Removal of Basic Dyes from Aqueous Solution by Chloroacetic Acid Modified Ferula Communis Based Adsorbent: Thermodynamic and Kinetic Studies

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ABSTRACT

This research aimed to propose an alternative cheap and abundantly available adsorbent (Ferula communis) for the removal of basic dyes from aqueous solutions. Chloroacetic acid modified Ferula communis (MFC) shows a great potential for the removal of basic red 9 dyes (BR9) from aqueous solution with the effects of solution capacity under pH, temperature, contact time, adsorbent dosage, and initial dye concentration condition on BR9 removal were examined. The adsorption equilibrium data were fitt to adsorption isotherm models and the pseudo-second order adsorption kinetics provides the best description of BR9 adsorption onto MFC. Thermodynamic evaluation of the adsorption parameters showed that the adsorption is endothermic and spontaneous. The experimental outcomes in the present research elucidated that MFC is suitable alternative to remove basic dyes.

Keywords: Ferula communis, Basic red 9, Adsorption, Kinetics, Thermodynamic studies

ÖZ

Bu araştırmanın amacı, sulu çözeltilerden bazik boyaların uzaklaştırılması için alternatif ucuz ve bol miktarda bulunabilen bir adsorban (Ferula communis) önermektir. Kloroasetik asit fonksiyonlandırılmıs Ferula communis (MFC), farklı pH, sıcaklık, temas süresi, adsorban bir dozaj ve ilk boya konsantrasyonu koşulları altında çözelti kapasitesinin etkileri ile sulu çözeltiden bazik kırmızı 9 (BR9) boyasının ortadan kaldırılması için önemli bir potansiyel göstermektedir. Adsorpsiyon denge verileri adsorpsiyon izotermi modellerine uygunlugu ve yalancı-ikinci derece adsorpsiyon kinetigi, MFC üzerine BR9 adsorpsiyonunu açıklamaktadır. Adsorpsiyon parametrelerin termodinamik olarak değerlendirilmesi, adsorpsiyonun endotermik ve kendiliğinden olduğunu göstermiştir. Mevcut araştırmadaki deneysel sonuçlar, MFC in bazik boyaların giderimi için uygun bir alternatif olduğunu göstermektedir.

AnahtarKelimeler: Ferula communis, Bazik Kirmizi 9, Adsorpsiyon, Kinetik, Termodinamik calisma

This thesis is dedicated to the most beautiful in my life:

my sons

LAZO & LARSA

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NOMENCLATURE

MFC	Modified Ferula Communis
CAA	Chloroacetic acid
BR9	Basic Red 9
FT-IR	Fourier Transform Infrared spectrophotometer
UV-VIS	Ultraviolet Visible spectrophotometer
q_e	Equilibrium concentration of adsorbed species in solid adsorbent (mg g^{-1})
C_e	Equilibrium concentration of adsorbed species in solution (mg L^{-1})
K_L	Langmuir isotherm constant (L mg^{-1})
C_o	Initial concentration (mg L^{-1})
K_F	Freundlich isotherm constant (mg g^{-1})(L.mg^{-1})$^{1/n}$
N	Adsorption intensity
k_1	Equilibrium rate constant of pseudo-first adsorption (min^{-1})
k_2	Equilibrium rate constant of pseudo-second order adsorption (g $mg^{-1}min^{-1}$)
K_i	The intra-particle diffusion rate constant (mg $g^{-1}min^{-1/2}$)
T	Time of diffusion (min)
$\Delta H°$	Enthalpy change (J mol^{-1})
$\Delta S°$	Entropy change (J mol^{-1})
$\Delta G°$	Gibbs free energy (J mol^{-1})
R	Universal gas constant (8.314J$mol^{-1}K^{-1}$)
T	Absolute temperature (K)

K_d	The distribution constant
R_L	Equilibrium parameter Langmuir isotherm

Chapter 1

INTRODUCTION

Dyes are broadly used in various industries such as leather, plastic, paper, food and textile to enhance the aesthetic values of their products. Very often these industries generate colored wastewater discharged into natural streams leading to unpleasant consequences to the environment. The presence of dyes in the water bodies can cause devastating harm to aquatic life by hindering the chemical oxygen demand and photosynthetic processes (Gupta et al. 2003). Some dyes, such as BR9 can cause serious injuries to animals and humans by inhalation (rapid breathing), ingestion (vomiting or mental confusion) or direct eye contact (Ho et al. 2005).

BR9 is widely used as suitable substrate in polyacrylonitrile textile fibers and as a colorimetric test for aldehydes. The extensive application of BR9 led to colored wastewater and effective treatments need to be embarked on for its removal from wastewater before being discharged into natural streams (Martins et al. 2006). Chemical structure and some physical properties of BR9 are shown in Figure 1.1 and Table 1.1 respectively.

Various physical or chemical methods have been used to treat wastewater containing dyes such as ozonation, filtration, adsorption, electrochemical annihilation,ion exchange, precipitation, and flocculation. Presently, biological treatment and adsorption technique are two effective industrially suitable techniques for treating pollutant containing wastewater due to the ease, ability to treat dilute solutions, insensitivity to toxic substances and effectiveness.

According to Basar, C. A. (2006), commercially available activated carbons are still considered as costly materials for many countries because of the use of non-renewable and comparatively costly starting material such as coal, which is unjustified in contamination control applications. Hence, this has incited a growing research interest in the production of activated carbons from renewable and economical sources which are mainly agricultural by-products, such as apricot shell.

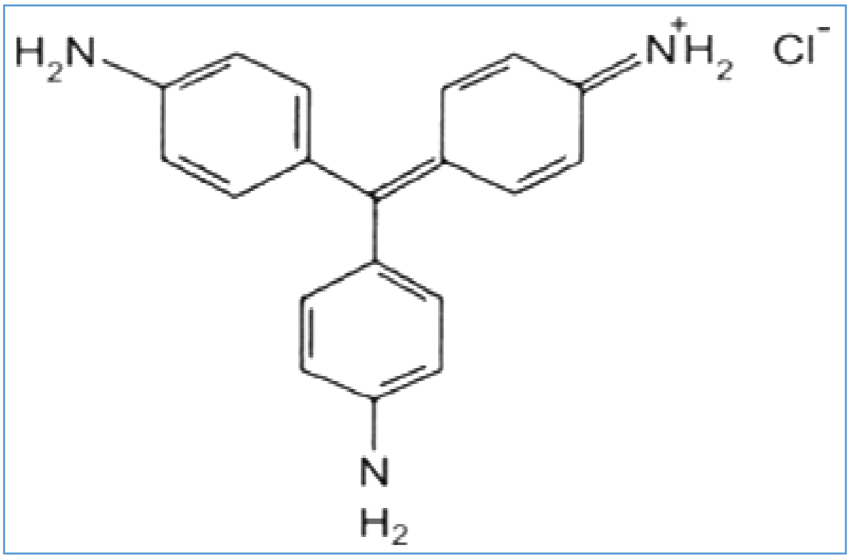

Figure 1.1: Chemical structure of BR 9

Table 1.1: Physical properties of BR9

Molecular formula	$C_{19}H_{18}ClN_3$
Molar mass	323.82 g/mol
Melting point	268-270 °C (541-543K)
Appearance	Green crystalline solid
Solubility in ethanol	5.9%
Solubility in water	Slightly soluble, 0.26%

In this study, adsorption properties of Ferula communis biomass were investigated. Ferula communis (FC) belong to the Apiaceae family and is found in the Mediterranean region extending to central Asia and northern Africa. Ferula communis plant has demonstrated to be medicinal with a rich history of curative application Zucca, P., et al. (2013). Ferula communis grow commonly on the Eastern Mediterranean mountainous regions of Turkey and Cyprus. It is a spring plant that flowers in March and April but dries during the summer period. Optical picture of the plant are given in Figure 1.2 and Figure 1.3. Majority of the people living in the region where FC grows dice the FC roots with honey and eat it due to its aphrodisiac role Zucca, P., et al. (2013); Mamoci, E.et al. (2012).

Figure 1.2: Typical specimen of Ferula communis from Cyprus

Figure 1.3: Ferula Communis plant in summer

1.1 Wastewater

Water contamination emanate from toxic organic compounds is disastrous to human and aquatic lives, increasing environmental concerns and regulations to protect the natural environment is of utmost interest to environmentalist. The issue for decontamination of pollutant wastewater can be classified in two types: physical (filtration, reverse osmosis systems, precipitation, adsorption and biological techniques) or chemical (ion exchange, oxidation, reduction and neutralization)(Grzechulska-Damszel, J., et al. 2010).

Lately, wastewater treatment and water reuse have been a great concern to environmental scientist and technologists. Biological treatments which are basic and most economical studies have been generally used to treat wastewaters, but much of the time these studies have been wasteful to degenerate toxin and resistance pollutants. Biological treatments have been preferred due to abundance of raw materials, ease of operation and its cost-effectiveness.

1.2 Adsorbent

Adsorbents used for water treatment are either origin or the result of an industrial production and activation process. Typical natural adsorbents are clay mineral, zeolites, oxides or biopolymers. A list of typical adsorbents is given in Table below.

Table 1.2: List of typical adsorbents

Organic adsorbents	Cellulose (the most spongy bio polymer in nature), chitin (the second most plenteous) collagen, fleece, starch polyacrylamide gels (which ingest commonly their own particular weight water of encompassing temperature, however discharge the vast majority of it by delicate heating), poly saccharides determine structure corn, and incidental types of biomass.
Inorganic adsorbents	Silicates ($MgSiO_3$), Sulfates ($CaSO_4$), Oxides (CaO, MgO, ZnO for life help in the space project), chlorides ($CaCl_2$). Also Alumina, silica's and zeolites. And even sodium bicarbonate and limestone (for pipe gas medicine). Some are utilized within anhydrous state while others hydrate.
Polymers	Most generally they are tan or whit, but some are orange, dark, or brown. Thusly, they were commonly polystyrene divinyl-benzene co polymers having a circular shape and high pore volume.

1.3 Type of Dyes

Dyes are substances that add color to materials; they act as substrate on textile fibers and other materials via synthetic reaction, absorption, or dispersion. Colors vary in their resistance to daylight, sweat, washing, gas, alkalis, and different executors; their fondness for diverse filaments; their reaction to cleaning operators and techniques;

and their solubility and technique for application. Dyes can be classified according to their performances in the dyeing processes as shown in Table 1.3.

Table 1.3: Industrial type of dyes

Group	Application
Basic	wool, cotton, silk
Acid Dyes	synthetic fibers, leather, wool, silk
Developed Dyes	fabric and cellulosic fibers
Solvent dyes	coloring oils, waxes, wood staining, solvent inks
Azoic	pigments and printing inks
Direct	cellulosic, blends and cotton
Vat dyes	cellulosic, blends and cotton
Reactive	fabric and cellulosic fibers
Dispersed dyes	synthetic fibers
Optical/Fluorescent Brighteners	leather, cotton, synthetic fibers, sports goods
Sulphur	cellulosic fibers and cotton
Organic pigments	cellulosic, blended fabrics, paper, cotton
Oxidation dyes	hair
Mordant dyes	fabric and cellulosic fibers, wool, silk

1.3.1 Dyes According to the Chemical Structure

According to the chemical structure, dyes are classified into two groups

- Cationic Dyes.
- Anionic Dyes.

1.3.2 Categorization based on the Source Material

Categorization of dyestuff is principally depending upon the nature of the source from which it made. Peters, A. T. (1984), the classification could be:

- Natural Dyes
- Synthetic Dyes

1.4 Brief explanation on adsorption techniques

1.4.1 Adsorption

Adsorption process can be referred to as adhesion of molecules, ions or atoms from dissolved solid, liquid or a gas onto a surface. A film of the adsorbate is created on the surface of the adsorbent in the adsorption process. There is a clear distinction between adsorption and absorption, the latter is a process in which the adsorbate is dissolved by the absorbent (a solid or liquid). Absorption involves the entire volume of the material while adsorption is a surface-driven process.

Adsorption involves surface energy and may occur as a result of electrostatic attraction and can be classified as chemisorptions (covalent bonding) or physisorption (weak van der Waals forces or hydrogen bonding).The reasons for choosing adsorption system over others, is because MFC has a very high surface area per unit mass that can adsorb pollutants.

Adsorption can remove a wide range of pollutant from wastewater, especially organic contaminants including industry solvents and some supplies may also introduce MFC treatment to deal with the toxic by-product dyes. Adsorption is not only efficient but also is the most effective and economical system. (Zhang, W. X., et al. 2011).

1.4.2 Filtration

This technique can be utilized to separate particles in step with their sizes. An application is that the removal of the precipitate when selective precipitation. Such solid-liquid laboratory filtrations square measure carried out through different grades of filter paper (those differing in pore size). Mixture is poured either onto a paper that rests during a funnel or onto another filtering (Ordonez, R., et al. (2014).

1.4.3 Electro coagulation

Electro coagulation is a procedure where an electrical current is connected to a sample to energize coagulation of solids in the sample; there are two essential provisions for this system: surgery, and also the treatment of wastewater and contaminated water. Organizations included in the preparation of electro coagulation supplies incorporate medicinal supply organizations, wastewater treatment organizations, and organizations included in ecological treatments.

1.4.4 Flocculation

Flocculation is a separation process where colloids come out of suspension as flake or floc spontaneously or in the presence of a flocculating agent. Flocculation is synonymous with aggregation gentle mixing and agglomeration, step up the rate of molecule collision and the unsettled particles are more accumulated and trapped into bigger precipitates. Flocculation is influenced by a few parameters, including mixing heat, mixing time, and mixing speeds. The result of the mixing time and mixing heat is used to define flocculation process. Paiva, C. T. and R. Z. L. Cancado (2008).

1.5 Activation of adsorbents

Chemical activation of the Ferula communis was completed using Chloroacetic acid. However, Chloroacetic acid is the most activity. The chemical activating agents act by dehydration of the sample during the chemical steps. The natural fiber was ground and sieved and then washed by absolute ethanol for 3 times following by distilled water for 10 times.

After that, the sample was dried in oven at 80C° for 24 hour. Then mixed with saturation of sodium hydroxide(to ensure all hydroxide group in the fiber cellulose was exchange by sodium ion) that's meaning dehydration of the sample, then added Chloroacetic acid drop wise with gentle heating for several hours to ensure complete adsorption of the solution by the biomass sample. Solution were allowed to be digestion at room temperature for 24 hour and then dried at 60 °C for 48 hour in a temperature controlled oven. After being cooled, the sample washed several times with deionized water and finally washed with cold water to remove remains chemicals (non-reactive materials).(Williams & Reed, 2004).

1.6 Objectives

The research has an point to be attained and due to this some targets:

- To synthesize modified FC so as to improve the adsorption properties of the biomass.
- To analyze the removal of BR9 from aqueous solution utilizing Ferula communis as adsorbent.
- To investigate the thermodynamic and kinetic parameters of the adsorption process.

Chapter 2

LITERATURE SURVEY

Presently there are various studies on the use of low-cost and environmental-friendly adsorbents for treatment of contaminated wastewaters. Altinisik, A., et al.(2010) states that different kind of adsorbents have been studied such as activated carbon, algae, red algae, green algae, macro fungus, sugarcane dust, saw dust, fly ash, bottom ash, de-oiled, maize cob, peat iron humate, lichen, microbial biomass and coal for removal of dyes and trace elements. Activated carbon which has high adsorption ability for removal of dyes in aqueous solutions remains an expensive material. Nandi & Patel (2013) performed a research on the removal of basic red 9 dyes from aqueous solutions by electro coagulation process.

They studied various treatment parameters, for example, initial dye concentration, salt concentration, inter-electrode distance, electrolysis time, initial pH and current density on dye elimination effectiveness. The test outcomes indicated that 99% dye elimination was obtained after 30 min of electrolysis for dye concentration of 100ppm at initial pH of 7.0 and current density of111.1 A/m^2. It was observed that a decreasing inter-electrode distance and increased current density and time of operation enhanced the dye elimination efficiency.

The kinetic study deduced that the dye elimination followed pseudo-first order reaction and phenomenological patterns were suggested to explain the reliance of dye removal capacity and specific electrical energy utilization on the investigated parameters as mentioned above.

Zhang, W. X., et al. (2011) investigated carboxymethyl cellulose as a viable adsorbent to remove cationic dyes. They assumed that carboxymethyl straw can be used to adsorb cationic dyes. Wheat straw materials were essentially modified using carboxymethylation to obtain anionic adsorbents, which were utilized to adsorb methylene blue, a sort of cationic dye.

The essential adsorption practices of modified straw for removal of methylene blue. Involve pH effect; adsorption isotherms, kinetics and column adsorption were studied, respectively. Then, after adsorption of methylene blue, the disposed of the deserted adsorbents turned into a trouble. Commonly, there are two typical techniques to treat with these deserted adsorbents: one is to reject also burn immediately; another way is to regain from dilute acidic or basic solution for reuse and gather some useful contaminants. Lately, a more productive and practical system has been investigated to treat with these rejected adsorbents.

The unused adsorbents were exercised as another kind of adsorbents for the modified surface structures. Hence, the surface structures of straws have been clearly become different after adsorption of methylene blue, and the methylene blue loaded adsorbents has been further re-utilized to adsorb methyl orange dye, a type of anionic dyes.

Gupta, V. K., et al.(2003) transformed waste carbon slurries and blast furance slag into low- cost adsorbents. The adsorbents has been described and utilized for the removal of basic red dye from aqueous solution. The research was conducted at varying pH to investigate the pH at which most extreme adsorption occurs. The adsorption results are related to Langmuir and Freundlich isotherms in each method. The kinetics of adsorption relies on the adsorbate concentration and the chemical and physical characteristic of the adsorbent. Studies were behavior to scheme the effect of initial adsorbate concentration, particle size of the adsorbent, pH, temperature and solid to liquid ratio. The adsorption of BR was discovered to be first- order and endothermic in nature.

Mittal, A. (2006) applied hen feather as prospective adsorbent to removal malachite green, a toxic triphenylmethane dye from wastewater. The adsorption parameters such adsorbent dosage, temperature, concentration of adsorbate, pH and contact time on the adsorption were examined. The adsorption isotherm constants obtained in the research were dependent on the initial concentration of the dye. The adsorption of malachite green was discovered to be intraparticle and film diffusion processes at lower and higher concentration respectively.

Gulnaz, O., et al. (2004) investigated the adsorption of basic dyes BR18 and BB9by dried activated sludge in a batch system. The data obtained showed that activated sludge had monolayer adsorption capacity of 285.71 and 256.41mg.g^{-1} for BR18 and BB9, respectively, Langmuir and Freundlich isotherm models were applied to deduce and understand the adsorption mechanism of the investigated dyes. The fitting of the kinetic equations for the adsorption process using activated sludge was examined as well. It was obtained that the pseudo second order kinetics satisfactorily explained the adsorption kinetics of both dyes onto dried activated sludge.

Zhang, W. X., et al. (2012) investigated the potential application of wheat straw modified by etherification process for removal of toxic dyes. The adsorption conducts of the modified straw for acid green 25 (AG25) and methyl orange (MO) removal were studied in both column and batch method. The adsorption ability of the straw for both dyes improved clearly after modification. The maximum AG25and MO adsorptions were obtained as 300 and 950 mg/g, respectively. Obtained data as recorded by the researchers indicated the adsorption process were chemisorptions in nature with an ion-exchange mechanism. Furthermore, after adsorption of anionic dyes, the loaded adsorbents were successfully applied in the secondary adsorption to remove a cationic dye directly at proper conditions. This was possible due to the change of the surface of the initially loaded adsorbents.

Ho, Y. S., et al. (2005) utilized tree fern for remove of basic red 13(BR13) from wastewater. The system has variable factors includes adsorbent temperature, particle size and data detected the effort of tree fern, an agricultural product as a low cost adsorbent. The Langmuir isotherm was found to represent the studied adsorption result well. The dye adsorption capability of tree fern increased as the adsorbent particle size decreased. Maximum saturated monolayer adsorption capability of tree fern for BR13 was 408mg.g^{-1}. Thermodynamic parameters suggested that the adsorption of BR13 was endothermic and spontaneous.

Chapter 3

EXPERIMENTAL

3.1 Materials and Instruments

Table 3.1: The materials that have been used and their manufactured

No	Chemicals	Company
1	Pararosaniline(Basic red 9)	Sigma - Aldrich
2	Chloroacetic acid	Sigma - Aldrich
3	Sodium hydroxide	Aldrich - Germany
4	Sodium hydrogen carbonate	Analar - UK
5	Hydrochloric acid	Aldrich - Germany
6	Acetic acid	Aldrich - Germany
7	Sodium acetate	Aldrich - Germany
8	Sodium dihydrogen phosphate	Analar - UK
9	Potassium dihydrogen phosphate	Aldrich - Germany
10	Sodium tetra borate	Aldrich - Germany
11	Potassium hydrogen phthalate	Analar - UK
12	Potassium chloride	Aldrich - Germany
13	Sodium sulphate	Analar – UK
14	Ethanol	Analar – UK

3.2 Instruments used for the experimental part

1. UV-Spectrophotometer (T80+UV/V is spectrometer) PG instrument Ltd.

2. Perkin Elmer spectrum (65-FTIR spectrometer).

3. Oven

4. Sensitive balance.

5. Mechanical agitator (shaker).

6. Stirrer-Hot plate (Heidolph MR Hei-Standard).

7. Water Bath.

3.3 Adsorbent Preparation

3.3.1 Adsorbent pre-treatment

In this study, Ferula communis (FC) used for this research is a native plant of Mediterranean region obtained from Famagusta in North Cyprus area, harvested in October 2013. The FC was modified with chloroacetic acid to produce anionic adsorbent under optimized preparation conditions. Raw material were washed severally, ground, dried in oven and sieved to obtain particles of diameter 500μm. The pre-treated material washed by absolute ethanol 2-3 times followed by distilled water 10 times, and then finally dried in the oven at 80°C for 24hr.

3.3.2 Adsorbent modification

10g of pre-treated FC was soaked in 0.5M of sodium hydroxide for 2hr at 80°C in a flask. 0.5MChloroacetic acid (CAA) was then added drop wise until a neutral pH was obtained. The modified adsorbent (MFC) was washed severally with distilled water and dried in oven at 60°C for 24hr.

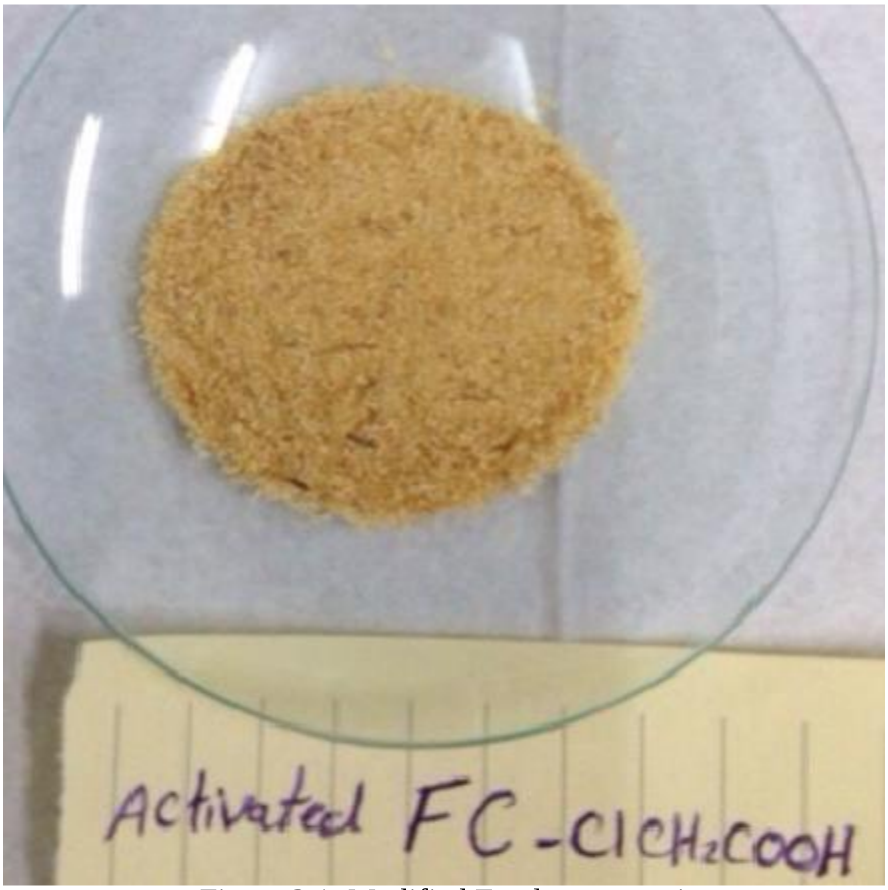

Figure 3.1: Modified Ferula communis

3.4 FT-IR Characterization

The Perkin Elmer /65- FTIR spectrometer/ was used to record and take IR spectrum (using KBr pellets of the sample) of sieved and activated Ferula communis.

3.5 Preparation of stock solution (Adsorbate)

BR9 dye was used as adsorbate and the different adsorption parameters such as adsorbent dosage, temperature, initial concentration, ion strength and pH were examined. A standard stock solution of BR9 were prepared by dissolving 0.5g of BR9 in 500 ml of distilled water, then working concentrations(500, 250, 125,62.5ppm) were prepared from the stock solution.

3.6 Adsorption Batch study

Adsorption batch experiments were conducted in 250ml flasks. Pre-determined amount of MFC was thoroughly mixed with40ml of different BR9 concentrations in conical flask on agitated shaker at 200 rpm. After specified time, 5ml aliquots were withdrawn from the flasks and the BR9 concentration were determined a UV/VIS-spectrophotometer (Beijing, T80+) at 540.00nm. The amount of BR9 adsorbed dye onto MFC was studied using the following equation:

$$q_e = (C_i - C_e)\frac{V}{W} \tag{1}$$

Where q_e: BR9 concentration in adsorbent at equilibrium.

C_i: Initial concentration of BR9 in (mg/L).

C_e: Concentration of BR9 at equilibrium (mg/L) in liquid phase.

V: Solution volume (L).

W: Adsorbent mass (g).

The percentage of BR9 removal was calculated using this equation;

$$R\% = \left(\frac{Ci - Ce}{Ci}\right) 100 \tag{2}$$

Where: R%: Percentage removal.

C_i: Initial concentration of BR9 in (mg/L).

C_e: Concentration of BR9 at equilibrium in (mg/L).

3.7 Error Analysis

The evaluation of the best fit for which isotherms to the obtained experimental equilibrium values in this present work was done by statistical error functions to determine the most convenient kinetic and isotherm equation to represent the experimental data using the linearized correlation coefficient R2.

The closer the value of R2to unity the more confident and favorable the experimental data is considered.

3.8 Adsorption Parameters

3.8.1 Effect of Initial Concentration of BR9 Dye

In order to investigate the effect of initial dye concentration 150 mg of modified Ferula communis (MFC) was added to 40 ml of different BR9 concentrations (20, 10, 5ppm). All of the samples were agitated on a shaker, then 5ml was taken from each of the solution after 3, 6 and 9 hours and at the end of the experiment, UV/VIS spectrophotometer was utilized for measuring the absorbance of BR9 in solution.

3.8.2 Effect of Adsorbent Dosage

In order to determine the effect of dye dosage, were used (50, 150 mg) of modified Ferula communis (MFC) added to 40 ml of (20, 10, 5 ppm) of the dye. All of the samples were agitated on shaker, then 5ml was taken from each of the solution after 3, 6 and 9 hours. Finally, UV/VIS spectrometer was utilized for the absorbance measurements of BR9 in solution.

3.8.3 Effect of pH

To find out the effect of pH on the BR9 adsorption, fresh buffer solutions were prepared (pH= 2, 4, 6, 8 and 10). 50mg of MFC was mixed with 40ml of buffer solution on a shaker, then 5ml was taken from each of the solution after 3, 6 and 9 hours and at the end of the experiment, UV/VIS spectrophotometer was utilized for measuring the absorbance of BR9 in solution.

3.8.4 Effect of Ion Strength

Prepared different concentrations of 0.5 , 1.0 and1.5 M of potassium chloride KCl , then 20 ml of each concentration mixed with 20 ml of dye solution(10 ppm) in existence of 50 mg of AFC, after 3 , 6 and 9 hours, 5 ml was taken for analyzing and measured the absorbance by using UV/VIS spectrometer.

3.8.5 Effect of Temperature

A 40 ml of 10 ppm dye solution containing 50 mg AFC in small conical flask placed in thermostat water bath of 25, 50 and 75 C° for 3, 6 and 9 hours, then measured absorbance by UV/VIS spectrometer.

Chapter 4

RESULTS AND DISCUSSION

4.1 Material Characterization

4.1.1 FT-IR Analysis for Adsorbent

Raw Ferula communis (FC), MFC and dye loaded MFC are analyzed by FTIR (PerkinElmer: model 65 spectrometer) in the range of 4000cm^{-1} and 400cm^{-1}. The FTIR spectra of FC and MFC are shown in Figure 4.1 (a) and (b), respectively. In Figure 4-1a, the broad peak at 3353.3 cm^{-1}is the characteristic peak of OH^- groups of cellulose. The strong C–O–C band at about 1025 cm^{-1}alsoconfirms the cellulose structure (C–O–C symmetric stretching at 1024-1199). The weak band at 2895 cm^{-1}is assigned to the stretch vibration of C–H bond in $-CH_2$ groups. The peaks at1737.6 and 1657 cm^{-1}confirmed the presence of C=O group in FC. Then after modification, -COOH groups were observed in MFC as shown in Figure 4-1b.The peaks at 1729 and1646 cm^{-1}in Figure 4-1b are indicative of –COOH group confirming successful modification of FC using Chloroacetic acid. In Figure 4-1c, the peaks at 1729 cm^{-1}disappeared, and a new peak appeared at about1595.6 cm^{-1}and this confirmed that BR9 molecules is chemically bonded to $–COO^-$ group on MFC. The FTIR analysis proved that the BR9 are chemisorptions in nature since there are drastic change in the spectra of MFC and dye-loaded MFC.

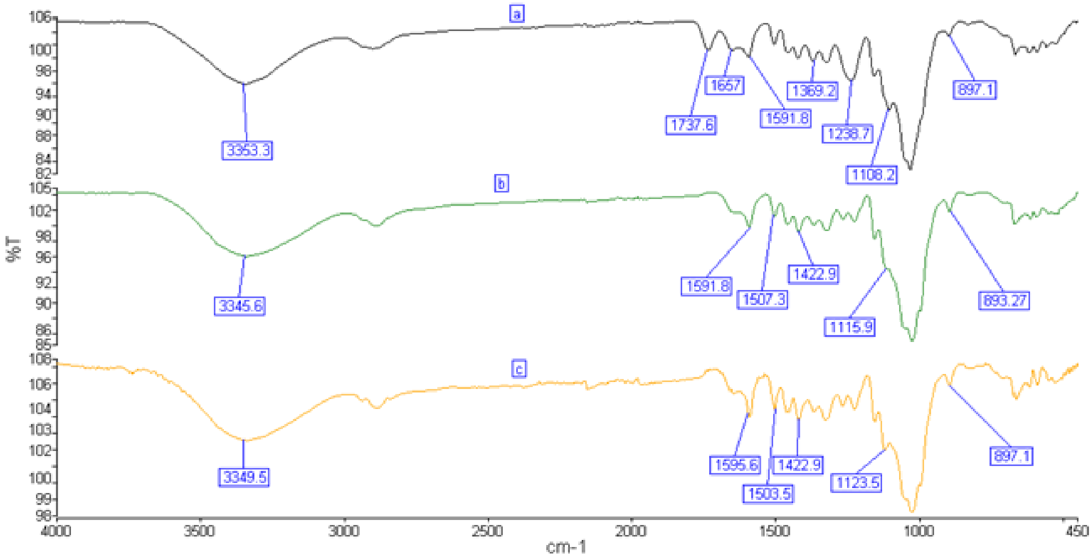

Figure 4.1 (a) FTIR spectra of Raw FC, (b) Modified FC and (c) BR9

4.1.2 Analysis of pH point Zero Charge (pH_{pzc})

The point of zero charge is an important feature that explains the condition when the electrical charge density on a surface of material is zero. The pH at point zero charge (pH_{pzc}) of MFC was studied by pH technique. Calculated amount of MFC was added to pre-determine solution of known pH in flasks. After 24 hrs, the pH of the solution was determined and differences in pH were noted. Plot of the final solution pH and initial pH was utilized to determine the $pH_{pzc}$of the material, which is the point at which the initial and final pH intersects (Oladipo, A. A., et al. 2014).

The pH_{pzc} of MFC was determined as 6.6. The surface of the adsorbent becomes positively charged at any pH below pH_{pzc}, which improves the adsorption of negatively charged dye anions through electrostatic force interaction. As the solution pH exceeds pH_{pzc}, the charge density on the surface of MFC reduces, leading to adsorption of basic dyes or positively charged species in solution.

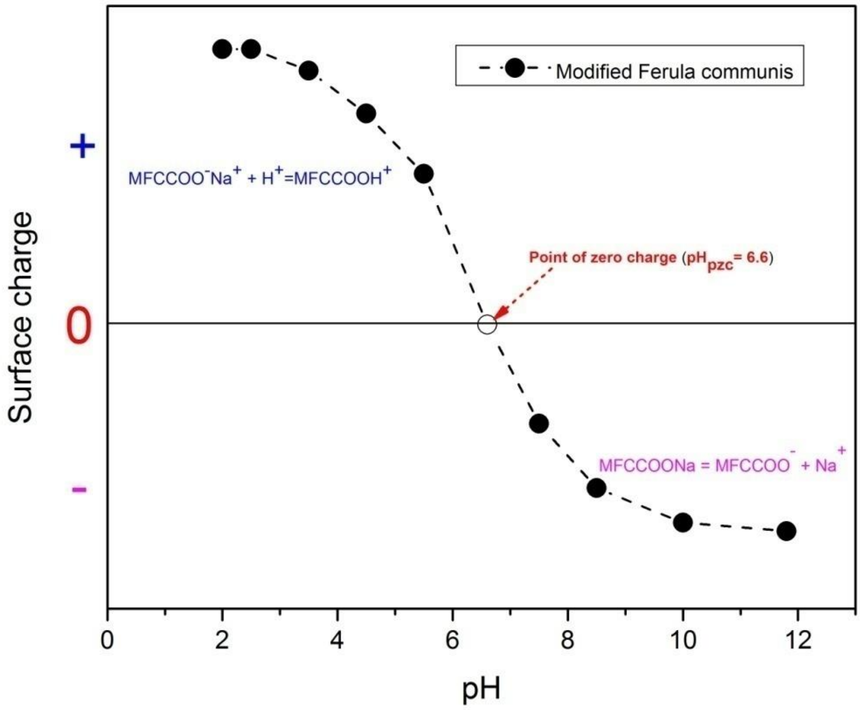

Figure 4.2: Determinations of pH_{pzc} of MFC by the pH float method

4.1.3 Adsorption Calibration Curve

Various concentrations of BR9 were prepared by serial dilution from the stock solution of 1000mg/L. The absorbance was determined for each dye concentration using the UV-VIS Spectrophotometer. The calibration curve (shown in Fig.4.3) was obtained by plotting the absorbance (Abs) against concentrations (mg/L) at pH7 and, the linear fit was determined. The concentration in solution was determined from the linear analysis.

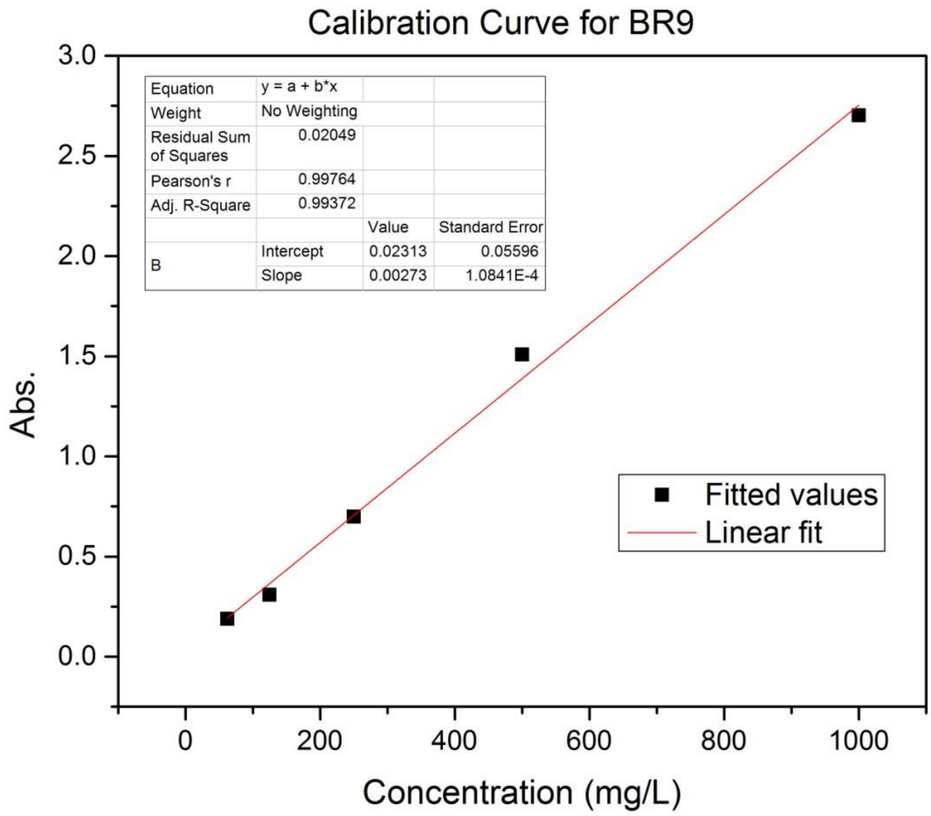

Figure 4.3: Calibration Curve of Basic Red 9 at Various Concentration at pH7.

4.2 Batch Investigation

The study of batch adsorption were examined an agitator at 200 rpm for 9 h as mentioned in section 3.5. UV/VIS-spectrophotometer was utilized for obtaining and analyzing for the adsorption capacity by the adsorbent using equations (1) and (2). Furthermore, the BR9 concentrations were investigated at wavelength 540 nm equivalent to the highest absorbance of each BR9 solution.

4.2.1 Operational Effect Parameters on BR9 Removal

4.2.1.1 Effect of Initial BR9 Concentration

Figure 4.5 shows that the uptake capacity of BR9 by MFC increased with the increasing initial concentration of dye during the batch adsorption studies. This increase in amount of adsorption with increased initial BR9 concentration is due to increasing driving force to dominate the resistances of mass transfer of the BR9 between the solid phases and bulk liquid. Increasing initial concentration results in increased diffusion of more dye molecules in bulk solution towards the MFC external surface and enhanced interaction between BR9 anions and MFC surface leading to increased adsorption uptake of BR9. The obtained data indicate that the removal efficiency of MFC was highly dependent on initial BR9 concentration.

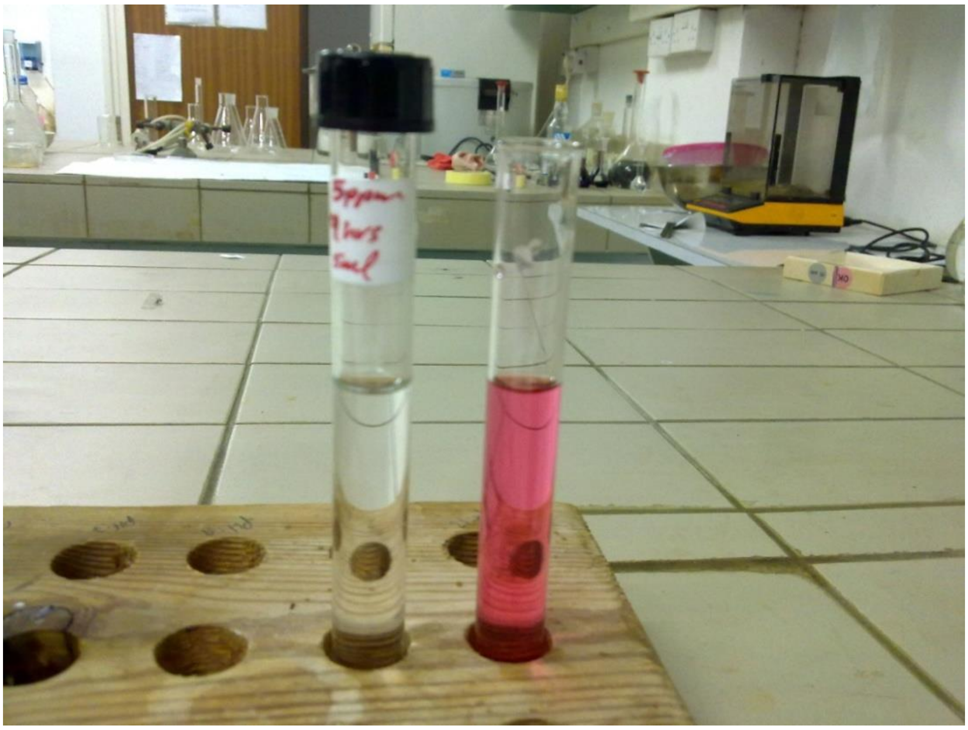

Figure 4.4: Dye Solution Become Colorless after Adsorption onto MFC

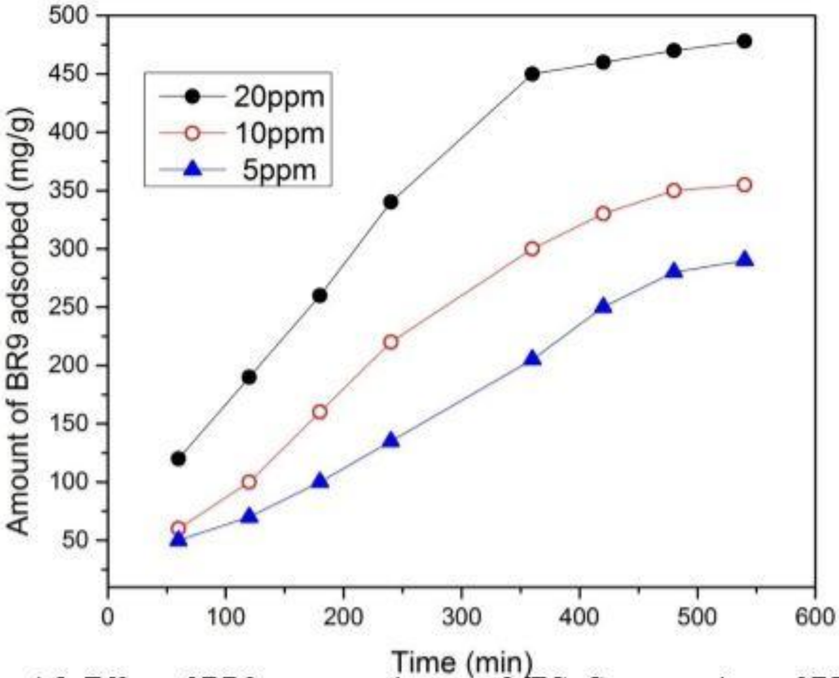

Figure 4.5: Effect of BR9 concentration onto MFC. Concentrations of BR9 = 5, 10 and 20 ppm; solution volume of BR9 = 40 ml; temperature = 25 °C; agitation = 200 rpm; MFC dosage = 100 mg; pH= 7.

4.2.1.2 Effect of Dosage on BR9

Investigation on the effect of MFC dosage indicated that the BR9 uptake increased from 220 to 340 mg/g with increased MFC dose until 200 min for 50 and 100 mg MFC respectively. This increment might be pointed to increased MFC surface area. Adsorption capacity increased from 210 to 340 mg/g after equilibrium was achieved. No significant increment was observed in the removal tendency after the adsorption process attained equilibrium showing that, all the available sites on MFC might have been fully occupied.

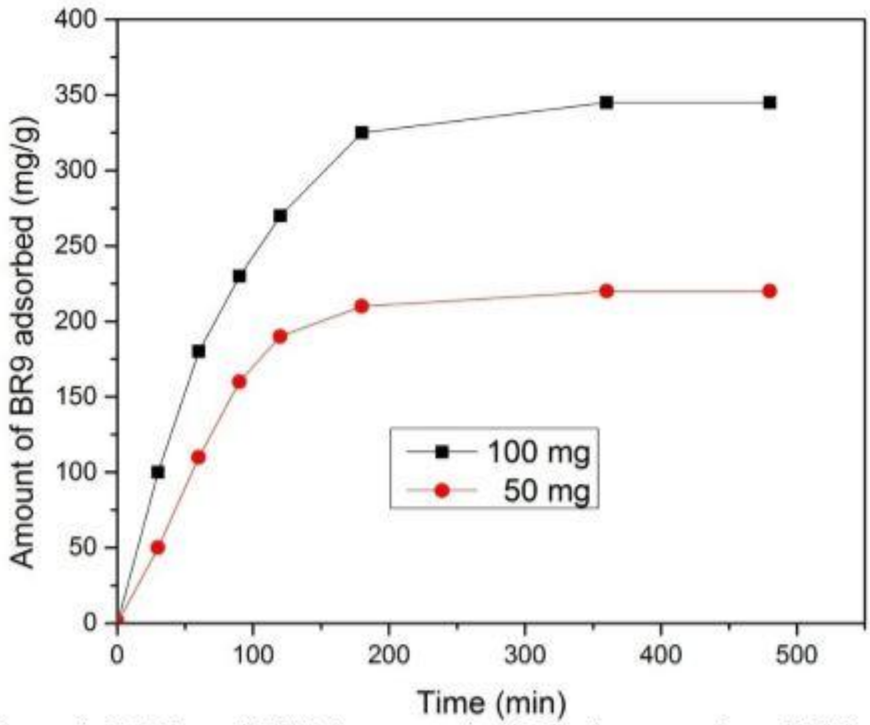

Figure 4.6: Effect of MFC dosage on the BR9. Concentration of BR9 = 10 ppm; solution volume of BR9 = 40 ml; temperature = 25°C; agitation = 200 rpm; MFC dosage = 50 and 100 mg; pH = 7

4.2.1.3 Effect of Solution pH

The pH is a significant parameter affecting the removal uptake of toxic pollutants from wastewater due to variation of H^+ and $OH^-$of the treatment medium Waranusantigul, P., et al. (2003). In the case of BR9, lower amounts of BR9 were adsorbed at lower pH range of 2-7, while larger amounts of BR9 adsorbed at higher pH range. The obtained results indicated that adsorption process of BR9 was favorable in basic medium as shown in Figure (4.7).

As determined, the pH_{pzc} of MFC was obtained as 6.6 and the surface of MFC will be positive at pH below this point. Hence, at lower pH the adsorption capacity is lower due to competition between the cationic dye molecule and the positive MFC surfaces. As the pH of the medium increased, the adsorption capacity increased steadily due to decreased protonation at the MFC surfaces which favor BR9 adsorption via electrostatics attraction between the negative MFC surfaces and the BR9 cations(El Haddad, M., et al.2012).

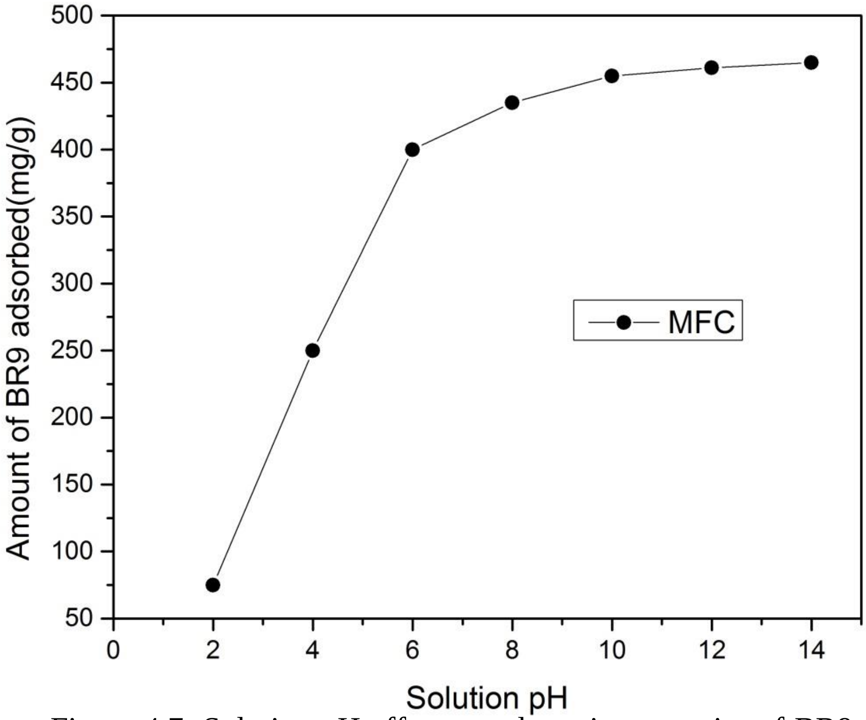

Figure 4.7: Solution pH effect on adsorption capacity of BR9 onto MFC; concentration of BR9 = 10 ppm; solution volume of BR9 = 20ml; temperature = 25°C; agitation = 200 rpm; MFC dosage = 50mg

4.2.1.4 Effect of Contact Time

The Figure 4.8 shows the amount of BR9 adsorbed onto MFC as a function of time. The BR9 adsorption was fast initially and gradually decreased with time until equilibrium attained.

Fast adsorption was observed during the first 50 min which may be attributed to abundant adsorption sites which attracted the dye particles from the bulk solution at the initial stages. From the figure it is obviously shown that adsorption reaction nearly attained equilibrium within 180 minutes and after which no substantial amount of BR9 was adsorbed with increasing contact time after equilibrium was achieved, indicating that all available sorption sites had been occupied.

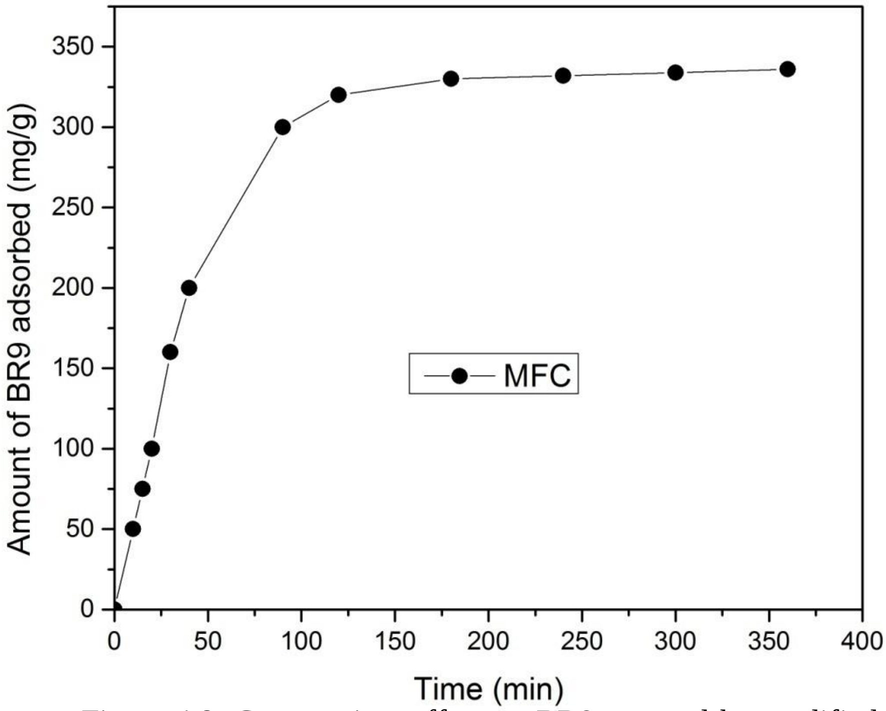

Figure 4.8: Contact time effect on BR9 removal by modified Ferula communis; MFC dosage = 50 mg; concentration of BR9 = 10ppm; temperature = 25°C; solution volume of BR9 = 40 ml; agitation = 200 rpm; pH =7.

4.2.1.5 Effect of Ionic Strength

The effect of ionic strength is significant parameter which has not yet been sufficiently described and which serves as threat to effective decolorization process. During dyeing techniques it is well-known that certain added substances, for example, surfactants and salts can either enhance or reduce color adsorption property of the fabric or material at equilibrium. Impact of ionic strength on adsorption of BR9 onto MFC was examined at room temperature. The interaction between the BR9 and MFC are mainly electrostatic, and it was notice that the adsorption amount of BR9 decreases with increasing ionic strength as shown in Figure 4.8. This could be ascribed to electrostatic competition between BR9 cations and K^+ ions for the available sorption sites.

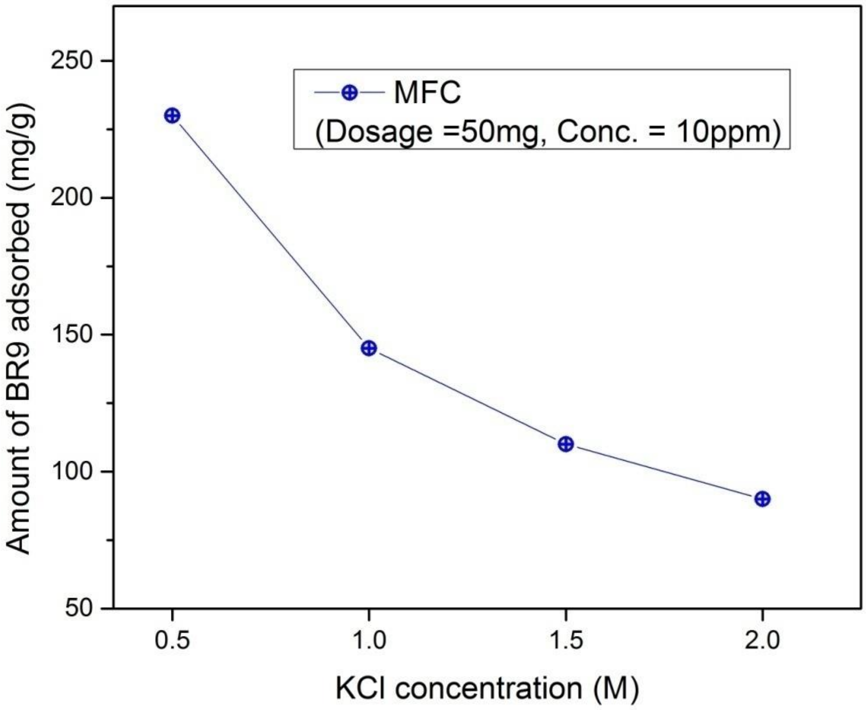

Figure 4.9: Effect of ionic strength. Concentration of BR9 = 10 ppm; solution volume of BR9 = 40ml; temperature = 25°C; agitation = 200 rpm; MFC dosage = 50mg; pH =7.

4.2.1.6 Effect of Temperature of BR 9 Adsorption

Adsorption process of BR9 were also conducted at different temperatures (25, 50 and 75°C) using 50 mg of MFC and BR9 concentration of 10 mg/L as shown in Figure4.10. The results indicated that the uptake capacity increased with increased solution temperature, which is attributed to enhanced diffusion of BR9 molecules towards the active sites of MFC leading to higher adsorption capacity (Han, X., et al.2011).

The obtained data indicated that the rate of BR9 removal increased steadily with temperature until 300 min, after which no substantial uptake was observed and this may be attributed to decreasing free active sites on MFC with time. The increased adsorption with the increase in temperature showed that the treatment process is endothermic in nature and may be ascribed to enhanced tendency of the BR9 molecules to escape from the bulk media to the MFC phase (Chiou, M. S. and H. Y. Li 2003).

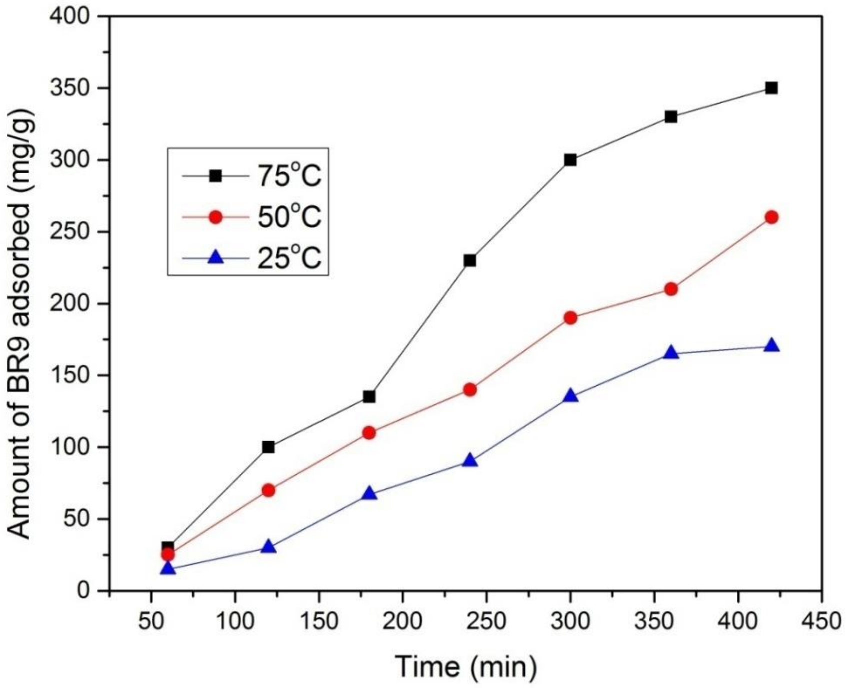

Figure 4.10: Effect of temperature on the dye adsorption onto MFC. BR9 concentration = 10 mg/L; MFC dosage = 50 mg; solution volume of BR9 = 40 ml; temperature = 25, 50 and 75 °C; agitation = 200 rpm

4.3 Thermodynamic Study

In general free energy changes were negative through the adsorption process as tabulated in Table 4.1, this confirmed the adsorption process of BR9 onto MFC was spontaneous. The more negative value of ΔG° as temperature increased, indicate higher temperatures favor the adsorption feasibility and spontaneity of the treatment process energetically. The values of ΔS°and ΔH°are positive and indicate increased randomness at the adsorbate-adsorbent interface, strong affinity of MFC towards BR9 and endothermic adsorption process respectively (Oladipo et al. 2014).

Table 4.1: Thermodynamic parameters for adsorption of BR9 onto MFC at different temperature

Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol. K)
298	-4.67373	9.9214	9.98
323	-8.41523	9.9214	9.98
348	-12.1573	9.9214	9.98

For thermodynamic attributes of the adsorption of BR9 on MFC adsorbent, the thermodynamic parameters such as change in free energy ΔG°, entropy ΔS°and enthalpy ΔH° have been examined from the equations below:

$$K_d = \frac{q_e}{c_e} \tag{3}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{4}$$

$$\Delta G^\circ = -RT \ln K_d \tag{5}$$

$$InK_d = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{6}$$

$$InK_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{7}$$

In addition, adsorption of BR9 is found to have negative values of ΔG°, positive value ΔH° represent that the adsorption process is endothermic and entropy has been determined as the degree of randomness of a process. The positive value of ΔS° indicates that some structural changes take place on the adsorbent and the randomness at the solid-liquid interface in the adsorption process increases during the adsorption process. Free energy change ($\Delta G°$) of the adsorption reaction is given by:

$\Delta G^{\circ} = -RT \ln K_d$ where ΔG° free energy change (Kj/mol), R universal gas constant (8.314 J/ mol. k), T temperature (K) and K_d distribution constant ($\frac{q_e}{C_e}$). The values of ΔH° and ΔS° could be calculated from the Van't Hoff equation.

4.4 Adsorption Isotherm Study

Langmuir model is widely applied in adsorption science and assumes that adsorption of solute is limited to a monolayer sites within the adsorbent and no interaction the between adsorbate substances Oladipo, A.A et al.(2014). The experimental data indicated satisfactory uptake of BR9 by MFC from aqueous solution. In addition, with increasing temperature the Q_m and K_L also increases, as shown in Table 4.2. K_L is the model adsorption constant, and adsorption process increases as the value of K_L increased.

Freundlich model assumes that the adsorption processes occur on heterogeneous surfaces of the adsorbent and the adsorbate particles may interact. Tan, I. A. W.,et al.(2008). The Freundlich constants, K_F and n represent the adsorption capacity and adsorption intensity respectively. The values of the constants are obtained by plotting log q_e against log c_e. The Langmuir model fit the experimental data well suggesting that monolayer coverage of BR9 occur on the MFC surface. As tabulated, Freundlich isotherm does not fit the experimental data well with lower correlation coefficient. The obtained values of Freundlich constant, $0 < 1/n> 1$ showed that the adsorption process is favorable.

Figure 4.11: Adsorbed Basic Dye onto MFC

Table 4.2: Isotherm parameters for adsorption of BR9 onto MFC at different temperature

Langmuir model	**T (°C)**	**Q_m (mg/g)**	**K_L (L/mg)**	**R_L**	**R^2**
$\frac{c_e}{q_e} = \frac{1}{q_m k_L} + \frac{c_e}{q_m}$	25	354.89	17.22	0.00289	0.9894
	50	421.98	24.99	0.00199	0.9983
	75	637.88	33.88	0.00147	0.9995
Freundlich model	**T (°C)**	**K_F (mg/g)**	**n**	**1/n**	**R^2**
$\ln q_e = \ln k_F + \frac{1}{n} \ln c_e$	25	124.11	2.3656	0.4227	0.9876
	50	111.45	3.6755	0.2720	0.6955
	75	135.86	5.1641	0.1936	0.9002

4.5 Adsorption Kinetic Modeling

In order to design an efficient adsorption process it is necessary to understand the adsorption kinetics for the investigated system. Pseudo-first order model is suitable for explaining physical adsorption and it assumes that the rate of adsorbate uptake with time is in direct relation to the difference in saturation concentration on the adsorbent surfaces (Mittal, A., et al.2009).

The pseudo-first order kinetic model can be expressed as:

$$\log(q_e - q_t) = q_e - \frac{K_1}{2.303}t \qquad (8)$$

Where: q_e and q_t are the amount of BR9 adsorbed at equilibrium (mg/g) and at contact time t (min) respectively, K_1: rate constant (min^{-1}).

As shown in Fig. 4.12, a linear plot of log (q_e-q_t) against time suggests the kinetic model is applicable to explain the adsorption process but low correlation coefficient (R^2) was obtained and there is no agreement between the calculated q_e and the experimentally obtained q_e, hence, BR9 removal does not follow first-order kinetic model.

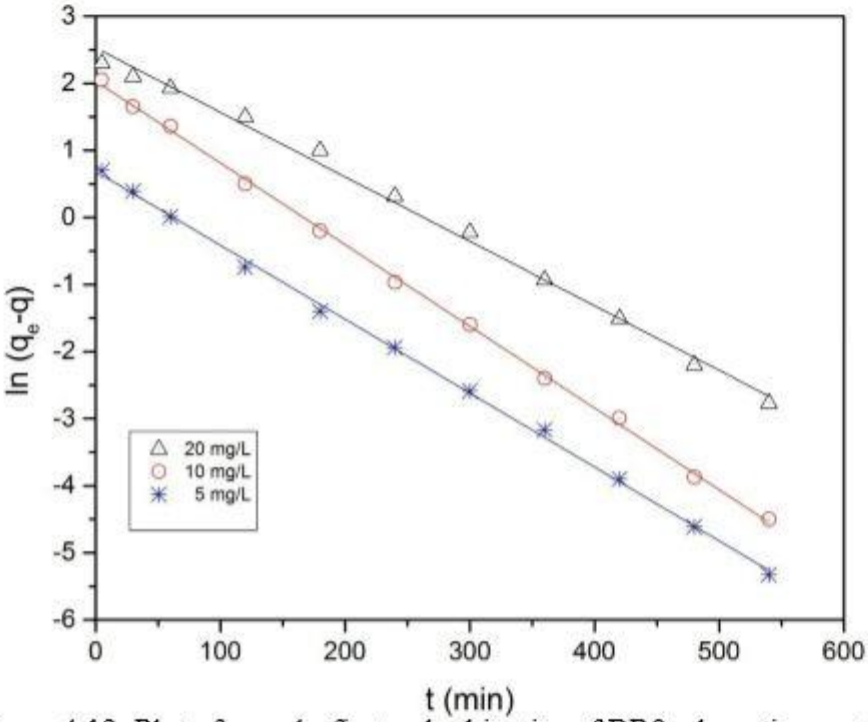

Figure 4.12: Plot of pseudo-first order kinetics of BR9 adsorption onto MFC

Additionally, the experimental results were fitted to the pseudo-second order kinetic equation as shown in equation 9. The pseudo-second order suggests that the adsorption process involves exchange or electrostatic sharing of electrons between the adsorbate and the adsorbent (Gupta, V. K., et al.2010).

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (9)$$

Where: K_2 is rate constant ($\frac{g}{mg \cdot \min}$) for pseudo-second order model. K_2 and q_e were calculated from the slope and intercept of the plot obtained by plotting ($\frac{t}{q}$) versus time t.

As tabulated the calculated q_e from pseudo-second order model were close to the experimental q_e, and the R^2 values obtained from the model are higher than those from pseudo-first order kinetics. Therefore, the adsorption process using MFC can be said to follow second-order kinetic model.

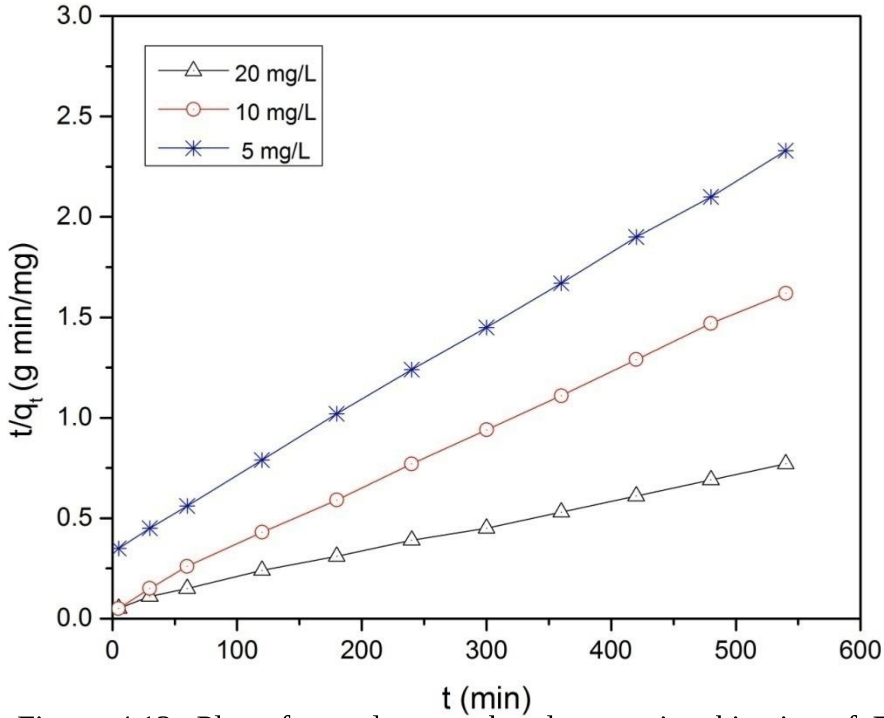

Figure 4.13: Plot of pseudo-second order sorption kinetics of BR9 adsorption onto MFC

Table 4.3: Adsorption kinetic parameters of BR9 dye onto MFC

BR 9 concentration	**5mg/L**	**10mg/L**	**20mg/L**
Pseudo-first order kinetic			
$q_{eexp.}$(mg/g)	399.67	411.22	445.86
$q_{e\ cal.}$(mg/g)	287.23	103.44	208.11
K_1 (1/min.)	0.0151	0.0126	0.0152
R^2	0.9623	0.9334	0.8597
Pseudo-second order kinetic			
$q_{eexp.}$(mg/g)	399.67	411.22	445.86
$q_{e\ cal.}$(mg/g)	387.11	413.67	486.12
K_2 (g/mg.min.)	0.0055	0.0015	0.0012
R^2	0.9999	0.9986	0.9996

Chapter 5

CONCLUSION

In the present work, a low-cost adsorbent was prepared, characterized and its adsorption capability were estimated. Conclusion can be drawn:

- MFC is efficiently suitable to treat wastewater containing basic dyes such as BR9.
- The adsorption process was spontaneous, endothermic in nature and obeyed Langmuir isotherm, as obtained from the thermodynamic parameters.
- The kinetic data showed that MFC can treat dye containing effluents in a short period making the process economical.
- Finally MFC can be utilized as alternative high capacity low-cost adsorbent.

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