JIMMA UNIVERSITY

SCHOOL OF POST GRADUATE STUDIES

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DEPARTMENT OF CHEMISTRY

M.Sc. THESIS ON

ADSORPTIVE REMOVAL OF SAFRANIN FROM AQUEOUS SOLUTION ONTO AVOCADO SEED

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JIMMA, ETHIOPIA

ADSORPTIVE REMOVAL OF SAFRANIN FROM AQUEOUS SOLUTION ONTO AVOCADO SEED

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Adsorptive removalofSafranin from aqueous solution onto avocado seed.

By

BizuayehuNigat

A Thesis Submitted to School of Graduate Studies, Jimma University, in Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemistry

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List of Abbreviations

FT-IR	Fourier transform infrared
UV-Vis	Ultra violet visible
XRD	X-ray diffraction

Abstract

The most naturally distinguishable pollutants in the environments are dyes or colored compounds. Maximum of the industries use dyes and pigments to color their products. Thus, the removal of dyes from effluents could be considered as an important issue for risk assessment.In this work, locally available biomass obtained from avocado seed was investigated as adsorbent for the removal of Safranin dye. The study employed a batch method to investigate the adsorptiveremoval of Safranin dye from aqueous solution. Parameters that influence adsorption such as pH, adsorbent dose, initialconcentration of Safranin dye, contact time and temperature have been studied. The Langmuir and Freundlich adsorption isotherm models were applied to describe the equilibrium isotherms and the isotherm constants were also determined. TheFreundlich adsorption isotherm model agrees with the experimental data well.The pseudo-first-order and pseudo-second-order kinetic models were used to describe the kinetic data and the rate constants were evaluated. The results of kinetic models showed that the pseudo-second order kinetic model best fitted with the experimental data and was found to have R^2= 0.9999. Thermodynamic parameters, enthalpy change (ΔH), entropy change (ΔS) and Gibbs free energy change (ΔG) were also calculated for the removal of Safranin dye. The results of thermodynamic parameters showed that the adsorption process is feasible, spontaneous in nature and endothermic. Maximum adsorption efficiencies was 98.48% for Safranin dye at pH 10.

Keywords: Adsorption, Safranin dye, Avocado seed, Isotherm, Kinetic, Thermodynamic

1. INTRODUCTION

1.1. Background of the study

Dyes are extensively used in different manufacturing industries, of which textile and leather industry is the largest consumer and, at the same time, a great generator of dye-loaded wastewater. Removal of dyes from wastewater is significant environmental importance, both from esthetic reasons and because of their adverse effects on aquatic life and human health, in terms of toxicity, mutagenicity and carcinogenicity [1].Industries from various sectors generate effluents containing substantial amounts of organic compounds.These compounds, when launched into water bodies without any prior treatment, can cause damage to the ecological balance in the environment, since its molecules may show carcinogenic properties or mutagenic actions on living organisms[2].Currently, dyes are one of the most important groups of chemicals widely used in paper, textiles, pharmaceutical, rubber, plastics, leather, cosmetics, and food industries, in order to color products. However, discharge of wastewater without proper treatment from these industries as a byproduct in to water bodies has been reported to impair the normal function of aquatic life and change in food web [3].

Dyes present in water bodies is toxic to aquatic as well as human lives, this is due to the presence of an aromatic structure and, in some cases, metals in their structure. The biodegradability of this type of pollution is generally difficult because dyes have a synthetic origin and a complex molecular structure which makes them more stable and difficult to be biodegraded [4]. Moreover, waste water containing dyes are one of the sources that diminish the esthetic value of rivers and causes eutrophication. The effluents are highly visible even at very low concentrations and undesirable. It might be also toxic and carcinogenic [5,6].

Synthetic dye stuffs are extensively used as coloring agents in the textile, paper, leather, gasoline, pharmaceutical, and food industries [7]. Most of the synthetic dyes and their degradation products are of great environmental concern due to their widespread usage, toxic and carcinogenic and their low removal rate during aerobic wastewater treatment [8, 9].Colored water can affect plant life, and thus an entire ecosystem can be destroyed by the contamination of various dyes in water. Some dyes are toxic and carcinogenic.

Due to this, dye-containing water to undergo treatment before disposal to the environment is necessary [10].

Safranin is one of the most commonly used cationic azine dyes, which is among the oldest known synthetic dyes. Safranin is mainly used as food dye in flavoring and coloring candies and cookies. It is also used for dyeing tannin, cotton, bast fibers, wool, silk, leather and paper [11]. Safranin can causes several acute health problems such as irritation to the skin, mouth, throat, tongue, lips, and eyes as well as stomach pain [9, 10]. Hence, the removal of Safranin dyes from aqueous solutions is highly significant.

Many physicochemical methods such as adsorption, coagulation, precipitation, filtration, and oxidation have been attempted for treatment of effluent containing dyes [12**]**.The potential of various methods for the removal of chemical dyes from effluents have been explored, and the adsorption process has proven to be the most effective. Among the treatment options, adsorption is one of the most commonly used techniques due to the easiness of design, operational simplicity and good efficiency in the removal of pollutants[13].Commercially available activated carbon as an adsorbent has yielded excellent results [14].However, taking into account the high costs involved in the preparation and regeneration process, the feasibility of alternate adsorbents has been studied recently by scientists. Therefore, other attempts that explore cheap, locally available and effective materials need to be made.

Plant biomass is widely distributed in nature, and bioadsorbents based on the relatively inexpensive plant biomass aroused wide concern. Biological materials are organized by sophisticated architecture developed from evolution. The unique microstructure is also desirable in adsorption, catalysis, and so on. On the other hand, plant biomasses have similar chemical composition composed of lignin and cellulose with unique surface chemistry with the presence of various polar functional groups, such as alcohols, aldehydes, ketones, carboxylic, phenolic and ether groups[15 - 17]. These functional groups have high affinity for pollutant from wastewater. For example, Henna plant biomass (stem) packed in an up-flow anaerobic bio-filter enhanced removal performance of azo dyes [18].In this direction, this research work reports the preparation of low-cost, active adsorbent from avocado seed, a waste agricultural biomass, and its utilization in the removal of color (Safranin as a model dye) from aqueous solution.

Removal methods of dyes in effluents may be divided into three main categories: physical, chemical and biological [19]. Physical methods are found to be easier and economical. Adsorption process belongs to this category and this is found to be very effective and is applied in liquid phase.

A considerable amount of interest has recently been focused on the adsorption technique for the removal of dyes from waste water onto various adsorbent such as treated ginger waste[20], activated carbon[21],untreated coffee husks[22],agriculture wastes[23], respectively.

Many researchers have studied the low-cost adsorbents from renewable and cheaper precursors which are mainly industrial and agricultural by-products [24], and their findings are quit conclusive. The use of agricultural waste material such pineapple peels [25], soybean hull [26], Thuja [27] , rice husks [28] and corncob [29] as a low-cost adsorbents for removal of Safranin in wastewater has been investigated and was found to be a potentialadsorbent.However,literatures have been found no work involving the use of avocado fruit as an adsorbent for the removal of Safranin dye from waste water. Thus, the main aim of this study is to investigate the removal of Safranin dye from aqueous solutions using avocado seed. Also the effect of pH, adsorbent dose, contact time, initial dye concentration and temperature on the adsorption has been investigated.

1.2. Statements of the problem

Dyes have wide application and found in all segment of environment. It is also used in chemical as well as radiochemical laboratories for the purposes of analytical means. The discharge of dye-bearing wastewater into natural streams and rivers posses' serious pollution problem, as dyes impart toxicity to aquatic life and are damaging the aesthetic nature of the environment.Safranin is considered as a highly toxic substance but found use in food, textile, paper, rubber industry, etc. The presence of high concentration of Safranin in aquatic system has a remarkable effect on the health of human, animals and plants. Contamination of Safranin in water can cause allergic dermatitis, skin irritation, cancer and mutation in human being[23]. Different lists of bioadsorbent for removal of Safranin dye such as spent coffee ground [23], pineapple peels [25], soybean hull [26], thujaorientalis [27]. Thus, looking material for the efficient removal of Safranin dyes from waste water is very important and this study was to carryout adsorptive removal of Safraninfrom aqueous solution onto avocado seed. Thus, the present study can put avocado seed is an alternative adsorbent for the removal of Safranin dye from aqueous solution.

1.3. Objectives of the study

1.3.1. General objective

The main objective of this study was to investigate the adsorptive removal of Safraninfrom aqueous solution onto avocadoseed.

1.3.2. Specific objectives

The specific objectives of this study were:

- Prepare low cost adsorbent from avocado seed.
- Characterize the adsorbent by FT- IR and XRD.
- Study the effect of different parameters on the adsorption of basic Safranin dye.
- Study removal ofSafranin from aqueous solution by using avocado seed.

1.4. Significance of the study

The main goal of scientific research is to equip the learners from solid knowledge of the science chemistry to practical aspects. It helps to grasp the global picture of the science in a tangible method. So, this has focused to investigate the locally available avocadoseed in order to study its removal efficiency of Safranin dye from aqueous solution. In similar way, it would have the significance in provide information about the adsorptive removal of Safranin from aqueous solution onto avocado seed as well as a reference for other researchers who want to study on adsorption.

2. REVIEW OF RELATED LITERATURE

2.1. Dye contaminated waste water and its treatment

Pigments and dyes are widely used in the textile and leather dyeing, paper, printing, pharmaceutical, and cosmetic industries. Many of these have been identifiedas toxic or even carcinogenic [30]. Discharge of these toxic substances into water bodies could pollute water and make it unfit for aquatic life. Further, the dyes could contaminate water and make penetration of sunlight to reach the lower layers impossible, thus affecting the possibility for aquatic plants to perform photosynthesis [31]. Polluted water not only damages plants and animals but also is harmful to the environment. A majority of these dyes are stable to light and oxidation.

Safranin is one of the most commonly used cationic azine dyes, which is among the oldest known synthetic dyes. Safranin is mainly used as food dye in flavoringand coloring candies and cookies. It is also used for dyeingtannin, cotton, bast fibers, wool, silk, leather and paper [11].Safranin can causes severalacute health problems such as irritation to the skin, mouth,throat, tongue, lips, and eyes as well as stomach pain [8, 11]. Hence the removal of Safranin dyes from aqueous solutions is highly significant.

Many physical and chemical processes have been used toremove synthetic dyes from industrial wastewaters such ascoagulation-flocculation [32], membrane filtration [33], adsorption [34,35,36]. Of these methods, adsorption and biosorption have been determined to besuperior due to their effectiveness, low cost, and ease of application[37].

2.2. Safranin dye Removal

This review is based on adsorptive mode of Safranin dye removal from wastewater using agricultural low cost adsorbent. Many scientist and researcher did many works for the removal of dye. A briefer view of work by the different researcher is presented. All researchers in the followed papers studied the physicochemical parameters such as solution pH, dye concentration, contact time and have been varied to study the adsorption phenomenon.

The evaluation of the efficiency of Safranindye removal with application of carbonized spent coffee ground as adsorbent was investigated [23]. The studies of sorption kinetics of the dye showed a rapid sorption dynamics by a second-order kinetic model with high correlation coefficient almost with a unit value 0.999. The experimental data were correlated reasonably well by Langmuir adsorption isotherm. The maximum adsorption capacity Q_O is found to be 3.76 mg/g. Adsorption percentage increase with increasing the adsorbent loading.

The pineapple peels as agricultural waste, for the removal study of Safranin in wastewater has been investigated [25]. Maximum adsorption capacity was reached after 90min, during which the adsorbate and adsorbent were in contact at 29^{o}C. The results obtained fitted Freundlich and Langmuir models; the Freundlich model better described the equilibrium dye uptake than the Langmuir.

Thuja biomass is a potential and cheap biosorbent for removal of Safranin from its aqueous solution and industrial wastewater remediation was investigated [27]. The sorption kinetics followed the pseudo-second order equation better than pseudo-first order rate model indicating that several processes were involved in dye sorption onto the biosorbent. The equilibrium sorption data are satisfactorily fitted in the order Freundlich>Temkin>Dubinin-Radushkevich> Langmuir. The changes in the standard enthalpy values are found to be negative indicating exothermic process, standard free energy of adsorption was found to be negative which means that the adsorption process is thermodynamically favored.

Sugarcane Bagasse was shown to be an inexpensive agricultural industrial adsorbent that can be appropriately used to eliminate Safranin in aqueous solution in a batch method. Untreated and sulfuric acid and hydroxide sodium-treated sugarcane bagasse were utilized in Safranin adsorption with different dye concentrations and pH as well as different contact times. The initial pH10 was obtained as the optimum pH for three adsorbents. The isotherm data indicated the best fit to the Langmuir model, giving evidence that the adsorption took the form of monolayer coverage. The kinetics results were fixed on the second-order kinetic model [38].

2.3. Adsorption.

Adsorption is a process that occur when a gas or liquid solute accumulates on the surface of a solid or a liquid, forming a molecular or atomic film. In other words, adsorption is the adhesion of atoms, ions, biomolecules or molecules of gas, liquid, or dissolved solids to a surface. It is a surface phenomenon and a consequence of surface energy. The atoms on the surface of the adsorbent are not wholly surrounded by the other atoms and thus, can attract adsorbate. Adsorption takes place primarily on the walls of the pores or at specific sites inside the particle. As the pores are generally small, the internal surface area is greater than the external area.Adsorption has found to be one of the most effective physicochemical methods for textile wastewater treatment.

Types of adsorption

Depending on the type of attractions between adsorbate and adsorbent and the exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as follows:

1.**Physisorption**: In case of physisorption/physical adsorption, molecules are attracted byweak van der Waals forces towards the adsorbent molecules.

2.**Chemisorption**: It is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond.

Contrary to physisorption, chemisorption occurs only as a monolayer and, furthermore, substances chemisorbed on solid surface are hardly removed because of stronger forces at stake. Under favorable conditions, both processes can occur simultaneously or alternatively. Physical adsorption is accompanied by a decrease in free energy and entropy of the adsorption system and, thereby, this process is exothermic [39].

2.4. Adsorption Variables.

2.4.1. pH

The pH of the dye solution is an important factor in the adsorption processes, especially on the adsorption capacity. It influences not only the surface charge, and the degree of ionization of the functional groups of the adsorbent, but also the dye chemistry. An effective change in pH values causes changing adsorption.It is the most important regulator of adsorption affecting the solution chemistry of the pollutants themselves, the activity of functional groups in the adsorbents, and competition with coexisting ions in solution [40]. The efficiency of adsorption is dependent on the pH of solution since variation in pH leads to the variation in the surface properties of the adsorbent and the degree of ionization.

It is known that ionic dyes upon dissolution release colored dye anions/cations into solution. The adsorption of these charged dye groups onto the adsorbent surface is primarily influenced by the surface charge of the adsorbent, which is in turn influenced by the solution pH.To study the effect of pH on adsorption, experiments are performed by using different an initial dye concentration. As the pH of the solution increases, the positive charge on the surface decreases and the number of negatively charged sites increases [41].Earlier works reported that cationic dye sorption increases with increase in pH [42].At lower pH range the decrease in adsorption is due to the electrostatic repulsion between the cationic dye species and the protonated adsorbent surface.

2.4.2. Dye concentration.

The amount of dye adsorbed highly depends on the initial dye concentration. Removal efficiency is greatly depended on the initial concentration of solution of adsorbate. This is the fact that increasing the initial dye concentration caused an increase in the adsorption driving force.

The effect of initial dye concentration in the removal of basic dyes the sorption rates of dye are rapid. Generally, when adsorption involves a surface reaction process, the initial adsorption is rapid. Then, lesser adsorption follows, as the available adsorption site gradually decreases [43].

2.4.3. Agitation time

Increase in the speed of agitation enhances the rate of adsorption. By increasing the speed of agitation, the randomness increases during the adsorption process, resulting in better contact between the adsorbate and adsorbent in the system and hence enhancing the rate of adsorption.Other researchers indicate that the adsorption of dye slowly increases and attained equilibrium at further agitation time showed no change in the adsorption process [44].The process of agitation of the adsorbate-adsorbent phase has the tendency of exposing active surfaces which otherwise, may be inaccessible.

2.4.4. Adsorbent dosage

The adsorbent dose is an important parameter in adsorption studies because it determines the capacity of the adsorbent for a given initial concentration of dye solution.

To investigate the effect of adsorbent amount, the adsorption of basic dyes increases with different adsorbent initial dye concentrations increases. This can be attributed to increased surface area resulting from the increase in adsorbent mass, thus increasing the number of active sites. Similar behavior for the effect of adsorbent concentration on basic dye adsorptions capacity was reported in the literature for other types of adsorbents [45].

The net equilibrium amount adsorbed however is an expression of the efficiency of an adsorbent which may not show increase in the amount adsorbed per unit mass as the adsorbate dose increases [46].As the adsorbent dosage increases, the adsorbent sites available for the dye molecules also increase and consequently better adsorption takes place.

2.5. Adsorption Isotherm Models

The equilibrium adsorption isotherm is important in the design of adsorption systems. The adsorption isotherm describes how adsorbates interact with adsorbents and therefore it is critical in optimizing the use of adsorbents.

The adsorption isotherm is an important technique providing precious information to predict the adsorbent efficiency for the removal of a specific adsorbate. It is reported in several studies that non-linear analysis should be considered as a better approach to obtain the isotherm parameters as sometimes linearization of non-linear experimental data may distort the error distribution structure of isotherm [47].

In this section two-parameter isotherm, models (Freundlich and Langmuir) examined to find out the best fit for the experimental data.

The Langmuir isotherm model is based on the assumption that there are a finite number of active sites which are homogeneously distributed over the surface of the adsorbent.The Langmuir isotherm is one of the most frequently used isotherm model and assumes uniform energies of adsorption [48]. The Langmuir equation can be written as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m\, b_L} \text{..} (1)$$

Where, q_m (mg/g)denote the maximum adsorption capacity and b_L(L/mg) is the constant related to the free energy of adsorption.

When the adsorption obeys the Langmuir equation, a plot of C_e/q_eversus$C_e$should be a straight line with a slope of $1/q_m$and intercept $1/q_m$b.This important characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless factor, R_L which is defined as:

$$R_L = \frac{1}{1+b_L C_o} \text{...} (2)$$

The$\boldsymbol{R_L}$values indicate the type of adsorption as either unfavorable ($\boldsymbol{R_L}$>1), linear($\boldsymbol{R_L}$=1), favorable (0<$\boldsymbol{R_L}$<1), or irreversible ($\boldsymbol{R_L}$=0).

The Freundlich isotherm mode applies to adsorption on heterogeneous surfaces with interaction between the adsorbed molecules, and is not restricted to the formation of a monolayer. This model assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases and, correspondingly, the sorption energy exponentially decreases on completion of the sorption centers of the adsorbent.

The Freundlich isotherm is an exponential equation and assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases [49].

The Freundlich expression can be represented as:

$$log q_e = log K_f \quad + 1/\text{n} \;\; log C_e \text{................................} (3)$$

Where, $K_f$is the Freundlich constant related to the bonding energy 1/nis a constant indicative of the intensity of the adsorption and $q_e$is the amount adsorbed at equilibrium (mg/g).The values of$K_f$and1/ncan be obtained from the slope and intercept of the plot of$logq_e$versus $logC_e$.Values of 1/n ranges from 0 to 1 and the closer this value to zero, the more heterogeneous the adsorbent surface.

This model is applicable to the adsorption on heterogeneous surfaces assuming different binding energies for the adsorption sites.

2.6.Adsorption Kinetic Studies

Adsorption is a time dependent process and it is very important to know the rate of adsorption for design and evaluate the adsorbent in removing the dyes in wastewater. The kinetics of adsorption based on the overall adsorption rate by the adsorbents is described by the first order Lagergren model and pseudo second-order.

The first-order rate expression of Lagergren[50] is given as:

$$\frac{dq_t}{d_t} = k_1(q_e - q_t) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Where q_e and q_t are the amount of Safranin dye adsorbed on adsorbent at equilibrium and time t, respectively (mg/g), and k_1 is the rate constant of the first order adsorption (min^{-1}). Integrating equation (4) for the boundary conditions t=0 to t = t is the following:

$$log(q_e - q_t) = logq_e - \frac{k_1}{2.303}t \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

The plot of$log(q_e - q_t)$ versustwill give a straight line and the value of k_1 can be obtained from the slope of the graph.

The second-order kinetic model is expressed as [51]:

$$\frac{dq_t}{d_t} = k_2(q_e - q_t)^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Where, k_2 is the pseudo-second order rate constant of adsorption ($g\ mg^{-1}\ min^{-1}$). The linearized integration form of (6) is given as:

$$\frac{t}{q_t} = \frac{1}{k_2{q_e}^2} + \frac{1}{q_e}t \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

If the pseudo-second order kinetics is applicable to the system, then the plot of $\frac{1}{q_t}$versus tof equation (7) will give a linear relationship with $\frac{1}{q_t}$and$\frac{1}{k_2 q_e{}^2}$as a slope and intercept respectively.The values of q_e and$k_2$can be determined from the slope and intercept.

3. MATERIALS AND METHODS

3.1. Instrument and Apparatus

pH meter (pH – 013,portable pH Meter),UV- Vis spectrophotometer (Model 6705 JENWAY), different sized volumetric flasks, mortar and pestle, beakers, measuring cylinders, drying oven (Model GENLABWIDNERS, England), filter funnel, conical flask, graduated cylinder, Thermostatic water bath shaker (Model Grant GLS400, England), Sieve (125µm), polyethylene containerflasks,Whatmanno.42 filter paper, analytical balance, Fourier transforms infrared (FT-IR) spectrophotometer (spectrum 65 FT-IR, Perkin Elmer model) and X ray diffraction (XRD) were used during the experiment.

3.2. Chemicals

The chemicals used for this study were: Safranin dye, $C_{20}H_{19}ClN_4$(BDH Chemicals Ltd, England), sodium hydroxide, NaOH (Fisher scientific, UK Limited, 99.3%), hydrochloric acid, HCl (BluluxLaboratories(P) Ltd, 35.4%).All chemicals used in this study were analytical reagent grade.

3.3. Preparation of Adsorbate

Stock solution (1000 mg/L) of Safraninwas prepared by dissolving 1 g of the dye in 1000 mL of distilled water. The stock solutions were diluted to obtain required standard solutions.

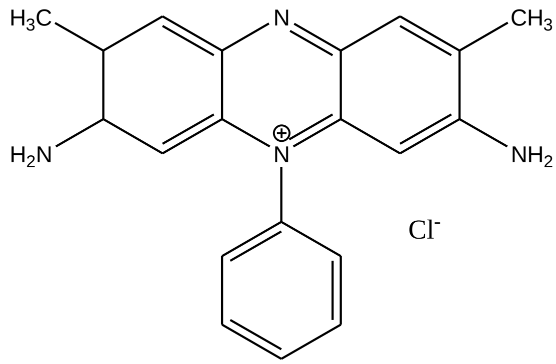

Figure 1: The structure of Safranin.

3.4. Preparation of Adsorbent

Avocado seed was collected from nearby juice house. It was then cut in to smaller pieces and washed with distilled water to remove the surface adhered particles. The sample was further dried in the sunlight for ten days. Then ground using mortar and pestle. The grounded sample was then sieved to ≤ 125 μm particle sizes.The resulting powder was oven dried for 24 hours at 105 ^{0}C [52]. Finally, the product was stored in a polyethylene plastic container flask and used in the adsorption studies.

3.5. Characterization of the adsorbent

Fourier transform infrared (FT-IR) spectra of dried unloaded avocado seed and Safranin dye loaded avocado seed were recorded wavenumber range at 4000-400 cm^{-1} to determine the surface functional groups and X-ray diffraction (XRD) to determine the crystal nature of the adsorbent.

3.6. Batch adsorption studies

For batch adsorption studies, the adsorption experiments were performed at room temperature.The adsorbent and the adsorbate were separated by filtration and the filtrate was analyzed for residual Safranin concentration spectrophotochemically using UV-Visible spectrophotometer at λ_{max} ~ 519 nm.

The percentage removal of Safranin dye from solutions was calculated by the following equation 8,

$$\% \text{ Removal} = \frac{(C_o - C_e)}{C_o} \times 100 \text{ .... (8)}$$

Where, C_o – Initial dye concentration (mg/L) and C_e – Equilibrium dye concentration (mg/L)

The amount of dye adsorbed on adsorbent q_e was determined by equation 9,

$$q_e = \frac{(C_o - C_e)V}{\text{W}} \text{.. (9)}$$

Where, V – Volume of dye solution (L) and W – Mass of adsorbent (g)

3.7. Analysis of Dye

The concentrations of Safranin dye before and after the adsorption processes was monitor using a UV-visible spectrophotometer.

3.8.Effect of pH on adsorption

The effect of pH on the adsorption of the dye solution was studies in the pH range 4 to 10. The pH of Safranin solution was adjusted before the experiments by using 0.1M NaOH and 0.1M HCl. This was done by contacting 0.5 g of avocado seed with 30 mL of 5 mg/L initial adsorbateconcentration. The optimum pH was determined as the pH with the highest percent adsorptionof Safranin.

3.9. Effect of initial concentration on adsorption

The initial adsorbate concentration effect on the adsorption by avocado seed was determined by ranging the initial concentration from 5 to 25 mg/L of 30mL.This study was conducted at optimum pH with adsorbent dose 0.5 g.

3.10. Effect of contact time on adsorption

The contact time effect on the adsorption of Safranin dye onto avocado seed was studied in the range of 5 to 90 minutes and at a concentration of 5 mg/L for Safranin.

3.11. Effect of adsorbent dose on adsorption

The adsorbent effect (avocado seed) dose on the Safranin adsorption was investigated by the varying the amount of dose from 0.1, 0.2, 0.3, 0.4, and 0.5g in 30mLof5 mg/L dye solution.

3.12. Effect of temperature on adsorption

The batch adsorption process was studied at different temperatures (20 – 40^0C) in order to investigate the effect of temperature on the adsorption process. This was done by contacting 0.5 g of adsorbent with 30 mL of 5 mg/L of Safranin dye at optimal pH and contact time.

3.13. Statistical analysis

All experiments were measured in triplicate during the determination of Safranin dye concentration using UV- Visible Spectrophotometer. And it was analyzed by averaging the values. The curve fittings of the data obtained were performed using Microcal Origin 6.0 software.

4. RESULTS AND DISCUSSION

4.1. Adsorbent Characterization

Fourier Transform Infra-Red spectroscopy (FT-IR)

Fourier Transform Infrared spectroscopy (FT-IR) is an important analysis technique that detects various characteristic functional groups available in any solid or liquid sample. Basically it is a spectroscopic analysis technique which is used for identification of chemical bonds in a molecule by producing an infrared absorption spectrum and from the functional groups present on the surface of sample.

During analysis the sample is irradiated by infrared radiations, some of the infrared radiations are absorbed by the sample and rest are passed (transmitted) through. The FT-IR spectra were collected generally in the range of 400-4000 cm^{-1} region with $8cm^{-1}$ resolution. Absorption in the infrared region makes changes in vibrational and rotational status of the molecules. The absorption frequency depends greatly on the vibrational frequency of the molecules. The absorption intensity depends on how the infrared photon energy can be transferred to the molecule. This depends on the change in the dipole moment that occurs as a result of molecular vibration. A molecule will absorb infrared light only if the absorption causes a change in the dipole moment.

This spectrum represents a fingerprint of the sample with absorption peaks corresponding to the frequencies of vibrations between the bonds of the atoms which make up the material. Thus, it gives an idea about the organic functional groups present in the sample.

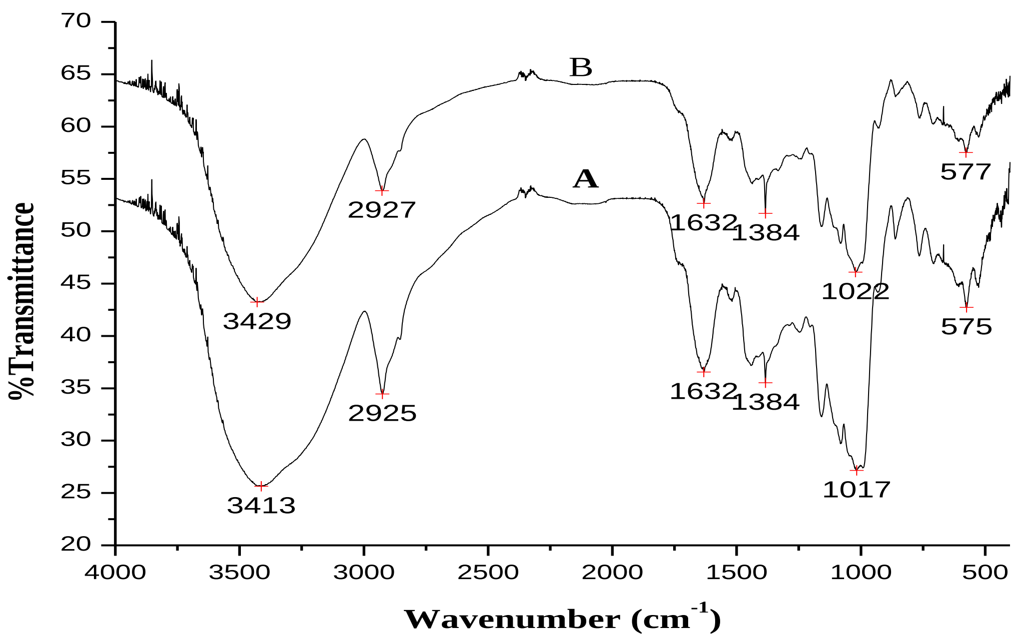

Figure 2:FT-IR spectra of avocado seed(A) before and (B) after adsorption of Safranin dye.

Fourier transformed infrared spectra in the range 4000 – 400cm^{-1}are shown in Figure 2 associated with the functional groups that are on the surface of avocado seed. FT-IR spectrum of before and after adsorption showed a strong peak shift of hydroxyl -OH group at wave number 3413 and 3429 cm^{-1}. The vibration of band 2925 cm^{-1} was attributed to aromatic C – H bending.

Region between 3200-2700 cm^{-1} indicates for organics and hydrocarbon, in this region are normally characteristics of carbon and hydrogen containing species which are assigned to various forms of C-H stretching. Peak no.2925 cm^{-1} Characteristic of carbon- and hydrogen containing species, with single bond and are assigned to various forms of C-H stretching, CH_3, alkane.After Safranin dye adsorption peak shifted to 2927 cm^{-1}.

The C-O stretching vibrations in alcohols and phenols produce a strong band in the 1260-1000 cm^{-1} region of the spectrum. Peakno. 1017 cm^{-1} characteristics of C-O stretching vibration of alcohols and phenols. After dye loaded the peak shifted to 1022 cm^{-1}. The presences of these groups are responsible for adsorption of Safranin dye on to the avocado seed (adsorbent) surface.

X-ray Diffraction (XRD) pattern

X-ray diffraction studies are used for determining crystal structures and the spacing between the atomic planes. X-rays are high-energy electromagnetic radiation produced by interactions between an external source of electrons and electrons in the shells of an atom. X-rays are produced in a vacuum chamber when a beam of electrons, created from heating a tungsten filament cathode, is accelerated towards a water-cooled anode. The loss of energy due to the collision is manifested as X-rays.

The detectors interpret the energy of the incoming X-ray as pulses and present the count rate as a series of peaks. Each peak corresponds to an X-ray diffracted from a specific set of planes in the specimen while their intensities are proportional to the number of X-ray photons of a particular energy that have been counted by the detector for each angle 2θ. The position of the peaks depends on the crystal structure while their quantity increases as the symmetry of the crystal decreases. Peak broadening of X-rays occurs when the crystallite or grain size of the studied material is <0.1μm and it increases with the decrement of crystallite size [53].

To analyze the structure and phase of avocado seed, XRD was performed as presented in Figure 3. The presence of amorphous phase with in the sample may result in irregular base line with noise and pulsed shape (being highly noisy line is the highly amorphous phase). The broad spectrum it may be due to the amorphous structure of the avocado seed. Additionally, the high intensity in low angle region (17.42^0) might be due to the rich micropores in avocado seed [54].

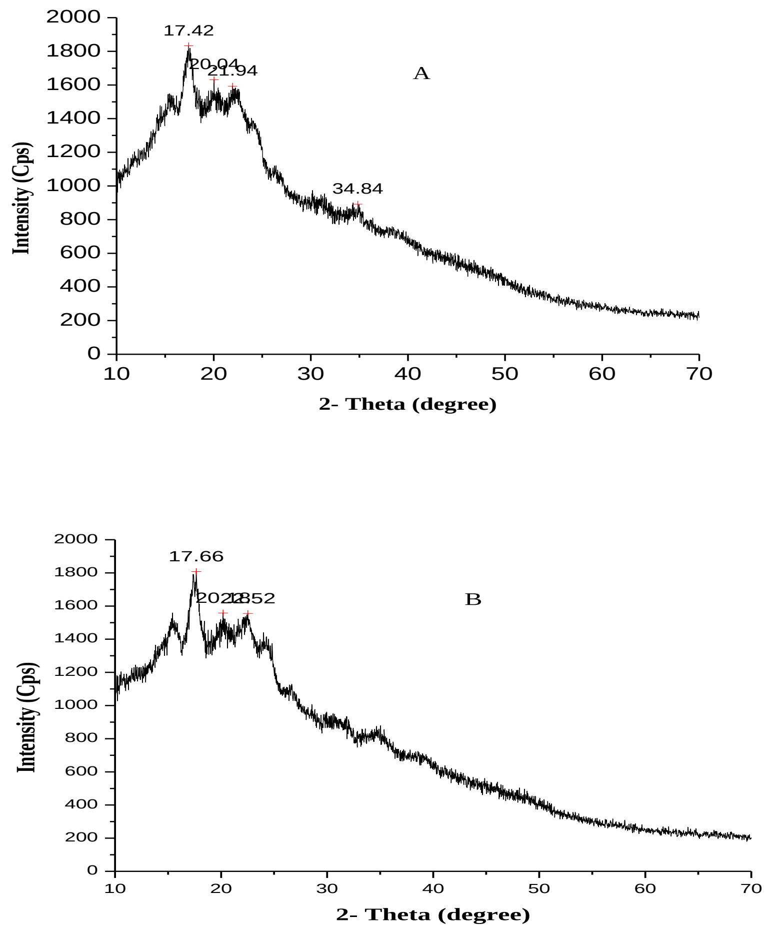

Figure 3: XRD pattern of avocado seed (A) before and (B) after adsorption of Safranin dye.

4.2 Calibration curve

A calibration curve shows us the relationship between the measured signal and the analyte's concentration in a series of standards.It knows as analytic signal as because of the calibration curve plotted according to the instrumental response and it changes with concentration of the measured substance (analyte). For most analyses a plot of instrument response versusanalyte concentration will show a linear relationship.

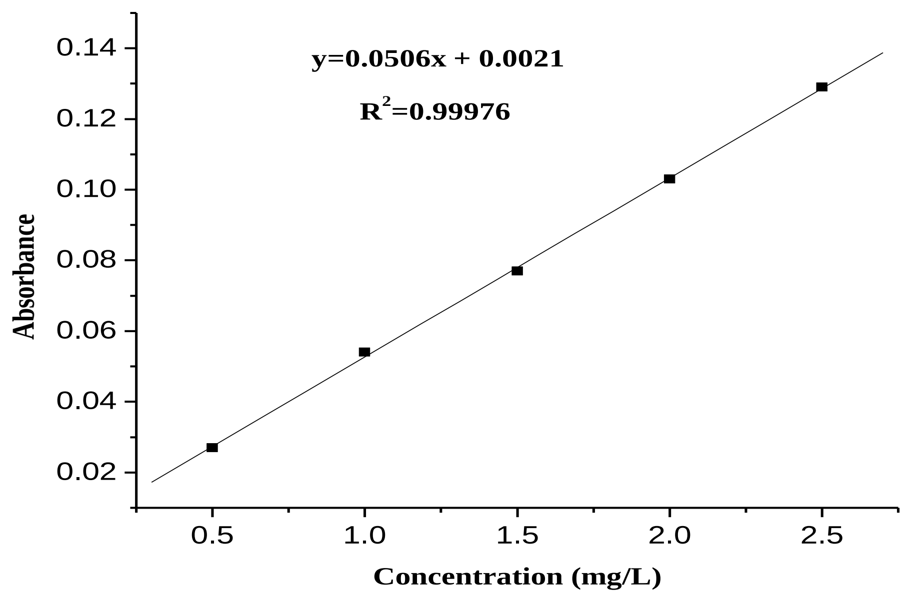

Figure 4: Calibration curve ofSafranin dye concentration, Co= 0.5- 2.5 mg/L at 519 nm.

4.3. Various parametric effects on the adsorption of Safranin dye onto Avocado seed.

4.3.1. Effects of initial pH of the solution

The effect of pH in aqueous solution is one of the potentially most important parameters in adsorption process [55].The effect of pH on the amount of dye adsorbed was studied by varying the initial pH under constant process parameters at equilibrium conditions.The pH of the dye solution is an important factor in theadsorption processes, especially on the adsorption capacity. It influences not only the surface charge, and the degree of ionization of the functional groups of the adsorbent, but also the dye chemistry. An effective change in pH values causes changing adsorption[42].

In this work, the effect of removal efficiency of avocado seed was studied at 5mg/L initial Safranin dye concentration and at 25^0C. In Figure 5 the results showed that the percent removal increases from 90.56% to 98.48% for Safranin dye with an increase in the pH from 4 to 10. Optimum pH for the adsorption of dye found to be in the range 7–10. It can be deduced that increasing solution pH increases the number of hydroxyl groups thus, increases the number of negatively charge sites and enlarges the attraction between dye and adsorbent surface.

The low Safranin adsorption under acidicpH could be due to the competition of dye cations with H^+ions, which restricted the access of cations to the adsorbent surface due to repulsive forces. As the pH increases, the competing effect of H^+ions decreased and the functional groups carrying negative charges were exposed and lead to electrostatic attraction between dye cation and adsorbent [56]. However, the Safranin dye adsorption increased linearly up to pH (7) and beyond this pH value, againSafranin adsorption slightly increased. Furthermore, the enhanced Safranin adsorption under slight basic pH is correlated with positively charged ions of dye in aqueous solution and negative charge on adsorbent surface, which are responsible for attraction between adsorbent surface and dye ions [57]. Similar trend for the adsorption of dyes have been reported previously [58, 39, 25,].

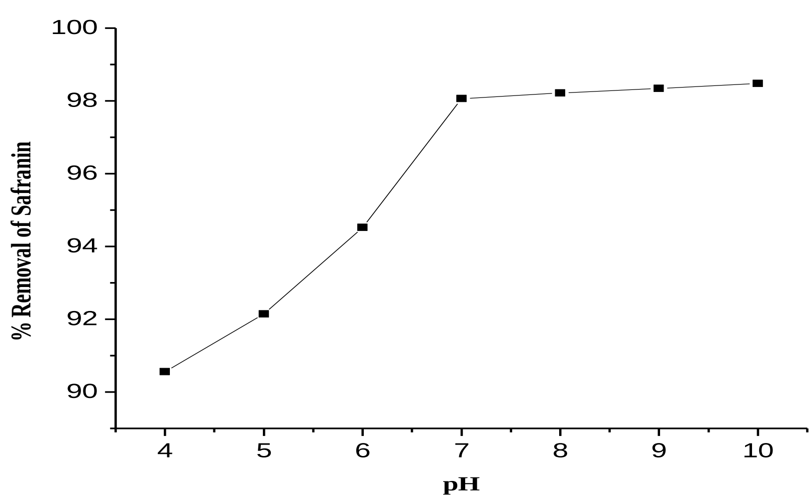

Figure 5: Effect of pH on adsorption of Safranin dye onto avocado seed (at initial concentration: 5 mg/L, adsorbent dose: 0.5 g, contact time: 30 min, shaking speed: 200 rpm, and temperature: 25^{0}C**).**

4.3.2. Effects of Adsorbent dose

The adsorbent dose is an essential parameter in adsorptionstudies because it determines the capacity of the adsorbent for a given initial concentration of dye solution. By varying the adsorbent dosage value from 0.1 g to 0.5 g keeping constant pH value (10), contact time (30 minutes), dye concentration (5 mg/L), the percentage of adsorption is minimum (95.3) for an adsorbent dose value of 0.1 g and reaches maximum (98.86) for a dose value of 0.5 g which is given in Figure 6. Due to the availability of large surface area, the percentage of adsorption increases with increase in adsorbent dosage. It is clear from Figure 4. The increase in sorbent dose at constant dye concentration and volume will lead to unsaturation of adsorption sites through the adsorption process. A similar result was reported on the removal of methylene blue dye from aqueous solution by mosambi fruit peel [59].The increase in adsorbent dose at constant dye concentration and volume results to increased availability of sorption sites and result to unsaturation of the sites. Greater adsorption rate was observed when the adsorbent/dye concentration ratio is greater than when the ratio is lower [60].

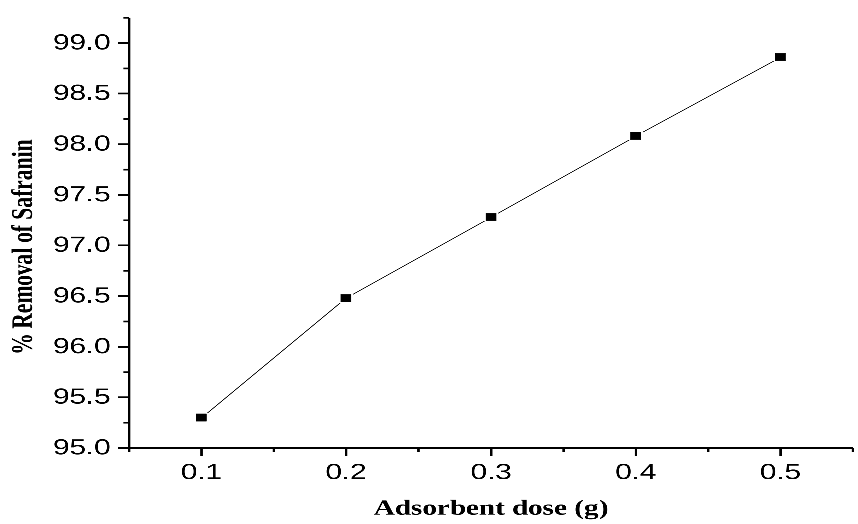

Figure 6: Effect on adsorbent dose on the removal efficiencies of avocado seed (at initial dye concentration: 5 mg/L, pH: 10, contact time: 30 min, shaking speed: 200 rpm,and temperature: 25^0C).

4.3.3. Effects of initial dye concentration

The initial dye concentrations are extremely depending on the extent of dye adsorbed. To study the effects of different initial concentration of Safranin dye, concentrations were varied from (5 mg/L – 25mg/L) with constant adsorbent dosage (0.5 g) value, pH:10 and contact time (30 minutes). The percentage adsorption of dye is maximum (98.46) at 5 mg/L and slowly decreased to (85.82) at 25 mg/L. This is because the increase of initial dye concentrations, the dye molecules gets highly resistant to the surface of the adsorbent which is clear from Figure 7. Similarly,at lower concentration there are sufficient active sites that the sorbet Safranin dye can easily occupy. However, at higher concentrations, active adsorption sites are not sufficiently available for the adsorbate to occupy. Hence, Safranindye was not completely adsorbed from solutions due to the saturation of binding sites. Similar trend was reported in the adsorption of methylene blue [61].

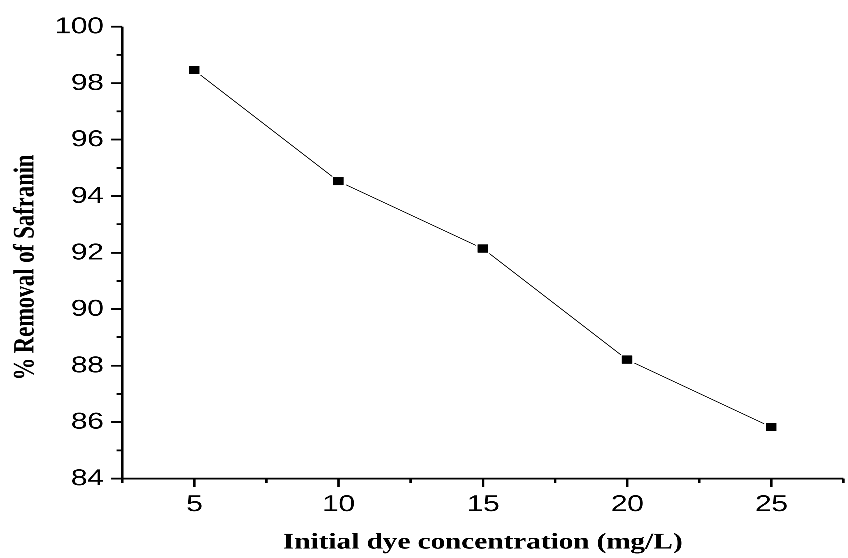

Figure 7: Effect of initial concentration on the removal of Safranindye by avocado seed (pH:10, adsorbent dose: 0.5 g, contact time: 30 min, shaking speed: 200 rpm, and temperature: 25^0C).

4.3.4. Effects of Contact Time

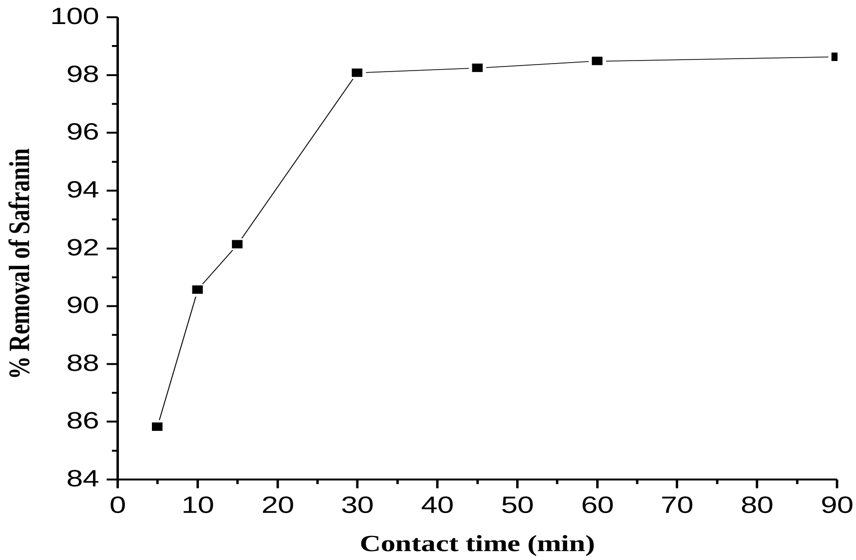

Figure 8: Effect of contact time on the Safranin dye removal by avocado seed (at initial concentration: 5 mg/L, adsorbent dose: 0.5 g, pH:10, shaking speed: 200 rpm and temperature 25^{0}C).

The results can be shown by Figure 8. It can be noticed that the adsorption is very fast and equilibrium between the aqueous solution and avocado seed established in less than 60 min. The time of 30 min. can be considered the saturation time.No meaningful improvement in the removalefficiency was observed after this time. This trend can be attributed to the high number of available adsorbent sites in the first thirty minutes. Similar trend was reported in the adsorption of methylene blue [61].

In general, the initial rate of adsorption is fast, and then a slower adsorption would follow as the available adsorption sites are slowly decreased. This is because initially a large number of vacant surface sites are available for adsorption; the adsorption rate is very fast, thus it rapidly increases the amount of adsorbate accumulated on the adsorbent surfacemainly within the first 30 minof adsorption. As a result, the remaining vacant surface sites are difficult to be occupied due to the formation of repulsive forces between the dye molecular on the solid and the bulk phase [27].

4.3.5.Effects of Temperature

Temperature is one of the most important parameter in adsorption process. Experiments were performed at different temperatures (20^0C, 25^0C,30 ^{0}C,35^0C and 40^0C) at optimum pH and contact time. As presented in Figure 9, the percentage removal of Safranin dye slightly increased with an increase of temperature from 20^0C to 35^0C and then decreased beyond 35^0C. The increased in the adsorption efficiencies for some range of temperature may be due to the chemical interaction between adsorbate and adsorbents, creation of some new adsorption sites. The decrease in percentage of adsorption at temperatures higher than 35^0C may be due to desorption caused by an increase of the thermal energy that may induces higher mobility of the adsorbate causing desorption [62].

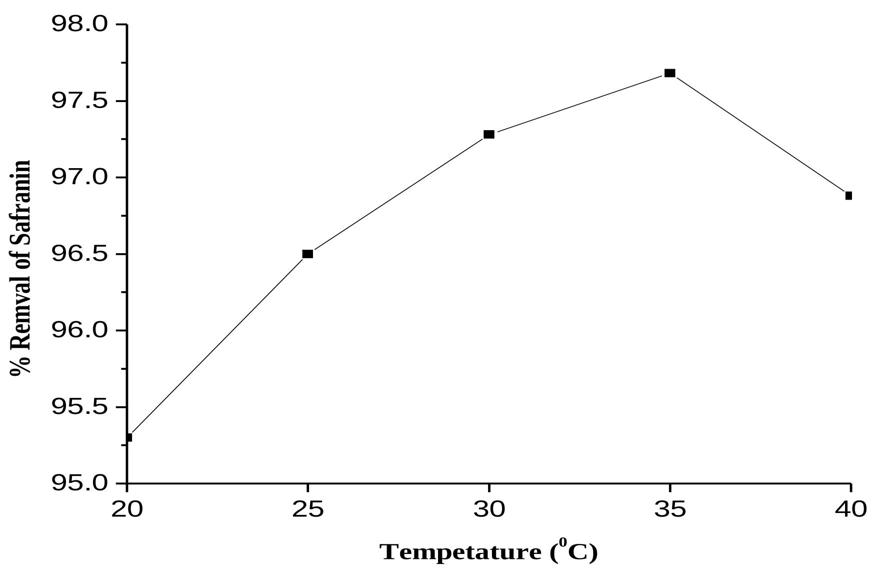

Figure 9: Effect of temperature on Safranin dye removal by avocado seed (at initial concentration: 5 mg/L, pH: 10,contact time: 30 min, adsorbent dose 0.5 g, shaking speed: 200 rpm).

The studies undertaken using natural biomasses showed that at higher temperature the adsorption was decreased and this decline in adsorption was correlated with damaging of active sites, the weakening of adsorptive forces between active binding sites of the adsorbent and the adsorbatespecies [63- 64]. It is also reported that earlier adsorbed ions ona surface tend to desorbs from the surface at elevated temperatures[65]. Other researchers also observed a similar effect of temperature on adsorption-desorption behavior for different biomasses[17].

4.4. Adsorption isotherms

The adsorption isotherm studies are an important technique to interpret the adsorption process sufficiently. Several models have been used to describe experimental data for adsorption isotherms. However, among these, the Langmuir and Freundlich isotherms are the most appropriate models for this study.

The Langmuir model is valid for monolayer adsorption. TheLangmuir isotherm model is based on the assumption that there are a finite number of active sites which are homogeneously distributed over the surface of the adsorbent. These active sites have the same affinity for adsorption of a monomolecular layer and there is no interaction between adsorbed molecules [66]. The linear form of Langmuir isotherm equation is given as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b_L} \qquad (10)$$

Where q_e (mg/g) is the equilibrium concentration of Safranindye in the adsorbed phase and C_e(mg/L) is the equilibrium concentration of Safranin dye in the liquid phase. Langmuir constants, which are related to the adsorption capacity q_m and energy of adsorption b_L can be calculated from the slope of the linear plot of $\frac{C_e}{q_e}$ versus C_e, a straight line with slope $\frac{1}{q_m}$ and intercept of $\frac{1}{q_m b_L}$ is obtained in Figure 10. The essential characteristics of the Langmuir equation can be which is given as:

$$R_L = \frac{1}{1+bC_o} \qquad (11)$$

Where, C_o is the highest initial Safranin dye concentration (mg/L).
The R_L values indicate the type of adsorption as either unfavourable (R_L>1), linear (R_L=1), favorable (0<R_L<1), or irreversible (R_L=0) [67].

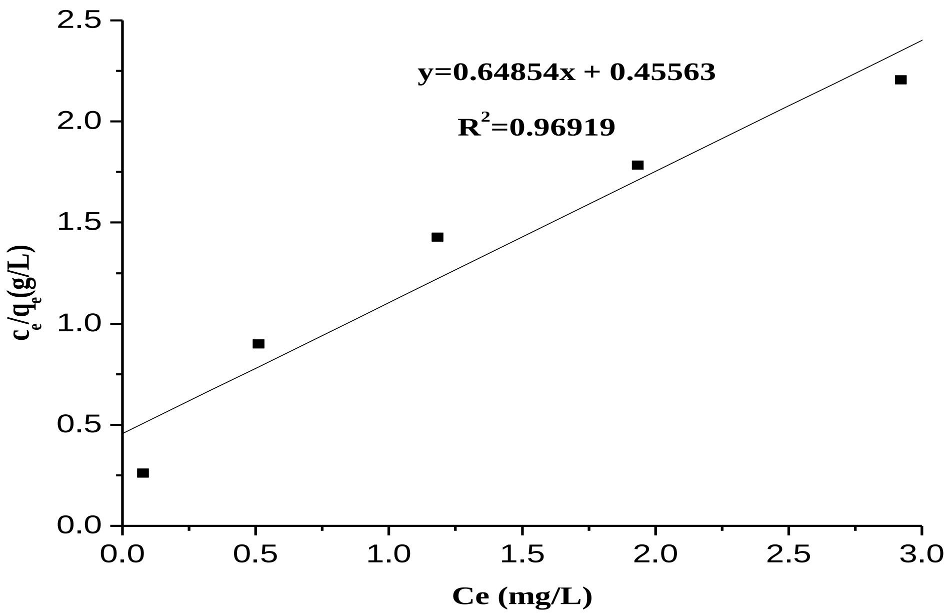

Figure 10: Langmuir Isotherm for the removal of Safranin dye.

Freundlich isotherm gives the relationship between equilibrium liquid and solid phase capacity based on the multilayer adsorption properties consisting of heterogeneous surface of the adsorbent [68].

The linear form of Freundlich isotherm is:

$$log q_e = log K_f + \frac{1}{n} log C_e \quad (12)$$

Where, q_e is the amount adsorbed at equilibrium (mg/g), K_f is the Freundlich constant related to the bonding energy and $\frac{1}{n}$ is a constant indicative of the intensity of the adsorption.

The values of K_f and $\frac{1}{n}$ can be obtained from the slope and intercept of the plot of $log q_e$ versus $log C_e$ in Figure 11.

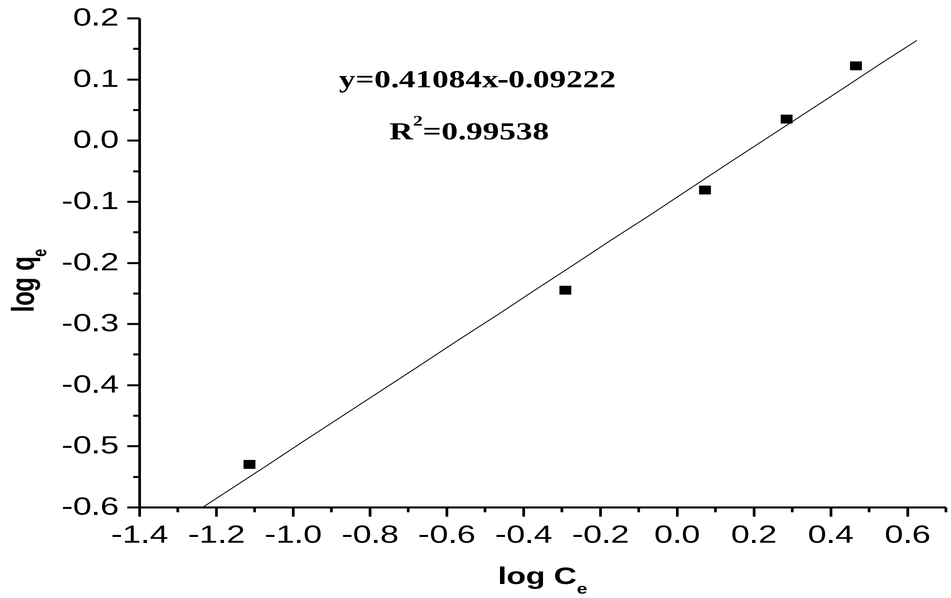

Figure 11: Freundlich Isotherm for the removal of Safranin dye**.**

Table 1: Calculated values of Langmuir and Freundlich constants.

Langmuir isotherm					Freundlich isotherm		
Dye	q_m (mg/g)	b_L (L/mg)	R_L	R^2	K_f	$\frac{1}{n}$	R^2
Safranin	1.542	1.423	0.027	0.96919	0.81	0.41	0.9907

Theresults from Table 1 clearly show that the adsorption of Safranin onto avocado seed fits well with the Freundlich model. The fact that the Freundlich model is a good fit to the experimental adsorption data suggests a heterogeneous distribution of active sites on the avocado fruit seed surface. The observed correlation coefficients for Freundlich isotherms were 0.9907. The other Freundlich constant, n,is a measure of the deviation of the adsorption from linearity. The n values between 2 and 10 represent good adsorption. The calculated n value of 2.437 indicates good adsorption of Safranin dye molecules ontoavocado seed. The value of $\frac{1}{n}$ is 0.41 which ranges between 0 and 1 represents the heterogeneous nature of avocado seed. i.e.the multilayer adsorption of dye molecules by avocado seed. The dimensionless equilibrium factor (R_L) value was 0.027 whichwas less than unity showing that the adsorption of dye molecules onto avocado seed was favorable. Similar phenomenon was observed in removal of leather dyes and hexavalent chromium by grape fruit peel [13].

4.5.Adsorption Kinetic studies

The study of adsorption kinetics is very important to determine the rate constants for the reaction and to know how quickly or slowly the reaction is proceeding. To evaluate the kinetic parameters, Pseudo first order and Pseudo second order were implemented to analyze the experimental data. The pseudo first order equation can be expressed as[69]:

$$log(q_e - q_t) = \ log q_e - \frac{k_1}{2.303} t \text{.................................. (13)}$$

Where,q_e and q_t represent the amount of adsorbed (mg/g) at equilibrium and at any time t, k_1 is the first order rate constant (min^{-1}). From the plots of $log(q_e - q_t)$versus t in Figure 12, k_1 can be calculated from the slope and theoretical q_e can be obtained from intercepts.

Table 2: Results of kinetic parameters for the adsorption of Safranin dye onto avocadoseed**.**

	Pseudo first order			Pseudo second order		
Dye	$\boldsymbol{q_e}$(mg/g)	$\boldsymbol{k_1}$(min^{-1})	R^2	$\boldsymbol{q_e}$(mg/g)	$\boldsymbol{k_2}$(g/mg.min)	R^2
Safranin	0.121	0.00299	0.79108	0.299	3.64	0.99997

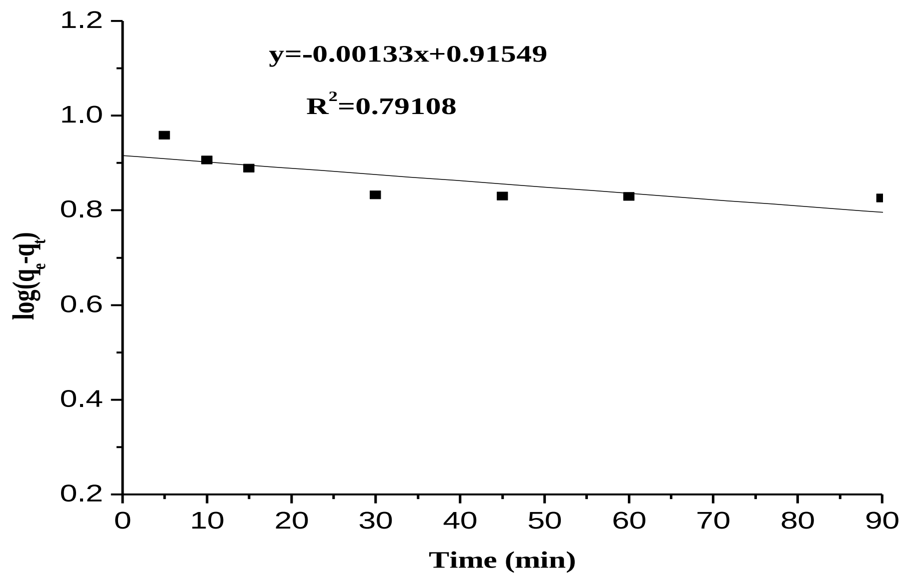

Figure 12: Pseudo-first order kinetics plot for the adsorption of Safranin dye onto avocado seed.

Pseudo second order equation can be given by [70]

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t \quad (14)$$

where, k_2 is the rate constant of second order adsorption. The linear plots of $\frac{t}{q_t}$ versus t determine $\frac{1}{q_e}$ as slope and $\frac{1}{k_2 {q_e}^2}$ as intercepts. The linear plots of pseudo second order model is shown in Figure 13

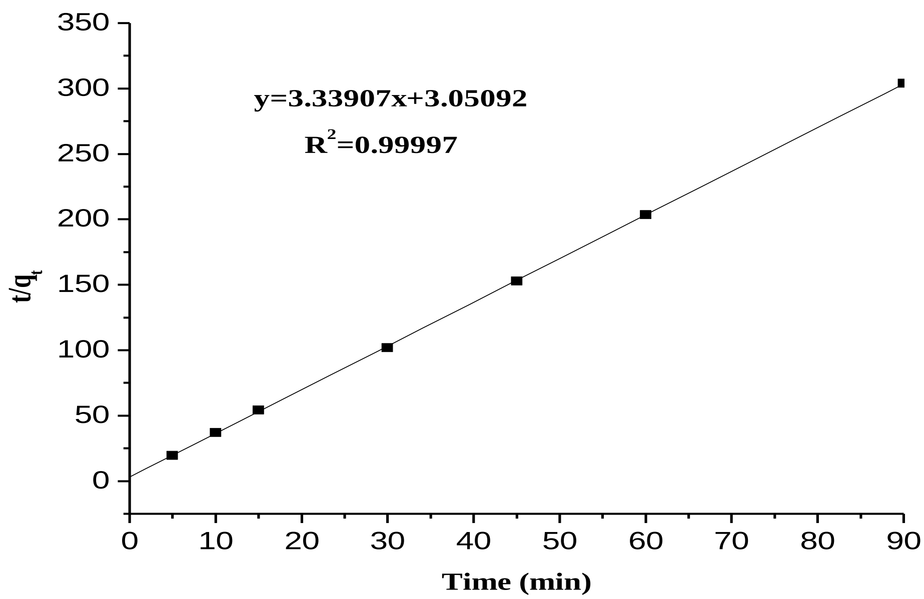

Figure 13: Pseudo- second order kinetic plot for the adsorption of Safranin onto avocado seed.

The correlation coefficient, R^2 of pseudo first order kinetics was 0.79108 for Safranin dye concentration in Table 2. Thus it can be concluded that it is not appropriate to use the pseudo first order kinetic model to predict the adsorption kinetics for Safranindye onto avocado seed for the entire adsorption period.

For the pseudo-second-order kinetic model, the correlation coefficient, R^2 were 0.9999 showing that the applicability of the model. Thus it appeared that the system under study is more suitably described by pseudo second order kinetics which was based on the assumption that the rate limiting step may be physisorption due to the presence of weak forces of attraction between adsorbent and adsorbate. The pseudo second order kinetics model has been successfully applied to several adsorption systems andmore suitable to describe the adsorption processas reported by [71]. Similar phenomenon has been observed in the adsorption of Safranin dye onto carbonized spent coffee ground [23].

4.6. Thermodynamic study

The thermodynamic parameters that help us to understand the nature of the adsorption of Safranin dye on adsorbent are the standard change in Gibbs free energy (ΔG^0), the standard change in entropy (ΔS^0), and the standard change in enthalpy (ΔH^0). These can be determined using the following equations:

$$\Delta G^0 = -RT \ln K_C \ldots\ldots (15)$$

Where R is the gas constant (8.314 J/mol.K), T is the absolute temperature in kelvin, and K_C (L/g) is the standard thermodynamic equilibrium constant defined by q_e/C_e. Similarly, the enthalpy change (ΔH^0) from 293 to 313 K was computed from the following equation [72].

$$\ln K_C = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \ldots\ldots (16)$$

ΔH^0 ($kJ.mol^{-1}$) and ΔS^0 ($kJ.mol^{-1}.K^{-1}$) were calculated from the slope and intercept of the linear plot of $\ln K_C$ versus 1/T as shown in Figure 14

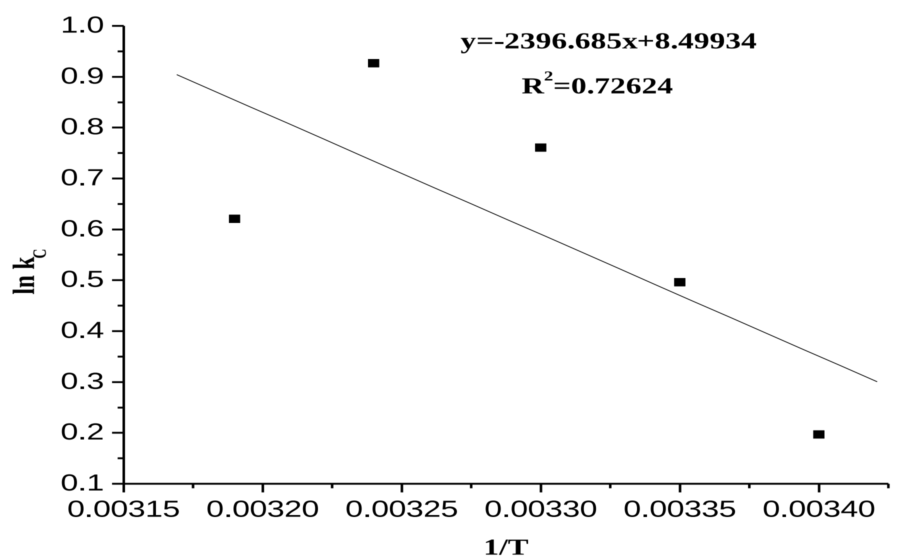

Figure 14:Plot of ln K_C versus 1/T for the estimation of thermodynamic parameters foradsorption of Safranin dye onto avocado seed.

Table 3: Thermodynamic parameters for the adsorption of Safranin dye onto avocadoseed at different temperatures.

ΔH(kJ/mol)	ΔS(kJ/molK)	ΔG(kJ/mol)				
		293 K	298 K	303 K	308 K	313 K
19.92	0.07066	-0.478	-1.228	-1.915	-2.371	-1.615

The thermodynamic parameters are listed in Table 3.The positive value of enthalpy indicates that the adsorption is endothermic in nature.The enthalpy value for adsorption process may be used to distinguish between chemical and physical adsorption. For chemical adsorption, values of enthalpy change range from 83to 830 kJ/mol, while physical adsorption they range from 8 to 25 kJ/mol. From this we concluded that Safranindye adsorption by avocado seed is a physical adsorption [73].The positive value of ΔS° (0.07066 kJ/mol.K) indicate that the increased in randomness at the solid/solution interface during the adsorption process. Similar types of observation were reported previously for decolourization of Cationic and anionic dyes from aqueous Solution by adsorption on NaOH treated eggshells [4].

The magnitude of Gibbs free energy change, ΔG° obtained is negative demonstrating that the adsorption is rapid and spontaneous. The negative value of ΔG° ensures the feasibility of the process. Generally, ΔG for physisorption processes ranges between -20 and 0 kJ/mol while the chemisorption is between -80 and -400 kJ/mol [74]. In this study, the ΔG° values ranges from -0.478 to-2.371 kJ/mol, indicating that adsorption is generallyphysical.Similar reported on adsorption of alizarin and Fluorescein dyes onto mango seed [75]. The values of Gibbs free energy also indicate the adsorption process of Safranin dye onto avocado seed is thermodynamically favored.Similar trend was reported for the adsorption of Safranin dye onto Thuja biomass [27].

4.7. Comparison of Safranin dye adsorption with different adsorbents.

The adsorption efficiencies of the adsorbents for the adsorption of Safranin dye has been compared with those of other reported in the literature and the values of adsorption efficiencies as presented in Table 4. Results of the study indicated that avocado seed has the highest percent removal.

Table 4: Comparison of adsorption efficiency of different adsorbents for the adsorption of Safranin dye.

Adsorbent	Adsorbate	Adsorption efficiency	Reference
Coffee spent ground	Safranin	92%	[23]
Jackfruit peel	Safranin	96%	[76]
Azadirachtaindica bark (treated)	Safranin	94%	[77]
Avocado seed	Safranin	98.48%	This work

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

In this study, the adsorption efficiencies of Safranin dye from aqueous solution using low-cost locally available untreated avocado seedwas investigated. The adsorption was found tobe dependent on pH, adsorbent dose, shaking time and initial dye concentration.The optimum pH for the removal of Safranin dye from aqueous solution under the experimental conditions used in this work was 10. Maximum adsorption efficiency was 98.48% for Safranin dye at pH 10. The adsorption efficiency increased with increased of shaking time and achieves equilibrium at 30 minutes.The removal of Safranin dye increases with increase of adsorbent dosage used but decreases with increased initial dye concentration. The adsorption equilibrium data obtained for removal of Safranin dye onto avocado seed showed best fit to the Freundlich isotherm model. The adsorption kinetic data fitted well to a pseudo-second-order model. Thermodynamic studies predict that the adsorption is feasible, spontaneous and endothermic in nature. The negative values of standard change in Gibbs free energy (ΔG^0) and positive values of standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0) are suggested that the adsorption is feasible, spontaneous and increased randomness at the solid-liquid interface during adsorption.The results revealed that the avocado seed is a natural, eco-friendly and low-cost adsorbent has relatively good removal efficiency and can be effectively used the removal of dyes from wastewater.

5.2. Recommendation

Avocado seed is a cheap and easily available material in large quantity in developing countries thus that can act as a good alternative to commercial activated carbon for removal of Safranin from aqueous solution. Being a naturally occurring environmentally friendly material, the use of avocado seed as adsorbent would be useful for the economic treatment of dyeing effluent.

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