, cellulosic etc (Christain, 2011).
Ability to form colors, solubility, fastness in coloring, bonding type (Iipupodhu and Obpazobahuemo, 2012).	

Dyes are used in the dyeing process, Textiles, paper or leather is usually heated in a solution or suspension of dyes. In printing, a dye or pigment paste is applied to the surface of the substrate and heated (Yener et al,2008).

1.4 Methods of Waste Water Treatments

Dye removal from textile effluents is an environmental issue that is of much concern these days, this is the reason why adequate method of treatment of dyes has been studied and has gained a lot of interest. Three ways by which waste water treatment can be made possible are physical, chemical and biological treatment (Gong et al, 2006).

1.4.1 Physical Methods of Waste Water Treatment

This method of treatment includes those processes irrespective of gross chemical or biological changes. It is strictly based upon a physical phenomenon of improvement of wastewater. Sedimentation and separation are common with this method, whereby solid particles are settled in a short time period by gravity.

Adsorption is a physical method which is very effective, whereby solute from waste water is transferred to the surfaces of an adsorbent which is usually porous. Dye adsorption can be influenced by the following:

- Interaction that takes place between the dye and adsorbent;
- Adsorbent surface area of exposure to dye in which it is in contact with;
- Particle size;
- Temperature at which reaction is taking place;
- pH;
- Contact time.

1.4.2 Chemical Method

In this method chemical treatment is possible through addition of some chemicals or by a chemical reaction to improve upon the quality of water. Commonly, chlorination was used whereby the added chlorine helps to kill bacteria and reduce the decomposition of wastewater. Industrially, chemical method is carried out by neutralization whereby balancing the pH of water is done by addition of an acid or a base. Possible chemical methods of treatments include; Coagulation, flocculation, precipitation, ion exchange, oxidation and ozonation.

Coagulation, Flocculation, Precipitation: these method separate colored colloids from textile effluents. Chemicals like ferrous sulphate, ferric chloride, poly aluminum chloride, cationic organic polymers are usually added to precipitate solids. The added chemicals also causes coagulation process (emulsions entrapping solids) and agglomeration of large particles sites i.e. flocculation where by non-ionic and ionic polymers are used. Electro-coagulation is an advanced method of dye treatment and color removal process. Its tasks are in the formation of flocs of metal hydroxides within the effluents. It involves electrolytic reaction at the electrodes, Coagulant formation in aqueous form of effluent, adsorption of soluble pollutants on coagulant and removal by sedimentation and flotation. For example electro coagulation treatment was applied with high efficiency for textile orange IV and acid red 14 dye containing effluents and 98% color removal was observed. (Merzouk et al, 2009).

Ion Exchange: This process has not been widely used for treatment of dye containing effluents because of the general opinion that ion exchange cannot accumulate a high range of dyes. The ionic exchange occurs due to interaction of ionic species from waste water treatment. In the waste water treatment, effluent

usually come in contact with the ion exchanger until the available exchange sites are filled up or saturated. It is a reversible process because the regenerated ion exchanger can be used again. (Robinson et al, 2001).

Oxidation Process: Chemical oxidizing agents are used in this process e.g. the use of chlorine, UV light and ozone , ferrous sulphate and peroxide or other oxidizing techniques are necessary for oxidative chemical treatment method . Main oxidizing agent is H_2O_2 activated by sunlight. Denton's reagent for example H_2O_2 and Fe (II) salts are best for treating waste water (Robinson, 2001).

Ozonation: process is also used in waste water treatment as it uses ozone that is capable of degrading chlorinated hydro carbons, phenols and pesticides (Forgacs et al, 2004).

1.4.3 Biological Method

In this method of wastewater treatment microorganisms like bacteria is used in the biochemical process of decomposition of wastewater. At the end of the process the sludge formed and other end products are converted into CO_2 , H_2O and other products.

Different biological treatment is performed for aerobic, anaerobic or both i.e. anaerobic/aerobic conditions. The most highly used biodegradation process involves aerobic microorganisms which use molecular oxygen as acceptor during respiration (Zaharia and Daniela, 2001). Biologically, dyes are degraded into less complicated materials and mineralized to carbon dioxide and water either in the presence or absence of oxygen (Zaharia et al 2012).

1.4.4 Adsorption Method

Adsorption process of removal of organic contaminants from waste water has being discovered as the most efficient method of waste water treatment. This method of

water treatment is advantageous over the rest of the methods such as filtration, electro coagulation, flocculation etc. This is because the operation and setting up of the plant is not complicated, it is very simple and less costly (Bhatnagar and Minocha, 2006). This method is capable of treating both organic and inorganic pollutants. Mostly low cost adsorbents are used in adsorption processes which are readily available. Due to the above advantages of adsorption over other methods, there has been an increased search for low cost adsorbents with high capabilities to bind with pollutants. Examples of some low cost adsorbents include; saw-dust, ginger, rice-straw and amongst others. Some agricultural and industrial waste are used as low cost adsorbents (Crini, 2006).

1.5 Activation/Modification of Adsorbent

By activation of adsorbent we aim at increasing the surface area, breaking particles to smaller pieces, and heating. Activation is therefore a means to improve upon the adsorbing power of an adsorbent. An example is activated carbon which is widely used nowadays. It is highly porous, amorphous solid of micro crystallites prepared in powder form which can be obtained either via physical or chemical activation (Rsubha and Namasivayam, 2009).

1.5.1 Physical Activation

Physical method of activation gives an idea of how the size and effectiveness of the pores vary. It is made up of two steps, carbonization and activation. In carbonization, there is heating to separate immediate products to tar and hydrocarbons and removal of generated gasses. Process is completed by heating between 400-600°C in an oxygen deficient atmosphere and the product of carbonization is mostly carbon. Activation is done by exposure to oxidizing agents at high temperature. This burns off pore blocking structures created in carbonization phase thus causing the

development of pores. The activated carbon is then used for waste water treatment due to its large macro pore and meso pore volume and high surface area.

1.5.2 Chemical Activation

Chemical activation of adsorbent is a one-step method used for the preparation of activated carbon. Chemical activating agents that are used include H_3PO_4 , KOH , NaOH , K_2CO_3 , H_2SO_4 . These agents help to increase the porosity by dehydration and degradation. (Abedi and Bahreini, 2010). Chemical activation is better than physical due to lower treatment temperatures and treatment time. Both carbonization and impregnation processes occur simultaneously. The products are of better porosity with larger surface area and produce due to prevention of the formation of volatile compounds including tar and because of dehydrogenation properties of chemical agents (Williams and Reed, 2004).

1.6 Literature Review

Several methods of treatment of effluent discharged from industries such as the textile, leather, plastic industries amongst others that are aimed at reducing the quantity of toxic effluents from waste water had several disadvantages such as high cost of operation, nonrenewability, and increase the amount of toxic waste in the environment.

Biosorption has been regarded as a better option because;

- Mostly low cost adsorbents are used in the process of adsorption.
- It gives a more efficient method of treatment.
- The biosorbents used in this process is renewable.
- It minimizes both chemical and biological sludge.
- Biosorbents are generated easily and metal recovery is also possible.

1.7 Terminology

1.7.1 Chemisorption: In chemisorption the adsorbate binds more specifically onto the solid surface, thus only monolayer adsorption is possible.

1.7.2 Physisorption: It occurs when an adsorbate loosely binds onto the solid surface through van de Waals type of interactions.

1.7.3 Langmuir Isotherms: It is used to describe the process of chemisorption and works on the following assumptions; Adsorbent surface is in contact with solution in which the adsorbate is present in. The surface of the adsorbent has a specific number of sites in which the solute molecules are adsorbed. Only monolayer adsorption is possible and all sites have equal energy Foo and Hameed,(2010).

1.7.4 Freundlich Isotherms: This is applied to multi-layer adsorption; it involves a non-uniform distribution of adsorbate on the sites present on the adsorbent .It is applied in heterogeneous systems Foo and Hameed,(2010).

1.8 Biosorption Processes

Pregnesh et al, (2011) used sewage sludge to adsorb basic red-12 from aqueous solution. In the experiment, a study on how the various effects such as the pH, dosage of adsorbent ,contact time, temperature and initial dye concentration affects the adsorption capacity of BR-12 dye was carried out. FTIR, XRD and SEM analysis of the adsorbent was done. This study showed that at an equilibrium state of adsorption was achieved at 120mins, adsorption process was exothermic i.e. increase in temperature resulted to an increase in the rate of the reaction. According to the researchers, intra-particle diffusion process was favored and the adsorption process followed a pseudo first order. Langmuir and Freundlich equations are applied to the data and the observed maximum adsorption capacity was found to be 295.85mg/g.

Fu and Viraraghavan utilized fungi biomass, *Aspergillus Niger* for the biosorption of four different dyes which are: basic blue 9, acid blue 29, Congo red and disperse red 1. Here adsorption of the above mentioned dyes is based upon the presence of functional groups such as carboxyl, amino, phosphate and lipids found in the fungal biomass *A.Niger*. These functional groups were modified using methanol and hydrochloric acid. It was realized that bio sorption by fungal biomass *A.Niger* is highly depended upon the type of functional groups present. The mechanism of biosorption of acid blue 29 was due to electrostatic attraction, and for disperse red, chemical and physical adsorption took place at the same time and lipid fractions were the main binding sites, with amino and carboxylic acid the minor binding sites. For Congo red amino groups are the major binding sites and the type of mechanism of reaction was electrostatic attraction. Carboxylic acid, phosphate and lipids could also be binding sites too. Disperse red 1 showed that the lipid fraction could be the major binding sites while the amino and carboxylic groups are minor binding sites. For basic blue carboxylic and amino groups are good binding sites while phosphates and lipids are minor binding sites (2002).

Mona et al., (2011) studied the biosorption of reactive red 198 using Cyanobacteria *Nostoc Linkia HA 46* as adsorbent. Calcium alginate was used to immobilize the biomass. In this experiment, the study was done at a pH range from 2 - 6, and at temperatures of 25°C to 45°C with a dye concentration of 100-500mg/L. A maximum adsorption was observed at 93.5 mg/L, at a pH of 2.0 with a temperature of 35°C and 100mg/L dye concentration with 94% of dye removal obtained. FTIR results revealed bio adsorption was as a result of the hydroxyl, amide, carboxylate, and methylene groups present.

Yuh-Shan et al, (2005) removed basic red dye from aqueous solution using tree fern biomass as biosorbant. In the study the sorbent particle size was varied with temperature to determine the adsorption capacity of tree fern when used as adsorbent. The result proved tree fern to be a low cost adsorbent that followed the Langmuir isotherm. Moreover it was observed that reducing the size of the particle resulted to an increase in the sorption capacity. An equilibrium monolayer sorption capacity was observed at 1.01mmol per gram at a temperature of 30 degree and particle size of 38 - 45micro meter. Sorption was maximum at 408mg/g and ΔG° , ΔH° , ΔS° calculated values showed process was exothermic and spontaneous.

Another research on dye removal by low cost adsorbent Hazelnut shells was conducted and its adsorption capacity was compared with wood sawdust. In this study hazelnut shells was ground to a powdery form and used to adsorb methylene blue dye of concentration up to 1000mg/L. Also, the adsorption using acid blue 25 made up to 500mg/L was also investigated. The result was then compared with the result obtained from adsorption using sawdust made from different wood types. Results showed that the adsorption kinetics followed a second order; the Langmuir isotherms were suitable to characterize the adsorption process. Methylene blue 25 dye adsorption was observed to have a higher adsorption capacity using hazelnut shells (Ferrero, 2007).

Another researcher Nityanand et al,(2005). Reported that dead biomass is more effective in adsorbing organic pollutants than live biomass .In this research, dead micro fungi *Fomes Fomentarius* and *Phellinus Ignirius* were used in the removal of methylene blue and Rhodamine blue from solution.The Freundlich and Langmuir isotherms showed Methylene blue had maximum adsorptions at 202.38mg/g and

232.73mg/g respectively, hence it was a mono layer adsorption, and Rhodamine at 36.82mg/g and 25.12 mg/g respectively. MB adsorption was higher than RB due to its larger molecular weight, larger ionic size, and presence of COOH in RB. Increase in pH sorption of MB increases while that of RB decreases.

Hairul and Kelly, (2011) investigated the adsorption of basic red 46 dye from waste water using a commercial grade granular activated carbon made in a fixed bed column. The initial concentrations of BR46 were in the range 50-250mg/L at a pH of 8.0, and the bed height was maintained at 100mm and flow rate 50ml/min. It was observed that the amount of BR46 adsorbed reduces from 65.71 to 36.06 mg/L as the initial dye concentration increases from 50-250mg/L. Percent adsorption was highest at lowest initial dye concentration, due to lower transport caused by a reduction in the diffusion coefficient as there is more time for binding of dye molecules to adsorption sites. Higher concentrations will result to saturation at adsorption sites and dye molecules ended up in the effluent. The adsorption followed the Freundlich isotherm model.

In a similar manner, this research work is focused on adsorption of basic red 9 dye from aqueous solution using *Ferula communis* as biomass and low-cost adsorbent. The aim of this work is to minimize cost using an efficient low cost adsorbent for the adsorption of basic red 9 dye. Modification of FC was done using phosphoric acid to increase the number of negative charges on the FC whose charge is opposite to that of BR-9 dye and thus increasing adsorption. Moreover, parameters such as pH, dosage effect, contact time, effect of concentration were studied, and thermodynamic parameters examined. Calculations were used to determine if adsorption followed a

pseudo first or second order reaction and the values of ΔG° , ΔS° , ΔH° was also be determined.

1.9 Objective

The objective of my research is;

- To prepare low-cost and high capacity adsorbent using FC biomass and to modify it using phosphoric acid.
- To examine the removal of Basic red dye from aqueous solutions using the modified FC as adsorbent.
- To understand the adsorption mechanism via the utilization of isotherm equations, thermodynamic evaluation and kinetic analyses.

Chapter 2

EXPERIMENTAL

2.1 Equipment

Mechanical stirrer (Heidolph Hei-Standard),

UV| Vis –Spectrophotometer (T80+ UV|Vis Spectrometer)

Mechanical Agitator

Electronic Balance

Heating Oven

Grinding Machine

Mechanical Stirrer

Hotplate Stirrer

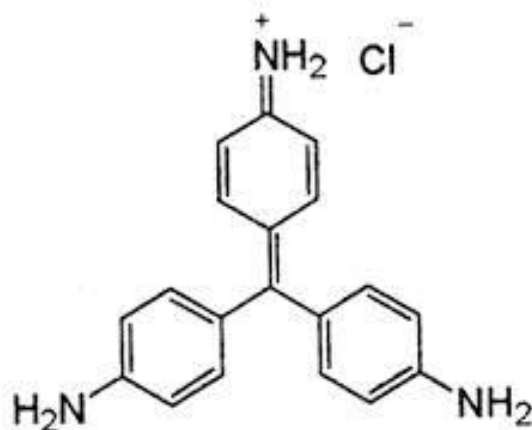
Perkin Elmer spectrum 65 FT-IR Spectrometer

Beakers, conical flask, measuring cylinders, round bottom flask, stirrer, pipettes, burettes etc.

2.2 Chemical Used

Table 3: Chemicals and Manufacturers

Materials	Manufacturers
Sodium Hydroxide	Aldrich-Germany
Basic red 9 Dye	Sigma-adrich.com
Potassium Chloride	Aldrich-Germany
Hydrochloric Acid	Riedel-deHaen-Germany
Sodium Hydrogen Carbonate	Aldrich-Germany
Potassium dihydrogen Phosphate	Aldrich-Germany
Disodium Hydrogen Phosphate	Aldrich-Germany
Sodium Sulphate	Aldrich-Germany
Phosphoric acid	Aldrich-Germany



Molecular structure of basic red 9 dye (C₁₉H₁₈ClN₃)
 Molecular Weight; 323.82g
Common names: Para magenta, Para Rosaline

Figure 2.0: Structure of Basic red 9 dye

2.3 Preparation of Stock Solution of Dye

A stock solution of basic red 9 was prepared dissolving 100mg of basic BR-9 dye in 500mL of distilled water to make a 200mg/L concentration. The solutions which were further used in carrying out the rest of the experiments were obtained by further diluting to required quantities using the equation below;

$$M_1V_1 = M_2V_2 \dots\dots\dots (1)$$

2.4 Adsorbent Synthesis

Ferula Communis plant was obtained from Pergamos area in the Famagusta areas of Cyprus was used as biomass. The biomass obtained was washed several times using distilled water to get rid of impurities like sand and dirt, it was then dried in an oven

at 50°C for 24 hours. It was cut into smaller sizes and grounded into smaller particles using a grinding machine. It was then sieved using a 500 μm sieve. Surface modification was done by weighing 30g of the ground FC into a beaker and adding 2.0M phosphoric acid into it and stirred at 80°C for an hour. It was further dried at 100°C for 24 hours. The FC obtained was cooled, washed again several times and treated with 0.1M NaOH for 60min. The excess NaOH is removed by washing several times with distilled water. It was then dried at 50°C for 24 hours to obtain modified FC.



Figure 2.1: Ferula Communis Plant

2.4.1 Effect of Dye Concentration

The adsorption experiment was done by shaking 200mg of modified FC with a 80mL of aqueous solution of basic red dye of different concentrations such as 20mg/L and 50mg/L. Shaking was done at 250rpm at a time interval of 3, 6 and 9 hours. 5mL of solution was pipetted and the absorbance using a UV-Spectrometer was taken.

2.4.2 Effect of Adsorbent Dosage

This effect was monitored by taking into consideration different dosages of the modified FC. Several masses 100mg, 200mg, 300mg, and 400mg were used. To each was added 40ml of aqueous solution of dye with agitation of 200rpm for a time period of 9hours. 5mL of the solution was pipetted and its absorbance measured using UV – spectrophotometer.

2.4.3 Effect of pH

In a similar manner the effect of pH was observed by measuring 20ml of buffer solution of pH 2, 4, 6, 8 and 10, adding 20ml of 50mg/L of dye solution in a volumetric flask and 100mg of the modified FC and agitating at 200 rpm. The buffer solutions were prepared as follows:

Preparation of Buffer pH 2

This was done by mixing 50mL of 0.2M solution of KCL and 13mL of 0.1M solution of HCL and diluted in a 200mL volumetric flask using distilled water.

Preparation of Buffer pH 4:

Mixing 7.1mL of 1M acetic acid solution with 12.5mL of 1M of sodium hydroxide solution and diluted with distilled water up to the 250mL mark.

Preparation of Buffer pH 6:

This was done by mixing 100mL of 0.1M of KH_2PO_4 and 11mL of 0.1M Sodium hydroxide, in a 200mL volumetric flask and distilled water added up to the mark.

Preparation of Buffer pH 8:

This was done by mixing 100ml of 0.1M KH_2PO_4 with 93.4mL of 0.1M Sodium Hydroxide and adding distilled water up to the 200mL mark.

Preparation of Buffer pH 10:

This was done by mixing 25mL of 0.05M Sodium carbonate solution with 5.35mL of 0.1M sodium Hydroxide solution and distilled water added to make it up to 250mL.

2.4.4 Effect of Ionic Strength

For this effect, 0.5M, 1.0M, 1.5M and 2.0M solution of potassium chloride were prepared. 40mL of 50mg/L dye concentration and 40mL of the different concentrations of potassium chloride were pipetted and put into four different volumetric flask .100mg of modified FC was added and shaking was achieved with the use of a mechanical shaker for 9 hours using 200rpm . Then 5mL of each solution was pipetted into a test tube and the absorbance was measured using the UV-spectrophotometer.

2.4.5 Effect of Temperature

40ml of BR-9 (50mg/L) was measured and put into a 3 necked round bottom flask. This was then transferred to hot plate and agitated at 200rpm; temperature was varied in the range of 35°C, 50°C, 65°C and 80°C. Then 100mg of modified FC was added and the result observed after 9hours, and the absorbance determined.

Chapter 3

RESULTS AND DISCUSSION

3.1 FT-IR Analysis

FT-IR analysis was carried out using the raw, modified and BR-9 Adsorbed on modified FC. All samples were prepared and analyzed in the powdered form. The results are shown in the diagram below (Figure 3.1).

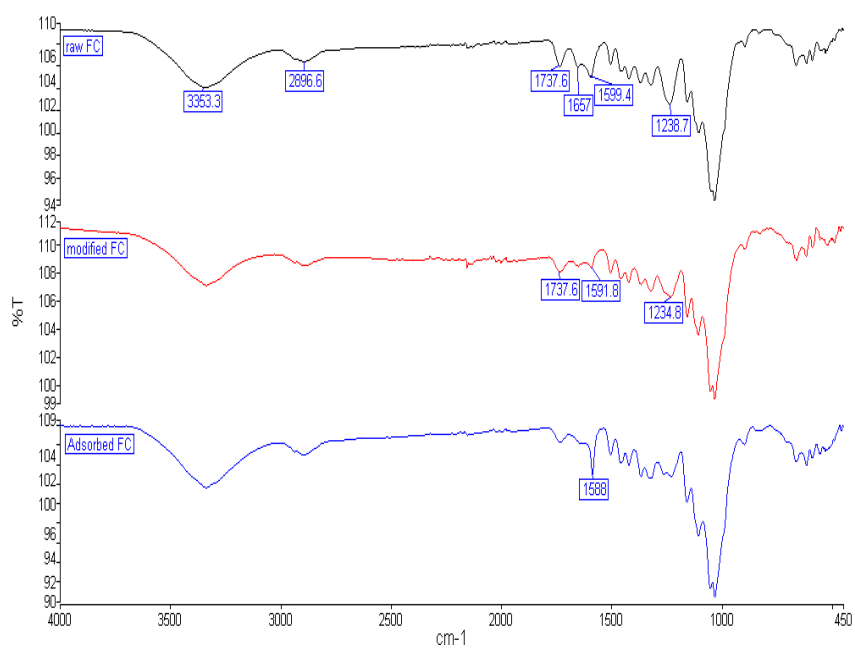


Figure 3.1: FT-IR Spectrum of Raw FC, phosphoric acid modified FC and BR-9 adsorbed dye on PFC

The FTIR for the three spectrums is represented above in Figure 3.1. This gave an idea of what was taking place at the active sites of the FC at different conditions. For the raw FC sample there is the presence of a peak at 3363.3cm^{-1} , this represents an O-H stretch, and the peak at 2896.6cm^{-1} indicates the presence of C-H bond. There is also a C=O stretch at 1737.6cm^{-1} , and the amide I and II bonds are present at 1657cm^{-1} and at 1599cm^{-1} respectively. The second spectrum shows the modified FC using Phosphoric acid. A reduction is observed at these peaks, 1737.6cm^{-1} , 1591.8cm^{-1} and 1234.8cm^{-1} . This could probably be due to the effect of adding phosphoric acid which could have resulted in the possible degradation or a reduction in the crystallinity of the modified FC. Finally the peak at 1588cm^{-1} observed on the spectrum labeled Absorbed FC could be as a result of interaction between the amide functional groups on PFC and the BR-9 dye.

3.2 Adsorption Calibration

Direct red dye of analytical grade of five different concentrations were prepared from stock solution of 5mg/L. Using the Perkin-Elmer UV-Vis spectrometer their respective absorbance's were determined. The calibration curve for the results of the absorbance at different concentrations were plotted.

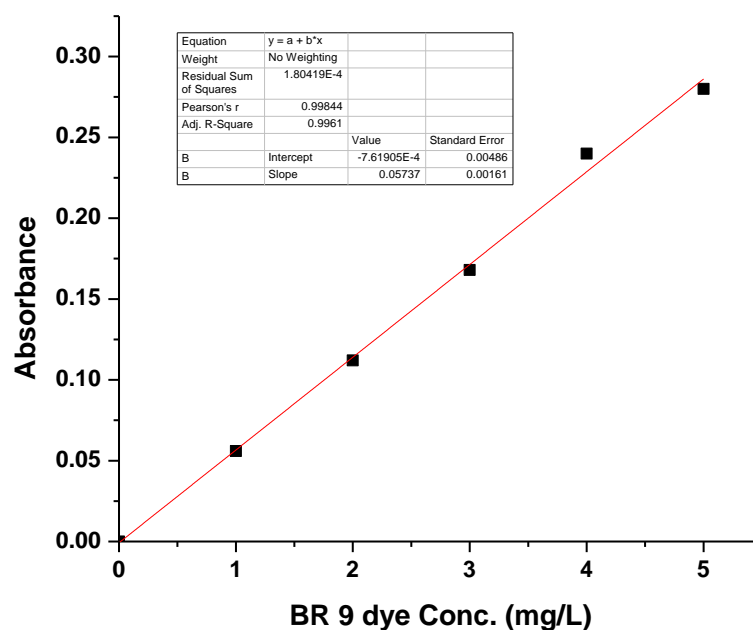


Figure 3.2: Calibration curve of basic red dye

3.3 Batch Adsorption Studies

The batch experiments were performed by using FC that was modified with phosphoric acid. In the experiments, various effects were taken into consideration to observe how it affected adsorption. Some of these effects include the effect of contact time, temperature, different dosage of modified *Ferula Communis*, effect of concentration, effect of pH amongst others.

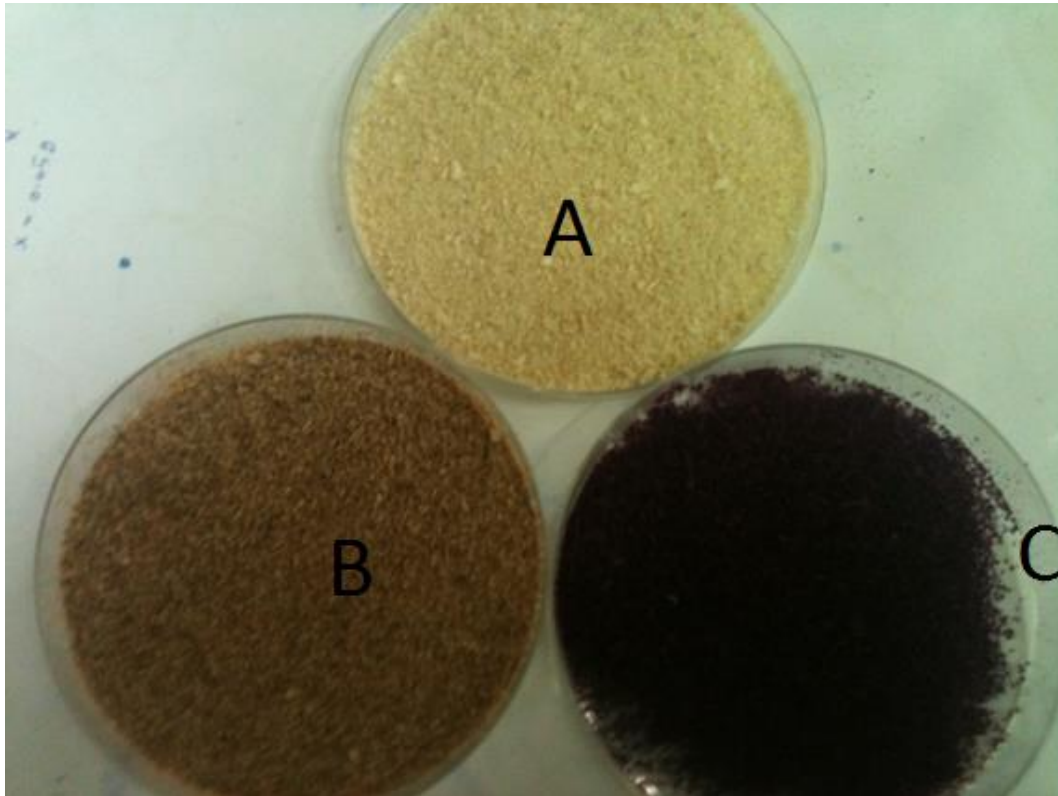


Figure3.3: A, B and C represent raw, phosphoric acid modified, and dye adsorbed Ferula Communis respectively.

3.3.1 Effect of Change in Concentration on Adsorption

Generally the amount of dye adsorbed per unit mass increases with increase in initial dye concentration as the concentration of dye increases from 20mg/L to 50mg/L, as shown by the plot of amount of dye adsorbed at 20ppm and 50ppm respectively, against time in minutes shown by Fig 3.3 bellow. The result graphically shows an increase from 25mg/g and 30mg/g to 135mg/g and 260mg/g at 250 minutes respectively for 20mg/L and 50mg/L of dye adsorbed. This increase is due to increase in the number of collisions between the anions of the adsorbate and the cations of the adsorbent thus increasing the sorption process. At 350minutes there is no tangible increase observed in the removal of BR-9 dye, and this could be as a result of saturation at the active site of adsorbent. A constant value of 380mg/g for 50ppm of dye, and 190mg/g for 20ppm of dye was observed between 400 to 540

minutes. This indicates that more adsorption was achieved at higher concentration due to increase in the number of moles as concentration increases.

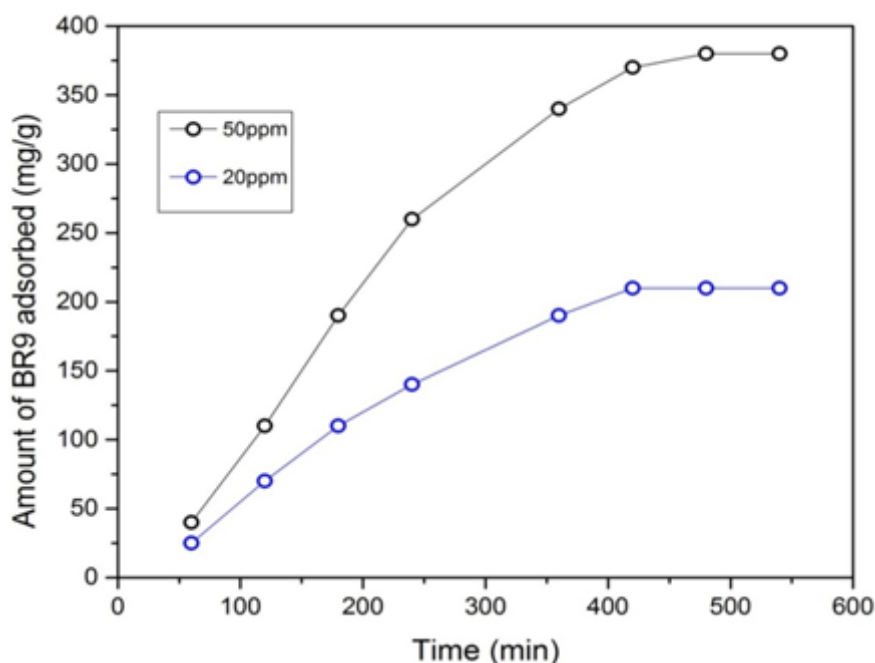


Figure 3.4: Effect of initial dye concentration on adsorption.

3.3.2 Effect of Contact Time on Adsorption

The results in figure 3.4 below showed that adsorption increases with contact time. This increase in contact time occurred in two different parts. In the first part, there is rapid increase in sorption reaching 200mg/g at a time interval of 80 minutes, after which in the second part of the reaction, adsorption increases slightly up to 230mg/g and then a plateau is observed at 260mg/g between time interval of 200 and 360 minutes. The explanation of this change is due to the fact that all the adsorption sites are exposed during the first phase of the reaction and slow down in the second phase as a consequence of diffusion progression from the bulk to the sites.

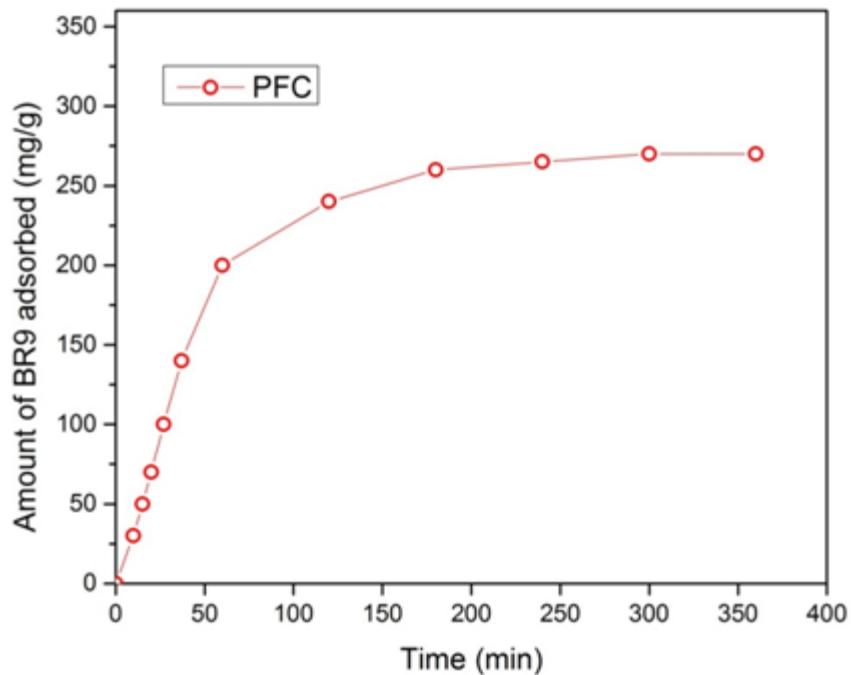


Figure 3.5: Contact time effect on adsorption of PFC

3.3.3 Effect of Dosage on Basic Red Dye Adsorption

The adsorption effect of MFC on BR-9 was studied at different doses of 100mg, 200mg, 300mg and 400mg at a constant BR-9 concentration of 50ppm, neutral pH and room temperature with an agitation speed of 200rpm. The result from the graph as shown below in figure 3.5 showed that increasing the adsorbent doses lead to a higher amount of dye removal. It is evident that the adsorption of BRD onto MFC increases from 120mg/g to 235mg/g as the doses of the adsorbent increases from 100 to 150mg. Further increase from 150 to 300 mg of MFC resulted to a higher dye removal amount of 375mg/g. This is as a result of the increase in surface area and number of sites available for adsorption. Further addition of adsorbent to dye will lead to saturation since the sites available for adsorption must have been completely used up.

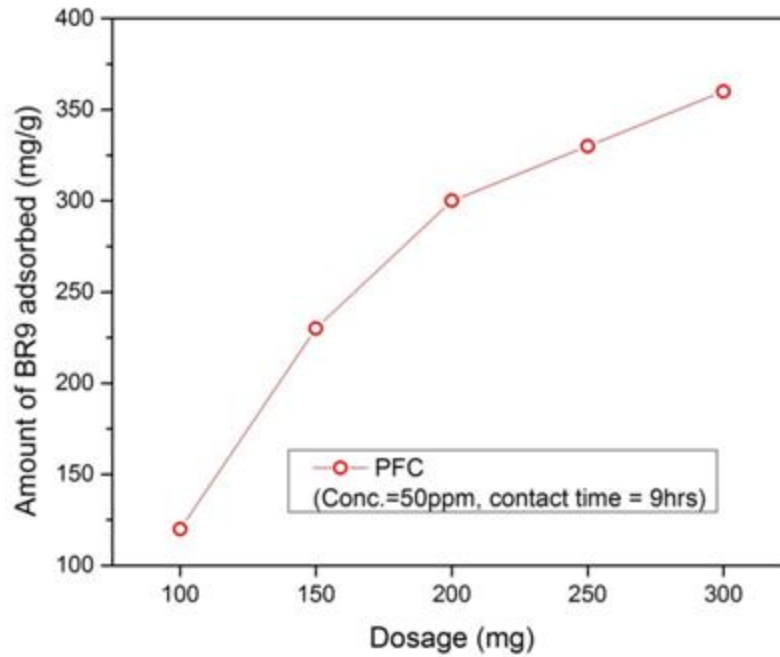


Figure.3:6 Effect of dosage upon the adsorption of basic red dye.

3.3.4 Effect of pH on Basic Red Dye Adsorption

The presence of either strong acids or bases in an adsorbate changes the surface characteristics and accumulation sites on the dyes. pH is regarded as an important parameter in the adsorption process of basic Red dye (Yu et al, 2009). There was an increase in uptake of BR-9 dye as the pH increased from 2-8 with 200mg/g of dye adsorbed as shown by figure 3.6 below. There was a slight increase observed at pH8-10 and a further increase from pH 10-14 with 300mg/g of dye adsorbed. The trend observed in BR-9 uptake as pH decrease was due to the presence of positive charges in acidic media (H^+) and since the surface of PFC is positive there was competition between the H^+ charges present in the acidic media, PFC and the BR-9 dye and a small amount of dye was adsorbed. As pH increased, the positive charges reduced and repulsion between the OH^- and the dye made adsorption to increase since there was only favorable interaction between the dye and PFC.

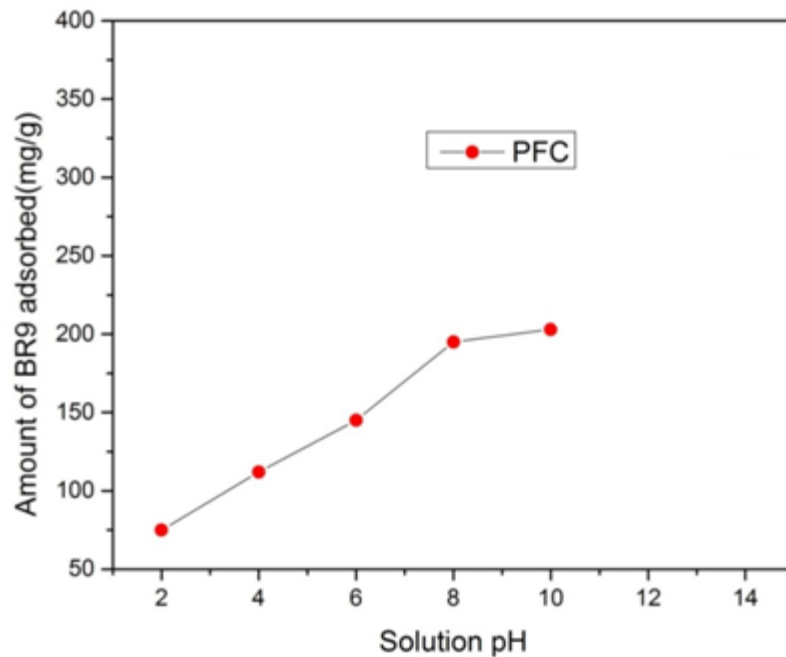


Figure3.7: Effect of PH upon adsorption of basic red 9 Dye from aqueous solution

3.3.5 Effect of Ionic Strength on Dye Adsorption

The effect of concentration of KCl salts upon the removal of BRD was studied by using different concentrations of KCl aqueous solution (0.5M, 1.0M, 1.5M, and 2.0M), 50ppm of dye solution and 50mg of PFC .The mixture was agitated using an agitation speed of 200rpm .The amount of dye uptake decreases with increase in KCl concentration due to competition between potassium ions and the positive charge of basic red 9 dye since they both have same charges.

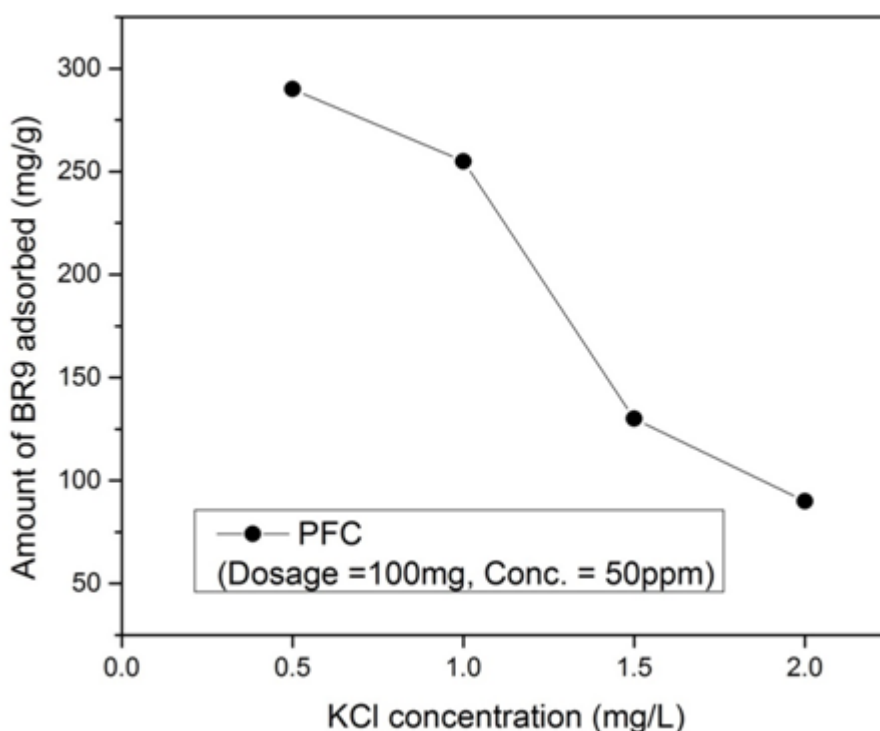


Figure3.8: Effect of Ionic Strength on Adsorption of Basic Red 9 dye

3.3.6 Effect of Temperature on the Removal of Basic Red 9 Dye

Effect of temperature was studied by varying temperatures such as 35, 50, 65 and 80°C using 50mg of PFC and 40ml of dye solution. The mixture was agitated for 9 hours with an agitation speed of 200rpm, and the absorbance was determined. The plot of amount of dye uptake with increasing temperature shows a decrease in adsorption as shown by the graph of figure 3.8 bellow. This can be explained as a result of increase in movement between dye and adsorbent, and thus less time is spent by adsorbent particles on its active sites leading to small amount of dye adsorption.

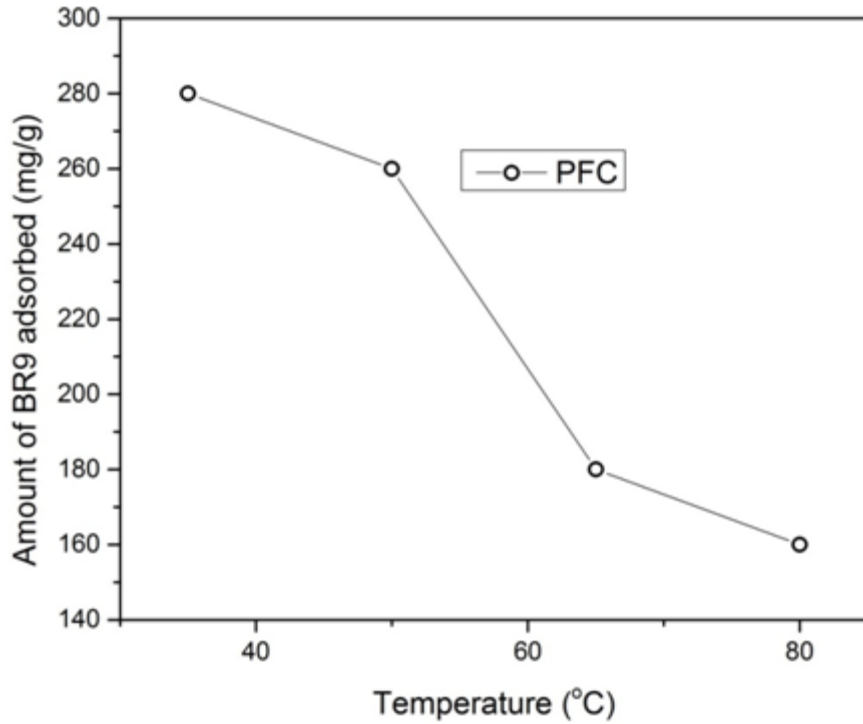


Figure 3.9: Effect of Temperature on Adsorption of Basic Red Dye

3.4 Adsorption Study

The adsorption capacities of PFC compared with other low cost adsorbents were studied using the calculations relating the amount of dye adsorbed and their percentage removal abilities.

The amount adsorbed is related as shown below, and the percentage removal is also calculated as well;

$$q_t = \left(\frac{C_0 - C_f}{m} \right) \times V \quad (2)$$

q_t = the measure of the uptake of dye by FC at time t , in mg/g

C_0 = the initial dye concentration in mg/L

C_t = concentration of dye at any time t in seconds

V is the volume of solution, and m the mass of *Ferula Communis* used

From the above calculations, the percent removal of dye from solution using PFC can also be calculated as shown.

$$\%removal = \frac{C_o - C_t}{C_o} \times 100 \quad (3)$$

3.4.1 Thermodynamic Study

Thermodynamically, parameters such as Gibbs free energy change, enthalpy, and entropy changes were calculated as they were gotten from the van Hoff's equation as shown below:

$$\Delta G^0 = -RT \ln k_o \quad (4)$$

Where: K_o and R are the apparent equilibrium constant and the universal gas constant respectively.

T is the absolute temperature in Kelvin.

(ΔH^0) is the apparent enthalpy and (ΔS^0) the entropy. The equation below was used to calculate the enthalpy and entropy of the process.

$$\ln k_o = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (5)$$

More so,

$$\lim_{C_e \rightarrow 0} \frac{q_e}{C_e} = K_o$$

as dye concentration approaches 0.

K_o is obtained by plot of $\ln (q_e/c_e)$. (Aljeboree et al .2014)

The value of the enthalpy change is negative (-19.96KJ/mol) showing that the adsorption process is exothermic.

The entropy change was negative (-49.98J/mol K) indicating that the entropy of the system decreased during the adsorption process.

The negative values of Gibbs free energy showed that the adsorption process was spontaneous. The decrease in the values of the Gibbs free energy with increasing temperature indicated that the adsorption became less favorable at higher temperature (Aljeboree et al.2014).

Table 4: Thermodynamic and kinetic parameters for adsorption of BR-9 onto PFC at different temperatures

Thermodynamic parameters for adsorption of BR9 onto PFC at different temperature

Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
308	-45.71	-19.96	-49.98
328	-38.21	-19.96	-49.98
338	-30.71	-19.96	-49.98
353	-23.22	-19.96	-49.98

Kinetic parameters for adsorption of BR9 onto PFC at different temperature

	Temperature (°C)			
	35	50	65	80
Pseudo-first order kinetic				
$q_e, \text{exp (mg/g)}$	234.45	211.98	185.76	160.45
$q_e, \text{cal (mg/g)}$	187.69	123.86	234.87	198.33
$k_1 \text{ (1/min)}$	0.0135	0.0136	0.0169	0.0187
R^2	0.8977	0.7865	0.6598	0.9873
Pseudo-second order kinetic				
$q_e, \text{exp (mg/g)}$	234.45	211.98	185.76	160.45
$q_e, \text{cal (mg/g)}$	237.99	213.44	184.67	168.03
$k_1 \text{ (1/min)}$	0.0035	0.0015	0.0012	0.0007
R^2	0.9876	0.9924	0.9998	0.9888

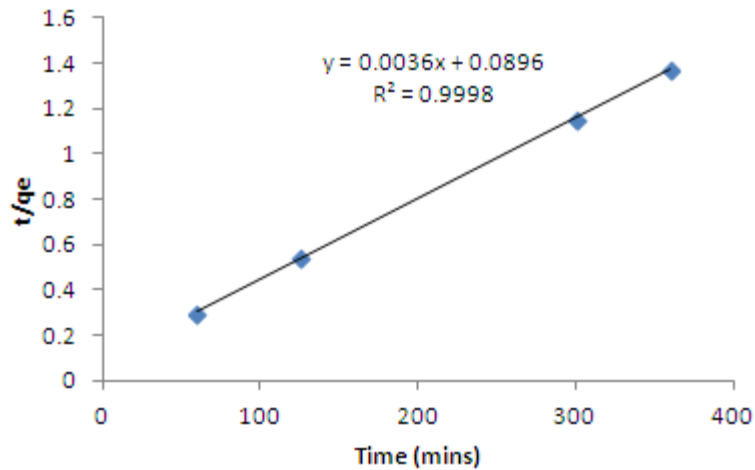


Figure 3.9: Pseudo Second Order Plot

3.4.2 Adsorption Isotherm Parameters for the Adsorption of Basic Red Dye

These parameters help to give an understanding of how the distribution of dye between the solid phase and the solution phase will vary at a particular temperature when equilibrium is attained.

The Langmuir assumes monolayer adsorption and that once the active sites are covered no other adsorption takes place. The Langmuir equation is as shown below.

$$q_e = \frac{q_m k_L c_e}{1 + k_L c_e} \quad (6)$$

q_e : equilibrium amount of dye adsorbed in mg/g

C_e : concentration of dye solution at equilibrium in mg/L

q_m : the maximum sorption capacity which occurs when sorbent surface is fully covered with monolayer sorbate molecules

K_L is obtained from the slope of a plot of C_e/q_e versus C_e (Ho, 2006).

Linearly it can be expressed as follows;

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \quad (7)$$

The Freundlich equation was linearized as follows:

$$\ln Q_e = \ln K_f + \frac{1}{n} (\ln C_e) \quad (8)$$

q_e = amount of dye adsorbed at equilibrium

C_e = the concentration of the dye solution at equilibrium

K and $1/n$ are empirical constants whose values were obtained from the intercepts ($\ln K$) and slopes ($1/n$) of linear plots of $\ln q_e$ versus $\ln C_e$ (Ho,2006).

The Langmuir adsorption model was found to fit the experimental data for the adsorption of basic red dye from aqueous solution with q_m value 354.8mg/g which is a constant representing maximum capacity of adsorption at equilibrium. The Langmuir model has a larger value of R^2 of 0.9997 compared to the Freundlich model value of 0.8876. The different values of K_L signify the difference in binding strength and capacity of dyes with the adsorbent surface, with the K_L value of 87.69L/mg at 308K for Langmuir. The values of K_L decreases with increase in temperature.

The Freundlich model failed to provide information about the saturation adsorption as opposed to Langmuir and has a lower R^2 value of 0.8876. The K_f and n values shows that there is an intense change in adsorption of BR-9 dye as temperature increases. Values of n are greater than 1 indicating adsorption of dye is not favorable under these this experimental conditions.

3.4.3 The Adsorption Kinetics of Basic Red Dye

Pseudo-first order, pseudo-second order and intra particle diffusion was used to examine the adsorption mechanisms.

Pseudo-first order kinetic model is represented as follows;

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (9)$$

q_t : the amount of adsorbate adsorbed at time t , and q_e in mg/g is the adsorption capacity at the equilibrium. k is the pseudo-first-order rate constant (min^{-1}), and t is the contact time (min). A plot of $\log(q_e - q_t)$ versus t gives a straight line with k_1 and q_e gotten from the slope and intercepts of the plot (Zeid et al, 2013).

Pseudo second order equation is expressed as;

$$\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{1}{q_e} t \quad (10)$$

Plots of t/q_t versus t gives a straight line with q_e and k_2 being the slope and intercept respectively (Zeid et al, 2013).

Comparing the R^2 values, the pseudo second order has a value of 0.9876 while pseudo first order is 0.8977. More so, the experimental values of q_e of 234.45 mg/g and the calculated value of 237.99 mg/g makes it acceptable for the adsorption of BR-9 dye onto PFC to be pseudo second order since they are higher and agree with each other as compared to the q_e values of pseudo first order equations which are 234.45 and 187.69 mg/g which do not agree. Therefore the pseudo second order equation kinetic model gives the better option for the BR-9 Adsorption mechanism.

Table 5: Isotherms Parameters for adsorption of BR-9 onto PFC at different temperature.

Isotherms parameters for adsorption of BR9 onto PFC at different temperature

	Temperature (°C)			
	35	50	65	80
Langmuir model				
q_m (mg/g)	354.89	321.98	297.88	260.22
K_L (L/mg)	87.69	63.53	44.99	38.87
R_L	0.0012	0.0016	0.0022	0.0026
R^2	0.9997	0.9988	0.9789	0.9979
Freundlich model				
K_F (mg/g)	64.42	41.66	35.86	30.66
n	1.3681	1.4764	1.2678	1.1303
R^2	0.8876	0.7989	0.8908	0.7895



Figure3.9: Basic Red Dye Stock Solutions Before and after Adsorption.

Chapter 4

CONCLUSION

This study was based upon the adsorption of BR-9 from aqueous solution using modified FC biomass as adsorbent. The FT-IR spectroscopy was used to characterize PFC, the kinetics studies and adsorption equilibrium isotherms were studied and the results were analyzed as follows;

The thermodynamic values of the Gibbs free energy and enthalpy were negative showing the process was an exothermic process and spontaneous.

Batch Analysis of the adsorption process showed that it is in line with the Langmuir model which is a monolayer adsorption with q_m observed at 354.89mg/g. Kinetic calculations showed it was a pseudo second order kinetics.

From the results obtained basic red dye adsorption was successful using Phosphoric acid modified FC plant, and the raw materials were non-toxic, eco-friendly, readily available and cheap, thus a adsorption of BR-9 dye using modified *Ferula Communis* was a better option for dye contaminated wastewater.

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