

JIMMA UNIVERSITY
COLLEGE OF NATURAL SCIENCES
SCHOOL OF GRADUATE STUDIES
DEPARTMENT OF CHEMISTRY



THESIS ON:

**KINETIC AND THERMODYNAMIC STUDIES OF CHLOROPHENOL ADSORPTION
ONTO *RICINUS COMMUNIS* PERICARP ACTIVATED CARBON IN AQUEOUS
SOLUTIONS**

November, 2013
Jimma, Ethiopia

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SOLUTIONS**

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Abbreviation

AC: - Activated carbon

RCAC: - Ricinus *cominnus* activated carbon

FT-IR: - Fourier transforms infrared

ΔG° : - Standard Gibbs free energy change

ΔH° : - Standard enthalpy change

ΔS° : - Standard entropy change

UV/Vis: - visible spectrophotometer

Abstract

This study reports the adsorption of 2-chlorophenol from aqueous solution using activated carbon prepared from pericarp of *Ricinus communis* by H₂SO₄ activation. The pericarp of *Ricinus communis* was activated by treating with H₂SO₄ solution followed by heating in an oven at 105 °C for 12 hrs. Batch adsorption experiments were also carried out as a function of pH, contact time, initial concentration of the adsorbate, adsorbent dosage and temperature of the solution. Adsorption of 2-chlorophenol by pericarp of *Ricinus communis* was observed to sharply increase from pH 2 to 6 then decreased up to pH 12. The adsorption of 2-chlorophenol was observed to decrease with the initial concentration increase and the adsorption increase with the dose of adsorbent increase. The 2-chlorophenol adsorption process was better represented by the Freundlich isotherm model than Langmuir, with correlation coefficient (r^2) of 0.996. The maximum adsorption efficiencies were obtained 99.87% at 60 minute, 98.75% at pH 6 and 99.25% at 30 °C. The Kinetic of 2-chlorophenol adsorption followed the pseudo-first-order kinetic model as determined by the correlation ($r^2 = 1$) and higher agreement between q_e and q_{exp} . Thermodynamic parameters, enthalpy changes (ΔH), entropy change (ΔS), and Gibbs free energy change (ΔG) were also calculated for the uptake of pericarp of *Ricinus communis*. These parameters showed that adsorption on the surface of *Ricinus communis* were feasible, spontaneous in nature, and exothermic between temperatures of 20 and 30 °C. IR spectrum for loaded and unloaded pericarp of *Ricinus communis* was characterized by using FT-IR spectrophotometer. The maximum adsorption capacity was obtained 24.9675 mg/g at 60 minute, 24.6875 mg/g at pH 6 and 24.8125 mg/g adsorption of 2-chlorophenol by pericarp of *Ricinus communis* AC adsorbent. It can be concluded that pericarp of *Ricinus communis* is a good and cheap adsorbent with high potential for the adsorption and recovery of 2-chlorophenol from contaminated water and could therefore serve as effective and efficient biomass for treating drinking waters in terms of high adsorption capacity.

1. INTRODUCTION

Water is mainly polluted with organics, inorganic, sediments, radioactive materials and heavy metals. The industrial and domestic wastewater is responsible for causing several damages to the environment and adversely affecting the health of the people. The main sources of water contamination are industrialization, civilization, agricultural activities and other environmental and global changes. Few hundred organic pollutants have been found contaminating water resources. The contaminations due to organic pollutants are very dangerous due to their various side effects and carcinogenic nature. Therefore, the importance of water quality preservation and improvement is essential in life and increasing continuously. The surface and ground waters at many places of the world are contaminated and not fit for drinking purpose¹.

Chlorophenols are a group of chemicals in which chlorines have been added to phenol. They are the most common organic pollutants used widely in agriculture, industry and public health. The most important chlorophenols sources are wastewaters from pesticide, paint, solvent, pharmaceuticals, paper and pulp industries as well as water disinfecting process. Chlorophenols are weak acids and permeate human skin by in vitro and are readily absorbed by gastro-intestinal tract. The acute toxicity of chlorophenols includes increased respiratory rate, vomiting and nausea. Chlorophenols also create complicated problems to water bodies such as bad odour and taste in drinking water, death of aquatic life, inhibition of normal activities of microbial population in wastewater treatment plant².

There are so many methods available for the removal of contaminant from effluents. The technologies are divided into three categories, biological, chemical and physical. The major method of industrial waste water treatment involves physical and chemical processes. They have their own advantages and drawbacks because of high cost and disposal problems. A combination of different processes is often used to achieve the desired water quality in the most economical way³.

Chemical methods involved coagulation combined with flotation and filtration, electro flotation, electro kinetic coagulation, conventional oxidation methods by oxidizing

agents, irradiation and electro chemical processes. These chemical technologies are very expensive have disposal problems. Although these methods are efficient for treatment of water contaminated with pollutants, they are very costly and commercially unattractive. The high electrical energy demand and consumption of chemical reagents are common problems. Physical methods are membrane filtration and adsorption. Membrane filtration processes are nanofiltration, reverse osmosis, electro dialysis etc. The major disadvantage of this membrane filtration is limited lifetime before membrane fouling occurs. Adsorption is one of the most popular methods for the removal of pollutants from effluents since proper design of the adsorption process will produce high quality treated effluents. This process provides an attractive alternative for treatment of contaminated water, especially if the adsorbent is inexpensive and does not require an additional pretreatment step before application. The disadvantage of the biological method, it requires large area and is constrained by sensitivity toward diurnal variation as well as toxicity of some chemicals and less flexibility in design and operation^{4,5}.

Adsorption has been found to be superior compared to the other techniques for water reuse in terms initial cost, flexibility and simplicity of design, ease of operation, and insensitivity to toxic pollutants and does not result in formation of harmful substances⁶. Adsorption is a surface phenomenon that occurs when a gas or liquid solutes accumulate on the surface of a solid or liquid forming a molecular or atomic film. Adsorption has been described as an effective separation process for treating industrial and domestic effluents. It is widely used as effective physical method of separation in order to eliminate or lower the concentration of a wide range of dissolved pollutants (organics or inorganics) in the effluent⁷. The adsorptions of various solutes on a solid remain an active area of research. However finding simple and easily performable experiments to illustrate the quantitative aspects of adsorption can be very difficult⁸. The common adsorbents include activated carbon, molecular sieves, polymeric adsorbents, and some other low-cost materials. When adsorption is concerned, thermodynamic and kinetic aspects should be involved to know more details about its performance and mechanisms. Except for adsorption capacity, kinetic performance of a given adsorbent is also of great significance for the pilot application⁹. Adsorption on activated carbon has been found to be superior compared to other chemical and physical methods for wastewater treatment

in terms of its capability for efficiently adsorbing a broad range of pollutants, fast adsorption kinetics and its simplicity of design. However, commercially available activated carbons are still expensive due to the use of non-renewable and relatively high-cost starting material such as coal, which is unjustified in pollution control applications^{10, 11}.

Phenol-containing wastewater presents a serious environmental problem since biological degradation of phenol occurs too slowly or does not occur at all¹². Consequently, there has been a growing interest in developing and implementing various adsorbents to remove phenols and other specific organic substances from water¹³.

Ricinus communis was originated in Africa and introduced in all continents, nowadays occurring worldwide as growing in trash species. Castor bean (*Ricinus communis*) is an important drought-resistant shrub belonging to the Family *Euphorbiaceae*. It is native to the Ethiopian region of tropical Africa and has become naturalized in tropical and temperate regions throughout the world¹⁴. Ricinus Communis seed shell (RCC) and Polypyrrole coated Ricinus Communis seed shell activated carbons (PPy/RCC) as an adsorbent. It is a polysaccharide, non-toxic, economically favorable one¹⁵. The pericarp of the fruits of *Ricinus communis* contains alkaloid, ricinine¹⁶. *Ricinus communis* is containing polymeric compounds and it is insoluble in water and alkali but soluble in strong mineral acids. Due to their wide variations in functionality, surface area, and porosity, polymeric adsorbents have been increasingly viewed as an alternative to activated carbon for the selective removal of specific organic substances from contaminated water¹⁷. Whereas, the adsorption results of aromatic organic compounds with high water solubility are dissatisfactory. The enhancement of adsorption capacity has been achieved by introducing functional groups such as amino groups, pyridine groups, carboxyl, phenolic hydroxyl, acetyl and so on, onto the surface of the hyper-cross linked polymers¹⁸.

In the present study, to evaluate the feasibility of *Ricinus communis* pericarp waste as a precursor for activated carbon production and employing the activated carbon thus prepared for the removal of 2-chlorophenol from aqueous solutions. The adsorption of 2-chlorophenol onto RCAC determined by using isotherm model, kinetic and thermodynamics parameters also calculated for the uptake of RCAC.

2. REVIEW LITERATURE

2.1. 2-Chlorophenol

There has been increasing concern and more stringent regulation standards pertaining to the discharge of persistence organic pollutants to the aquatic environment, due to their toxicity and detriment to living species including humans. Persistence organic pollutants are non-degradable and can accumulate in living tissues, so they must be removed from polluted water. Chlorophenols are one of these harmful and toxic persistence organic pollutants, which are commonly used in a number of industrial applications such as biocides and wood preservation, in addition produced as by-products of many other processes. Chlorophenols are sparingly soluble in water (less than 1g/L at 25°C) but the removal of these toxic compounds from aqueous systems represents a problem, especially when it is present at very low concentrations¹⁹.

2-chlorophenol is a derivative of phenol. It is used as a disinfectant and pesticide. 2-chlorophenol is a liquid at room temperature, but all other chlorophenols are solids. 2-chlorophenol is used as bactericides, fungicides and preservatives. The water solubility of chlorophenols is low, in the presence of chlorine in drinking water, phenols form chlorophenol, which has a medicinal taste that is quite pronounced, and objectionable²⁰.

Chlorine substitution on phenols does not only increase water taste and odour, but also its toxicity effects²¹. Residues of 2-chlorophenol have been found worldwide in soil, water, air sample, food products, human, animal tissues and body fluids. Due to their slow degradation, 2-chlorophenol represent a major threat to ecosystems²². Chronic toxic effects due to phenolic compounds reported in humans include vomiting, difficulty in swallowing, anorexia, liver and kidney damage, headache, fainting and other mental disturbance. Among the different organic pollutions of aquatic ecosystems, phenols, especially the chlorinated ones, are toxic to animals and human even at low concentration²³. Current methods for removing chlorophenols from polluted water include microbial degradation, adsorption on activated carbon, biosorption, chemical oxidation, deep-well injection, incineration, solvent extraction and irradiation²⁴. Among these methods, adsorption is a promising and widely applied method due to its cost-

effectiveness and the ability to recycle both of the pollutants (adsorbate) and the adsorbents.

2.2. Adsorption

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film of the adsorbate. It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term sorption encompasses both processes, while desorption is the reverse process. Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification. The pollutant is adsorbed on the surface (mostly the internal surface) of a granule, bead, or crystal of adsorbent material²⁵.

2.2.1. Types of Adsorption

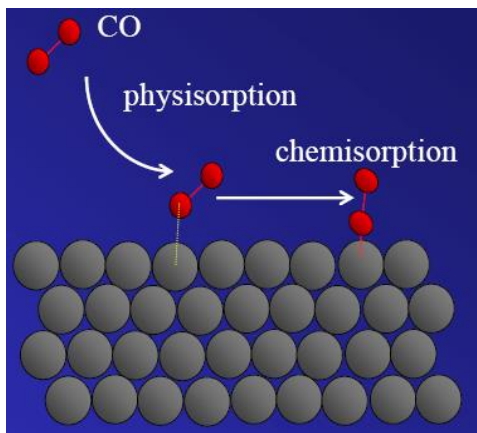
The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorption.

Physisorption or physical adsorption is a type of adsorption in which the adsorbate adheres to the surface only through Van der Waals (weak intermolecular) interactions, which are also responsible for the non-ideal behavior of real gases²⁶.

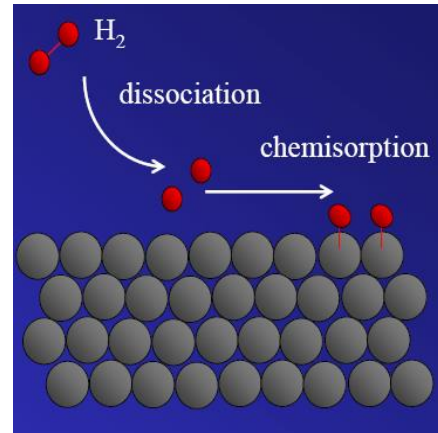
Chemisorption is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond, as opposed to the Van der Waals forces which cause physisorption²⁶.

Typical Characteristics of Adsorption Processes

	Chemisorption	Physisorption
Temperature Range (over which adsorption occurs)	Virtually unlimited (but a given molecule may effectively adsorb only over a small range)	Near or below the condensation point of the gas (e.g. Xe < 100 K, CO ₂ < 200 K)
Adsorption Enthalpy	Wide range (related to the chemical bond strength) - typically 40 - 800 kJ mol ⁻¹	Related to factors like molecular mass and polarity but typically 5-40 kJ mol ⁻¹ (i.e. ~ heat of liquefaction)
Crystallographic Specificity (variation between different surface planes of the same crystal)	Marked variation between crystal planes	Virtually independent of surface atomic geometry
Nature of Adsorption	Often dissociative May be irreversible	Non-dissociative Reversible
Saturation Uptake	Limited to one monolayer	Multilayer uptake possible
Kinetics of Adsorption	Very variable - often an activated process	Fast - since it is a non-activated process



Physisorption + molecular chemisorption chemisorptions



Physisorption + dissociative

2.3. Activated carbon

Activated carbon (AC) is a carbonaceous material that can be prepared by the pyrolysis of many inexpensive materials that have a high carbon content and low inorganic content. On a commercial scale, activated carbon is produced by the pyrolysis and activation of high-cost starting materials, such as wood, petroleum and coal, making it expensive and unjustified as a method of pollution control^{10, 11}. To reduce the production cost, the utilization of renewable and less expensive precursors for the preparation of activated carbon is attracting the interest of researchers all over the world. The precursors of interest are primarily industrial and agricultural byproducts and forest wastes, such as coconut shell²⁷, sugar beet bagasse²⁸, rice straw²⁹, bamboo³⁰, rattan sawdust³¹, molasses³², rubber wood sawdust³³, oil palm fiber³⁴, waste apricot³⁵, coconut husk³⁶. Waste plastics and tires, which are organic materials, can also be converted into activated carbon.

Activated carbons (ACs) are effectively used not only in drinking water purification and various industrial applications but also in hemoperfusion- and hemofiltration-based therapies. Recent technological advances have allowed the production of ACs in both granular and monolithic forms that can be used for direct contact with blood without the need for an additional biocompatible coating. The adsorption kinetics displayed by smaller AC micro particles ($\sim 1\text{--}50\mu\text{m}$) interacting with both low ($\approx 10\text{--}100$ atoms in molecules) and high-molecular (e.g., proteins, lipoproteins) compounds is more effective than that provided by larger AC granules or monoliths. This is due to the difference in the surface area accessibility and working layer thickness of smaller and larger AC particles³⁷.

Activation occurs by selectively removing carbon groups from the surface of carbons, creating more voids between carbon atoms which enlarge the pores, where molecules can be adsorbed or attaching functional groups to the surface of carbon. There are two conventional means of carbon activation: physical activation (or gasification) and chemical activation.

Physical Activation: Physical activation processes involve the treatment of pyrolyzed carbonaceous materials at temperatures between 700-1000°C, a carbonaceous material is carbonized under the oxygen-free atmosphere (carbonization process) and then activated with an activating gas such as an oxidizing gas is used to induce gasification. Common activation gases include CO₂, steam, and air.

Chemical activation: In chemical activation, both carbonization and activation processes occur simultaneously at a lower temperature and a shorter time than that in physical activation. Therefore it saves time and energy. Moreover chemical activation is reported to give activated carbon with higher specific surface area and much better developed porosity than physical activation³⁸. In chemical activation, several types of chemicals are used as the activating agent including ZnCl₂, H₃PO₄ and KOH. Different activating agents provide activated carbons with different properties. Hayashi and coworkers found that the greatest specific surface areas of activated carbons were obtained at the carbonization temperature of 600 °C with ZnCl₂ and H₃PO₄ activation³⁹. In contrast, the maximum surface areas of activated carbons were obtained at the carbonization temperature of 800°C with alkali metal (KOH, NaOH, K₂CO₃ and Na₂CO₃) activation. Hideharu, I. et al.⁴⁰ activated carbonaceous materials, to obtain activated carbonaceous materials with an oxidizable chemical, such as, zinc chloride, phosphoric acid, or sulfuric acid at a temperature greater than 100°C and less than 500°C. Activation process occurred with the assistance of librated CO₂ and heat. These represent activating agents which most commonly used in physical activation. By impregnating with concentrated H₂SO₄ more effectively sulfonated carbon atoms can be made at the active sites to increase porosity of activated carbon and increase its adsorptive capacity.

2.4. Application of Adsorption

Adsorption plays a significant role in the environmental pollution control and life supporting systems or planetary bases, where adsorbents may be used to process the habitat air or to recover useful substances from the local environments. Adsorption processes are good candidates for separation and purification by virtue of high reliability, energy efficiency, design flexibility, technological maturity and the ability to

regenerate the process by regenerating the exhausted adsorbent. Development and application of adsorption cannot be considered separately from development of technology used to manufacture adsorbents applied both on laboratory and industrial scales. The adsorbent can take a broad range of chemical forms and different geometrical surface structures⁴¹.

A large specific surface area of the adsorbent pores provides a large adsorption capacity. The creation of a large internal surface area in a limited volume inevitably gives rise to large numbers of small sized pores between adsorption surfaces. Materials such as activated carbon and zeolite can be specifically engineered with precise pore size distributions and hence tuned for a particular separation application.

2.5. Adsorption Kinetics

The study of adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. When adsorption is concerned, thermodynamic and kinetic aspects should be involved to know more details about its performance and mechanisms. Except for adsorption capacity, kinetic performance of a given adsorbent is also of great significance for the pilot application. From the kinetic analysis, the solute uptake rate, which determines the residence time required for completion of adsorption reaction, may be established. Also, one can know the scale of an adsorption apparatus based on the kinetic information. Generally speaking, adsorption kinetics is the base to determine the performance of fixed-bed or any other flow-through systems. Both adsorption reaction model and adsorption diffusion model which are mathematical models can apply for kinetic adsorption⁴². It can provide some information about mechanism of the reaction between adsorbate and adsorbent and useful in understanding the adsorption process. The kinetics of 2-chlorophenol adsorption on the activated carbons were analysed using pseudo first-order⁴³, pseudo second-order⁴⁴, Elovich⁴⁵ and intraparticle diffusion and liquid film diffusion⁴⁶ kinetic models. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (R^2 , values

close or equal to 1). A relatively high R^2 value indicates that the model successfully describes the kinetics of 2-chlorophenol adsorption.

Pseudo first order

A pseudo first order kinetics is present to describe the rate of adsorption process in liquid-solid phase. It can be described as the following equation (1)

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \text{-----} 1$$

Integrating eq. (1) for the boundary conditions of $t=0, q_t=0$, and $t = t, q_t = q_t$.

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \text{-----} 2$$

Where q_e is the amount of 2-chlorophenol adsorbed at equilibrium (mg/g), q_t is the amount of molecule adsorbed at time t (mg/g), k_1 is the first order rate constant (min^{-1}) and t is time in (min). The straight line plot of $\log (q_e - q_t)$ against time t , should give a linear relationship from which the pseudo –first order rate constant (k_1) and equilibrium sorption capacity (q_e), can be calculated from the slope and intercept respectively.

Pseudo-second order

The Pseudo-second order kinetic model is expressed as:

$$\frac{dq}{dt} = K_2(q_e - q_t)^2 \text{-----} 3$$

The linearized form of the kinetic rate expression for a pseudo second-order model was applied to the experimental data using (eq. 3) ⁴⁷.

$$\frac{t}{qt} = \frac{1}{h_0} + \frac{1}{q_e} t \text{-----} 4$$

Where q_t is the amount of 2-chlorophenol molecules on the activated carbon surface (mg/g) at time t , q_e is the amount (mg/g) of 2-chlorophenol sorbed at equilibrium, the initial sorption capacity (mg/min), h_0 , is obtained as shown in equation

$$h_0 = k_2 q_e^2 \text{-----} 5$$

Where k_2 is the Pseudo-second order rate constant (g/mg/min). The parameters h_0 and k_2 are determined experimentally from the slope and intercept of a plot of $\frac{t}{qt}$ against t .

In this case, $\frac{t}{qt}$ versus time was taken to obtain straight lines. From the slopes and intercepts of these plots, the pseudo-second order rate constants K_2 (g/mg/min), the equilibrium sorption capacity q_e (mg/g) and the initial sorption capacity, h_0 (mg/min) were computed. The pseudo second-order kinetics model has been successfully applied to several biosorption systems⁴⁸

Elovich model

The linearized form of the Elovich equation is mainly applicable for chemisorptions kinetics.

The equation is often valid for systems in which the adsorbing surface is heterogeneous⁴⁹. The Elovich model is generally expressed as

$$\frac{dq}{dt} = \alpha e^{-\beta qt} \text{-----6}$$

Integrating eq. (6)

$$qt = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \text{-----7}$$

A plot of qt versus $\ln t$ should give a linear trace with a slope of $\frac{1}{\beta}$ and an intercept of $\frac{1}{\beta} \ln(\alpha\beta)$. Where α is the initial adsorption rate (mg/g min) and β is related to the extent of surface coverage and the activation energy for chemisorptions (g/mg) and are calculated from the slope and intercept respectively.

Intraparticle diffusion

To investigate if intra-particle diffusion was the sorption rate limiting step, intra-particle diffusion model⁵⁰. The Intraparticle diffusion model is generally expressed as according to this expression of equation (8) given as:

$$qt = K_{id} t^{0.5} + C \text{-----8}$$

Where, k_{id} is the intraparticle diffusion rate constant (mg/g/min^{1/2}) and C (mg/g) is a constant that gives idea about the thickness of the boundary layer, i.e. the larger the value of C the greater the boundary layer effect. If Srivastava plot of qt versus $t^{1/2}$ gives a straight line, then the sorption process was controlled by intra-particle diffusion only

and the slope gives the rate constant K_{id} . However, if the data exhibit multi-linear plots then two or more steps influenced the sorption process⁵¹.

Liquid film diffusion

The liquid film diffusion model was also employed to investigate, if the transport of the sorbet molecules from the liquid phase up to the solid phase boundary plays a major role in the adsorption as shown in equation

$$\ln(1 - F) = -k_{id}t \text{-----} 9$$

Where F is the fractional attainment of equilibrium $F = \frac{q_t}{q_e}$, K_{id} is the adsorption rate constant. A linear plot of $-\ln(1 - F)$ versus t with zero intercept would suggest that the kinetics of the sorption process is controlled by diffusion through the liquid surrounding the solid sorbent.

2.6. Adsorption isotherms

There are several isotherm equations available for analyzing experimental adsorption equilibrium parameters, the most common being the Langmuir and Freundlich models. 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. These active sites have the same affinity for adsorption of a mono molecular layer and there is no interaction between adsorbed molecules⁵².

A well known linear form of the Langmuir equation can be expressed as

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \text{-----} 10$$

Where: - C_e is the equilibrium concentration of solute in solution (mg/l),

q_e is the amount of solute adsorbed at equilibrium (mg/g),

q_m (mg/g) and K_L (L/mg) are the Langmuir constants, and q_m signifies adsorption capacity and K_L is related to energy of adsorption process.

A plot of $\frac{C_e}{q_e}$ against C_e yields a straight line and q_m and K_L are obtained from the slope and intercept respectively.

This important characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless factor⁵³, which is defined as: R_L

$$R_L = \frac{1}{1+K_L C_o} \text{----- 11}$$

Where K_L is the Langmuir constant and C_o is the initial concentration of the adsorbate in solution. The values of R_L indicates the type of isotherm to be irreversible ($R_L=0$), favorable ($0 < R_L < 1$), linear ($R_L=1$) or unfavourable ($R_L > 1$).

The Freundlich isotherm model 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 well-known expression for the Freundlich model is given as⁵⁴:

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \text{----- 12}$$

Where: - q_e is the adsorption density (mg/g),

C_e is the concentration of the adsorbate in solution at equilibrium (mg/dm³),

K_F and n are the Freundlich constants.

If a plot of $\log q_e$ against $\log C_e$ yields a straight line, then the sorption process obeys a Freundlich adsorption isotherm. The K_F and $1/n$ can be obtained from the intercept and slope of the straight line. The exponent (n) is an index of the diversity of free energies associated with the sorption of the solute by multiple components of a heterogeneous sorbent. When $n < 1$, the isotherm is concave and sorbates are bound with weaker and weaker free energies, $n > 1$, the isotherm is convex and more sorbate presence in the sorbent enhance the free energies of further sorption and $n=1$, the isotherm is linear and system has a constant free energy at all sorbate concentrations.

The good fit of freundlich isotherm to an adsorption system means there is almost no limit to the amount adsorbed and there is a multilayer adsorption⁵⁵.

2.7. Thermodynamic study

Experimental data derived from the effect of temperature on the sorption process was analyzed using different equations which make it possible to determine some thermodynamic parameters such as Gibb's free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°). The adsorption equilibrium constant K_o was estimated from the expression

$$K_o = \frac{C_e}{C_o} \text{-----13}$$

The thermodynamic parameters was determined according to equations (14 and 15) as given below

$$\Delta G^\circ = RT \ln K_o \text{-----14}$$

$$\ln K_o = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \text{-----15}$$

The values of ΔH° and ΔS° can be calculated from the slope and intercept of the linear plot of $\ln K_o$ against reciprocal of temperature ($1/T$).

2.8. Statement of the problem

Access to potable water is one of the main problems in world especially in industrial areas. These areas are highly affected by high concentration of 2-chlorophenol in water. 2-Chlorophenol are one of the most important groups of priority contaminants because they are not readily biodegradable and are highly toxic, causing problems with the human respiratory and nervous system. Chlorinated organic compounds (COCs) have been so widely used that they can be found in nearly all major environments such as in various waste oils and other organic liquids. Due to their reactive nature, they are highly toxic, mutagenic and possibly carcinogenic. Furthermore, they are biorefractory and tend to accumulate in animal tissues. Once released into the environment, they will accumulate in the surrounding areas and pose a great health threat to humans and ecosystems over a long period of time⁵⁶. Therefore, the efficiency of traditional biological treatment method is not satisfying due to 2-chlorophenol's structural stabilization and toxicity⁵⁷. As one type of the most hazardous materials, they are carcinogenic, mutagenic and resistant to biodegradation, and thus have to be

decomposed before discharging into receiving waters, in order to avoid the biomagnified toxicity to aquatic flora and fauna through various food chains. Thus, the present research work can answer the following questions:

- ✓ What is the efficiency and adsorption capacity of activated carbon prepared from *Ricinus communis* pericarp waste to remove 2-chlorophenol from aqueous solution?
- ✓ What kind of adsorption mechanisms responsible for adsorption of 2-chlorophenol onto activated carbon?

2.9. Objectives of the Study

2.9.1. General Objective

To evaluate the feasibility of *Ricinus communis* pericarp waste as a precursor for activated carbon production and employing the activated carbon thus prepared for the removal of 2-chlorophenol from aqueous solutions.

2.9.2. Specific Objective

- ❖ To prepare activated carbon from pericarp of *Ricinus communis*.
- ❖ To determine the effects of pH, dose of pericarp of *Ricinus communis*, contact time, and temperature on the adsorption efficiency of activated carbon.
- ❖ To determine adsorption efficiency of 2-chlorophenol from aqueous solution.

2.10. Significance of the study

The study was focused on kinetics and thermodynamics of 2-chlorophenol adsorption onto *ricinus communis* pericarp activated carbon in aqueous solutions. Therefore, the outcome of this research:

- ✓ In contributing alternative operational method of advanced technologies for removal of 2-chlorophenol by using activated carbon from aqueous solution.
- ✓ Emphasis how to treat wastewater by using environmentally friendly, locally available and economically low cost materials.
- ✓ And also it will give more information on adsorption by using *ricinus communis* pericarp activated carbon for further study.

3. MATERIALS AND METHODS

3.1. Instrumentation and Apparatus

A Shimadzu model 180 UV-Visible spectrophotometer was used to analyze the concentration of 2-chlorophenol. GRANT GLS 400 shaker was used for shaking mixtures. pH meter (HANNA instruments, pH 211), Electronic balance (ADAM AFP-110L), Filter paper (5971/2 S&S Folded of 185 mm), Centrifuge, Oven (Model GENLAB WIDNES, England), Thermostatic water bath (Model Grant GLS400, England), Sieve (150 μ m), Conical flasks, volumetric flask, Fourier transforms infrared [FT-IR] spectrophotometer, Petri dish, Crucibles and mortar and pestle were used for ground the pericarp of *Ricinus communis* sample.

3.2. Reagents and Solutions

All chemicals used in this study were used without any purification. Distilled water was used for the preparation of stock standard solution of 2-chlorophenol and de-ionized water also was used for all subsequent dilutions. A stock solution of 2-chlorophenol (1000 mg/L) was prepared by dissolving 1 gm of 2-chlorophenol (98%, sigma Aldrich) in 1000 ml distilled water. Working solutions of the desired concentrations were prepared by serial dilution of the stock solution. Sulfuric acid (H_2SO_4 , 98% analytical reagent) and sodium bicarbonate ($NaHCO_3$, sigma Aldrich) for activation of pericarp of *Ricinus communis* sample. Glacial acetic acid (Riedel-de Haën, Germany) sodium acetate (Riedel-de Haën, Germany), Potassium hydrogen phosphate (Finkem, India), Potassium dihydrogen phosphate (Finkem, India) conc. NH_3 , (Mumbai, India), ammonium chloride (Riedel-de Haën, Germany), were used throughout the experiments to adjust the pH of solutions and also were used for preparation of buffer solutions of pH 4, 7 and 10 which were used for calibration of the pH meter.

3.3. Preparation of Activated Carbon

The pericarp of *Ricinus communis* sample was collected from local seller (vendor) N/Wollo in Gobalafto woreda 600 km away from Addis Ababa to Northern direction. It was used for the preparation of activated carbon. The sample was dried and activated chemically by pouring 50% sulfuric acid with constant stirring (w/v). The charred

material was kept in hot air oven at 105 °C for 12 h. This was washed with redistilled water and this was soaked in 10% sodium bicarbonate solution and was allowed to stand overnight to remove the residual acid from the pores of carbon. The material was washed with distilled water, until the pH of the adsorbent reach 6.8. Then it was dried in a hot air oven at 105 °C for 12 h, ground and was sieved to obtain the particle size of 150 μm⁵⁸. The sieve adsorbent was stored in an airtight container for further experiments. Redistilled water was used for the whole period of experimental studies.

3.4. Characterization of Activated Carbon

Fourier Transform Infrared (FTIR) analysis was used to detect the available functional groups on the pericarp of *Ricinus communis* surface.

Proximate analysis of total ash content, moisture content, volatile matter, pH, Conductivity, pore (Void) Volume, specific gravity, porosity/ bulk density, carbon Yield and fixed carbon were also performed.

Determination of pH and Conductivity

1.0 gm of each carbon was weighed and transferred into a 250 ml beaker and 100 ml of distilled water was added and stirred for 1 hr. Samples were allowed to stabilize and then pH measured using an electronic pH meter. The same samples were further used for electrical conductivity (EC) and results read off in mS/cm⁵⁹.

Pore (Void) Volume Determination

Each AC sample (1gm) was immersed in water and boiled for 15 minute in order to displace air from the pores. The samples were dried and reweighed. The pore volume was calculated as increase in weight (Δw) divided by the density (ℓ) of water at 20°C.

$$pore\ volume = \frac{\Delta w}{\ell_{t20}} \text{-----} 1$$

Ash Content Determination

Dry AC sample (1.0 gm) was placed in to a crucible and transferred into a preheated muffle furnace set at a temperature of 1000 °C. The furnace was left on for one hour

after which the crucible and its content was transferred to desiccators and allowed to cool for 30 minute. The crucible and content was reweighed and the weight lost was recorded as the ash content of the AC sample (W_{ash}). Then the % ash content (dry basis) was calculated from the following equation

$$Ash = \frac{100\% W_{ash}}{W_o} \text{-----} 2$$

Where W_0 and W_{ash} is the dry weight of carbon sample before ashing and ash content of the AC sample respectively.

Moisture Content Determination

Thermal drying method was used in the determination of moisture content of the samples. 1.0 gm of the dried activated carbons were weighed in triplicates and placed in washed, dried and weighed crucible. The crucibles were placed in an oven and dried at 105 °C to constant weight for 4 hr according to the method of Rengaraj⁶⁰. The percentage moisture content (%MC) was computed as follows:

$$Moisture(\% = \frac{loss\ in\ weight\ on\ drying(g)}{intial\ sample\ weight} \times 100 \text{-----} 3$$

Volatile matter Determination

Thermal drying method was used in the determination of volatile matter of the samples. 1.0 gm of the dried activated carbons were weighed in triplicates and placed in washed, dried and weighed crucible. The crucibles were placed in an oven and dried at 105 °C to constant weight for 24 hr. The percentage moisture content (%VM) was computed as follows:

$$volatile\ matter(\% = \frac{weight\ of\ volatil\ component(g)}{oven\ dry\ weight\ (g)} \times 100 \text{-----} 4$$

Specific gravity determination

The relative density bottles were cleaned, dried and weighed empty. One third of the activated carbons were put into it and weighed again. The relative density bottles were filled with water and reweighed. Finally the bottles were emptied, cleaned of the

activated carbon particles filled with water alone and weighed. The specific gravity was calculated in triplicate.

$$G_s = \frac{M_2 - M_1}{(M_2 - M_1) - (M_3 - M_4)} \text{-----5}$$

Where G_s = specific gravity

M_1 = mass of empty bottle

M_2 = mass of bottle and activated carbon

M_3 = mass of bottle, activated carbon and water

M_4 = mass of bottle and water

Determination of porosity/ bulk density

A cylinder and a petridish plate were each weighed. A sample of activated carbon was put into the cylinder and reweighed. The samples were transferred into the petridish plate and put into an oven so as to dry it to constant weight at a temperature of 105 °C for one hour. The weight of the dried samples was taken again after drying. A clean dry well corked density bottle was weighed. The bottle was filled with water, corked and reweighed, small quantities of samples of activated carbons were taken and ground to powder, sieved using 150 μm and gradually put into the bottles with little amount of water and weighed again. The bulk density, dry density and porosity were calculated using the following expressions

$$\text{Bulk density} = \frac{\text{mass of wet sample}}{\text{volume of cylinder}} \text{-----6}$$

$$\text{Dry density} = \frac{\text{mass of dry sample}}{\text{volume of cylinder}} \text{-----7}$$

$$\text{Porosity } (\eta) = \frac{V_v}{V_t} \text{-----8}$$

Where V_v = volume of void, V_t = total volume

The volume of void V_v was obtained by first determining the total volume of the cylinder ($V_t = \pi r^2 h$) used for the experiment and also determining the volume of solid i.e. the activated carbon used ($V_s = M_s / G_s P_w$).

r = radius of cylinder

h = height of cylinder

Ms = mass of solid

Gs = specific gravity

Pw = density of water

Then, volume of void (Vv) was obtained as $Vv = Vt - Vs$

Fixed Carbon Determination

The fixed carbon content (FC) was given as:

$$\% \text{ FC} = 100 - [\% \text{ ash content} + \% \text{ volatile matter content} + (\% \text{ Moisture content})]$$

Where, FC= fixed carbon (%), VC = Volatile Content (%), Ash = ash content (%) and U = Moisture content (%)

Carbon Yield

The total yields were determined after sample processing in terms of raw material mass. The dried weight, W_o of each pre-treated sample was determined and the carbon yield calculated as

$$Y_{ch} = \frac{W}{W_o} \times 100 \text{ ----- 9}$$

Where Y_{ch} = Carbon yield (%); W = dried weight of AC prepared; W_o = pre-treated sample used in the carbonisation and activation processes.

3.5. Effect of initial concentration

Equilibrium studies were carried out by contacting 0.2gm activated carbon with 50 ml 2-chlorophenol was prepared in de-ionized water from the stock solution of different initial concentrations (40, 60, 80, 100,120,140,160,180 and 200 mg/L) in twenty seven (250 ml) conical flask. The pH of the solutions was adjusted to 6.0 by adding phosphate buffer solution. The suspensions were agitated at 150 rpm on a shaker at room temperature (30°C) for 1 hr. At the end of the agitation period the samples was centrifuged for 5 min and the supernatant 2-chlorophenol solution, was filtered through filter paper. 2-Chlorophenol concentrations in the filtrate were analyzed using a UV/Vis spectrometry measuring absorbance at the wavelength of maximum absorption of (280nm). Determinations were run in triplicate.

3.6. Effect of pH

0.2 gm each of activated carbon was weighed and introduced into eighteen (250 ml) conical flasks. 50 ml of 100 mg/L solution of 2-chlorophenol was prepared in de-ionized water from the stock solution was added to the activated carbon. The pH values of these suspensions were adjusted to 2.0, 4.0, 6.0, 8.0, 10.0 and 12.0 by adding a solution of potassium chloride and hydrochloric acid for pH 2.0, acetic acid and sodium acetate for 4.0, K_2HPO_4 and KH_2PO_4 for pH 6.0 and PH 8.0 and NH_3 and NH_4Cl for pH 10 and 12. The flasks were tightly covered and shaken for 1 hr at 150 rpm. The suspensions were filtered through filter paper, centrifuged for 5 minutes and analyzed. Determinations were run in triplicate.

3.7. Effect of contact time

0.2 gm each of RCAC was weighed and put in thirty-three (250 ml) conical flasks. 50 ml of 100 mg/L concentration of 2-chlorophenol solution was prepared in de-ionized water from the stock solution was added to the biomass. The pH values of these suspensions were adjusted to 6.0. The flasks were labeled for time interval of 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120 minutes. The flasks were tightly covered and shaken at 150 rpm for the appropriate time intervals on an electric shaker. The suspensions were filtered through filter paper and centrifuged for 5 minutes. The supernatants were analyzed using UV-Visible spectrophotometer. Determinations were run in triplicate.

3.8. Effect of temperature

50 ml of 2-chlorophenol solutions with an initial concentration of 100 mg/L was placed in twenty-one (250 ml) conical flasks. 0.2 gm each of activated carbon was added to these solutions. The conical flasks were labeled at temperatures of 30, 40, 50, 60, 70, 80 and 90 °C respectively. The flasks were agitated at 150 rpm and heated on a thermostat water bath to the appropriate temperatures for 1h. The suspensions were filtered using filter paper and centrifuged for 5 minute. The supernatants were analyzed using UV-Visible spectrophotometer. Determinations were run in triplicate.

3.9. Effect of adsorbent dosage

Different masses of activated carbon ranging from 0.1 to 0.7gm was accurately weighed and transferred into twenty-one (250 ml) conical flasks. 50 ml of 2-chlorophenol was added to each of the conical flasks. The flasks were tightly covered and shaken for 1 hour at 150 rpm. At the end of 1 hr, the suspensions were filtered using filter paper, centrifuged for 5minute and analyzed. Determinations were run in triplicate.

3.10. Adsorption Study

The adsorption study was carried out by contacting 0.2gm of the activated carbon with 50 ml and 100 mg/L initial concentration of the 2-chlorophenol solution under different conditions for a period of time. The adsorption studies are conducted at 30 °C using thermo stated water bath to determine the effect of pH, contact time and initial concentration on the adsorption. The residual 2-chlorophenol was analyzed using UV/Vis spectrophotometer measuring absorbance at the wavelength of maximum absorption of (280 nm). All experiments were carried out triplicate, and the concentrations given are average values. The initial concentration in the test solution and the adsorbent dosage were varied to investigate their effect on the adsorption kinetics. The adsorption studies were carried out at different temperatures. This is used to determine the effect of temperature on the thermodynamic parameters. The amount of adsorption at time t, q_t (mg/g), was calculated using the following relation:

$$q_t = \frac{(C_o - C_t)}{M} V \text{----- 10}$$

Where C_t (mgL^{-1}) is the liquid phase concentrations of 2-chlorophenol at any time, C_o (mg/L) is the initial concentration of the 2-chlorophenol in solution. V is the volume of the solution (L) and M is the mass of dry adsorbent (g).

The amount of adsorption at equilibrium, q_e (mg/g) and the percent adsorption (%) was computed as follows:

$$q_e = \frac{(C_o - C_e)}{M} V \text{----- 11}$$

$$\text{percent of adsorption} = \frac{(C_o - C_e)}{C_o} \times 100\% \text{----- 12}$$

Where C_o and C_e are the initial and equilibrium concentrations of 2-chlorophenol (mg/L) respectively.

4. Result and Discussion

4.1. Characterization of the adsorbent

Activated carbons are widely used as adsorbents due to their high adsorption capacity, high surface area and micro porous structure. Some important physico-chemical characteristics of RCAC are given in Table 1. The activation process of RCP by adopting sulphuric acid treatment leads to the corrosion of the surface of a carbonaceous material and the appearance of micro-, macro- and meso-pores.

Moisture content: - Moisture content of the carbon has no effect on its adsorptive power; it dilutes the carbon which is necessary to use of additional weight of carbon during the treatment process. The RCAC samples were determined using standard test method for moisture in AC⁶¹.

Ash content: - Ash content can affect activated carbon performance that is; it reduces the overall activity of activated carbon. It also reduces the efficiency of reactivation⁶². Therefore, the lower the ash content the better the activated carbon for use as adsorbent.

Porosity: Porosity describes the number of pores present in a sample. Therefore porosity enhances adsorption capacity of an adsorbent, and the higher the porosity, the higher the adsorption capacity of the adsorbent.

pH value: The pH value of activated carbon is a measure of whether it is acidic or basic. Activated carbon, when coming out of the kiln tends to be a bit basic, with a pH of around 8. Too high a pH indicates too much contaminant. Too low a pH, especially for acid washed activated carbon, means that the acid has not been properly rinsed away. For most applications, activated carbons are specified for a pH of 6-8. The pH values of the activated carbon samples are therefore within the specified pH range of activated carbons⁶³.

Bulk density: Bulk density is the mass of carbon that can be contained in a filter of a given solid capacity and the amount of treated liquid that can be retained by the filter cake. The higher the density the better the filterability of activated carbons.

The lower ash content, moisture content and volatile matter is attributed to lower inorganic content and higher fixed carbon. Higher value of fixed carbon shows that the adsorbent is having more efficiency and stability. The samples were determined using standard test methods for ash, moisture and volatile matter contents of AC. A higher percentage adsorption for smaller particle size adsorbent (150 μm) is due to the availability of more surface area. The high surface area is considered to be most suitable adsorbent for adsorption.

Table 1: Physico-chemical characteristics of *Ricinus cumminus* pericarp activated carbon (RCAC)

Parameters	Value
pH	7.1
Conductivity mS/cm	0.683
Moisture content (%)	17.5
Volatile matter (%)	16.2
Ash content (%)	19.75
Bulk density (gm/cm^3)	0.241
Pore volume(cm^3)	1.053
Porosity	0.9475 (94.75)
Specific gravity	2.766
Particle size (μm)	150
Fixed Carbon, %	46.55
Yield (%)	48.9

FTIR characterization

The FTIR spectrum of pericarp of *Ricinus communis* before adsorption and after adsorption shows that some peaks were shifted (Fig. 1). The FTIR spectrum of *Ricinus cominnus* displays a number of absorption peaks indicating the presence of different types of functional groups. The absorption peaks at 2923 cm^{-1} , $1623 - 1559\text{ cm}^{-1}$, 1099 cm^{-1} and $760 - 656\text{ cm}^{-1}$ corresponds to carboxylic, amides, halogens and amines⁶⁴.

The region between $3000 - 2800\text{ cm}^{-1}$ exhibits the C-H stretching vibrations of CH_3 and CH_2 functional groups. There is a strong peak at 3429cm^{-1} representing the -OH stretching of the phenol group of cellulose and lignin, and the peak at 3004cm^{-1} indicates the presence of -CH stretching of an vinyl functional groups. The appearance of peaks at 1627 and 1387cm^{-1} indicates the presence of C=O stretching of an aldehyde group and the C—H stretching of CH_2 functional groups, respectively. The peaks at

1270, 1029 and 624 cm^{-1} might be due to C-O stretching of the phenolic group, the ester group of cellulose and long chain band of lignin respectively⁶⁵.

The FTIR spectrum after adsorption, shown in Fig. 1 (Chlorophenol loaded AC) and Fig. 1 (Real Sample loaded AC) indicates that the peaks due to the above functional groups are slightly affected in their position and intensity. It indicates that the adsorption of 2-chlorophenol on the surface of pericarp of *Ricinus communis* is affected either through complexation or through physical impacts which might be weak electrostatic interaction and Van der Waals forces. But, FT-IR spectrum of after adsorption show that the main adsorption peaks of RACC activated carbon spectrum has not much changed compared to the spectrum of before adsorption. The results indicate that the adsorption process between RCAC activated carbon and 2-chlorophenol is a physical adsorption and not a complex reaction.

The drift spectra of RCAC show that both types i.e. acidic and basic surface functional group are present on its surface. The results given above suggest that only a fraction of the RCAC surface is available for adsorption contributes to the removal. In the literature, the 2-chlorophenol adsorption on AC was determined by the so-called π - π interactions (dispersion forces between 2-chlorophenol π electrons ring and π electrons of AC) and “donor-acceptor complex” formation between the surface carbonyl groups (electron donors) and the aromatic ring of 2-chlorophenol acting as the acceptor^{66, 67}.

These changes observed in the spectrum indicated the possible involvement of those functional groups on the surface of pericarp of *Ricinus communis* in adsorption process. The presence of those functional groups on the surface of pericarp of *Ricinus cominnus* carbon can be attributed to its leguminous plant origin as evident from high content functional group. However, selective acid base neutralization method gives more information on the oxygen surface functionality of the activated carbon studied.

Table 2: FT-IR Spectral Characteristics of *Ricinus communis* pericarp activated carbon (RCAC) before and after adsorption of 2-chlorophenol

Sample	Absorption bands(cm^{-1})			Functional groups
	Before adsorption	After adsorption	difference	
2-Chlorophenol	3429	3435	6	O-H stretching
2-Chlorophenol	3004	2931	73	C-H stretching
2-Chlorophenol	1627	1624	3	C=O asymmetric stretching
2-Chlorophenol	1387	1388	1	In plan C-H bending
2-Chlorophenol	1270	1207	63	COOR, ester stretching
2-Chlorophenol	1029	1030	1	C-O stretching
2-Chlorophenol	624	538	86	Long chain band

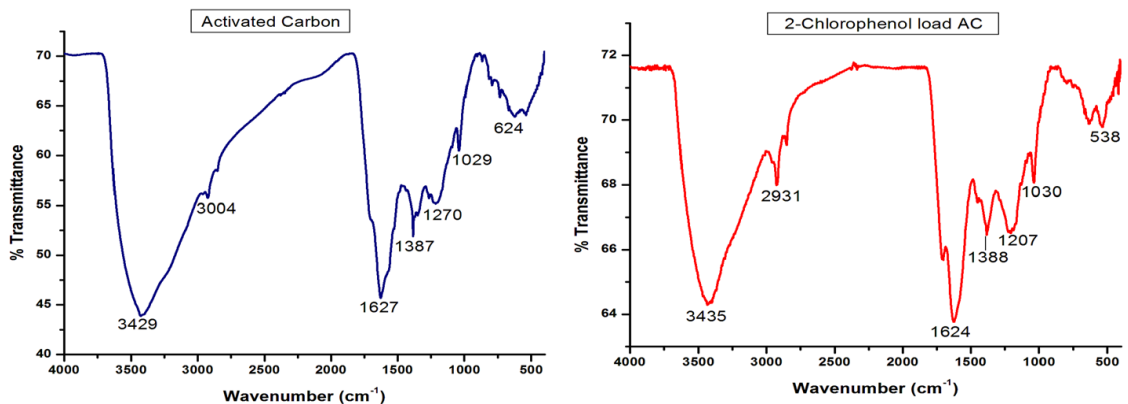


Figure 1: FT-IR spectra of AC before and after adsorption of 2-chlorophenol

4.2. Adsorption equilibrium

The influence of initial concentration on the removal of 2-chlorophenol by RCAC was studied at initial concentration of 40-200 mg/L with constant dose of adsorbent 0.2 gm and the result presented in Fig 2. It is observed that the percentage removal of 2-chlorophenol is more than 97.65% achieved at all concentration on RCAC. It was also observed that the percentage 2-chlorophenol removal increased with decreasing concentration till 40 mg/L. For example, the percentage removal is calculated 99.97 % using the initial concentration of 40 mg/L, while it is found 97.65 % using high-level of 200 mg/L. At high-level concentrations, the available sites of adsorption become fewer. This behavior is connected with the competitive diffusion process of the 2-chlorophenol through the micro channel and pores. This competitive will lock the inlet of channel on

the surface and prevents the 2-chlorophenol to pass deeply inside the AC *i.e.* the adsorption occurs on the surface only. These results indicate that energetically less favorable sites by increasing 2-chlorophenol concentration in aqueous solution.

The initial 2-chlorophenol concentration also plays an important role in the adsorption capacity. The initial 2-chlorophenol concentration provides the necessary driving force to overcome the resistance of mass transfer from the aqueous phase to the solid phase. The higher the initial concentration is, the greater the driving force becomes. The increase in initial 2-chlorophenol concentration also enhances the interaction between molecule and AC. Therefore, an increase in initial concentration of 2-chlorophenol enhances the adsorption capability of AC for 2-chlorophenol.

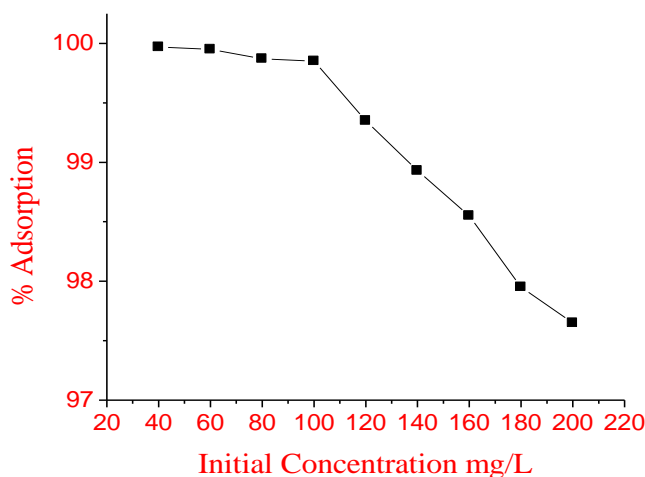


Figure 2: Effect of adsorbent dose on adsorption of 2-chlorophenol onto pre carp of *Ricinus cominnus* (Initial concentration of 2-chlorophenol =100 mg/L, pH= 6 contact time = 60 min agitation speed = 150 rpm and temperature of 30 °C).

4.3. Effect of contact time

In order to find out the time for equilibrium adsorption, the interaction period for 2-chlorophenol on the RCAC was varied the contact time from 10-120 minute at a fixed concentration of 100 mg/L, a dosage of adsorbent of 0.2 gm, agitation speed 150 rpm, temperature 30 °C and pH of 6. It was found that at the initial stage, rate of adsorption of 2-chlorophenol is quite high and reaches a maximum after 60 minute that does not change with further elapse of time (Fig 3). The saturation curves rises sharply in the initial stages, indicating that there are plenty of readily accessible sites. Figure 3 shows

that the contact time needed for 2-chlorophenol solutions of 100 mg/L to reach equilibrium is 60 minutes and the adsorption capacity of 24.9675 and 99.87% of adsorption. Almost, no remarkable improvement was observed after longer contact time. After this equilibrium period, the amount of solute adsorbed did not change significantly with time, indicating that 60 min is sufficient to attain equilibrium for the maximum removal of 2-chlorophenol from aqueous solutions by *Ricinus cominnus*. So the optimum contact time was selected as 60minutes for further experiments⁶⁸.

It can be explained that the AC surface was progressively blocked by the 2-chlorophenol reaching pseudo equilibrium in about 60 min. Generally, the adsorption capacity increases with time and reaches a constant value where no more 2-chlorophenol is removed from the solution at some point in time. At this point, the 2-chlorophenol amount being adsorbed onto the material is in a state of dynamic equilibrium with the 2-chlorophenol amount desorbed from the adsorbent.

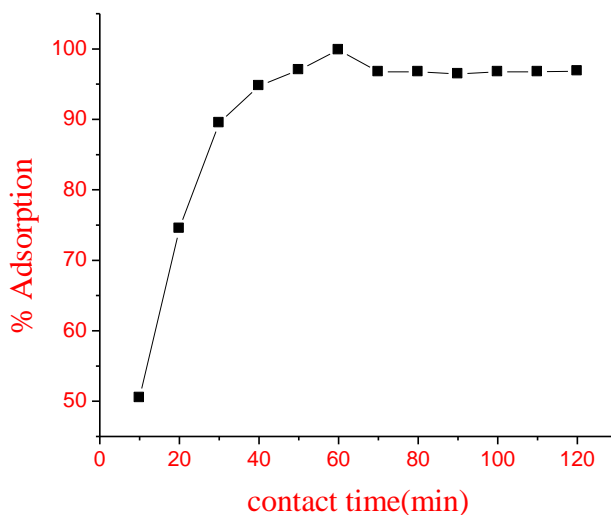


Figure 3: Effect of contact time on adsorption of 2-chlorophenol onto precarp of *Ricinus cominnus* (Initial concentration of 2-chlorophenol =100 mg/L, pH= 6 adsorbent dose= 0.2 gm, agitation speed = 150 rpm and temperature of 30 °C).

4.4. Effect of pH

In any adsorbate - adsorbent system, pH of the solution affects the surface charge of the adsorbents, effects ionization and the extent and rate of adsorption⁶⁹. Change in pH affects the adsorptive process through dissociation of functional groups. This

subsequently leads to a shift in reaction kinetics and equilibrium characteristics of adsorption process. The effect of pH of 2-chlorophenol on their adsorption onto RCAC is given in Fig 4. The effect of pH on the adsorption of 2-chlorophenol was studied varying the pH from 2 to 12 at initial concentration of 100 mg/L. It can be observed that the removal of 2-chlorophenol increase with increasing pH from minimum at pH of 2 (62.5%) to maximum at pH of 6 (98.25%) and at pH 12 (56.75%) was occurred. It was observed that the relative amount of phenolic compound adsorbed was significantly affected by pH with an increase in the percentage of 2-chlorophenol removed from solution. The maximum adsorption occurs at pH 6.0; with further increase in pH a significant decline in removal efficiency was observed which may be attributed to formation of 2-chlorophenolate anion. The maximum uptake of adsorbate was highest at optimum pH of 6.0, with the adsorption capacity of RCAC (24.6875 mg/g) and the 98.75% of adsorption.

The 2-chlorophenolic compound considered in this study, viz, 2-CP, have pKa values of 8.3, thus at optimum conditions of pH 6 the protonated species appear to be more readily adsorbed on the negative surface of the carbon. The donor acceptor complex mechanism was reported earlier for the adsorption of 2-chlorophenol on activated carbon⁷⁰. In this mechanism carbonyl oxygen on the carbon surface acts as the electron donor where as the aromatic ring of the phenol acts as the electron acceptor. When the pH of a solution goes beyond the pKa, 2-chlorophenol chiefly exists as negative 2-chlorophenolate ion, whereas this exists as neutral molecule below the pKa. 2-chlorophenol adsorbed on the surface of activated carbon due to the electron withdrawing inductive effect of chlorine and electron rich nature of the hydrogen atom in 2-chlorophenolate ion, the hydrogen bonding efficiency decreases. Therefore, 2-chlorophenol effectively adsorbed on to the adsorbent as molecules but not 2-chlorophenolate ion⁷¹. From the experimental results pH 6 was selected as an optimum pH.

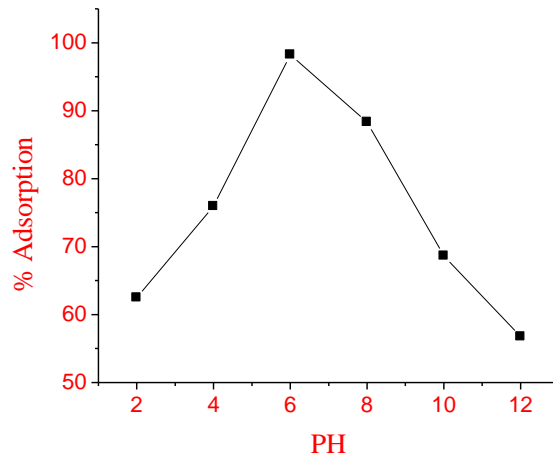


Figure 4: Effect of pH on adsorption of 2-chlorophenol onto precarp of *Ricinus cominnus* (Initial concentration of 2-chlorophenol =100 mg/L, adsorbent dose=0.2 gm contact time = 60 min agitation speed = 150 rpm and temperature of 30 °C).

4.5. Adsorbent dosage

The determination of optimum dose is essential for optimization of the removal process. It is observed that the removal of 2-chlorophenol increased with increasing dose of the activated carbon (0.1 to 0.7gm) (Fig 5). The % removal of 2-chlorophenol increases from 98.25 to 99.91 % for an increase in adsorbent dose from (0.1 to 0.7 gm). Initially, a rapid increase of adsorption with the increasing adsorbent dosage is attributed to the availability of more adsorption sites. After the critical dose (about 0.4 gm), the rate of 2-chlorophenol removal increases much more slowly (only from 98.25 % to 99.83 %). This can be attributed to the splitting effect of flux (concentration gradient) between adsorbent and adsorbate. This may be due to the fact that increasing the adsorbent mass may affect the adsorption as it increases the exposed surface area and the number of binding sites which are available for adsorption and hence increased the %

Removal of 2-chlorophenol adsorbed from aqueous solution⁵⁰. The study of the effect of adsorbent dose is necessary to observe the maximum adsorption with the minimum possible amount of adsorbent. This is because a fixed dose of activated carbon can only adsorb a certain amount of molecule. Therefore, the higher the adsorbent dosage, the larger the volume of effluent can be purified with a fixed dosage of AC.

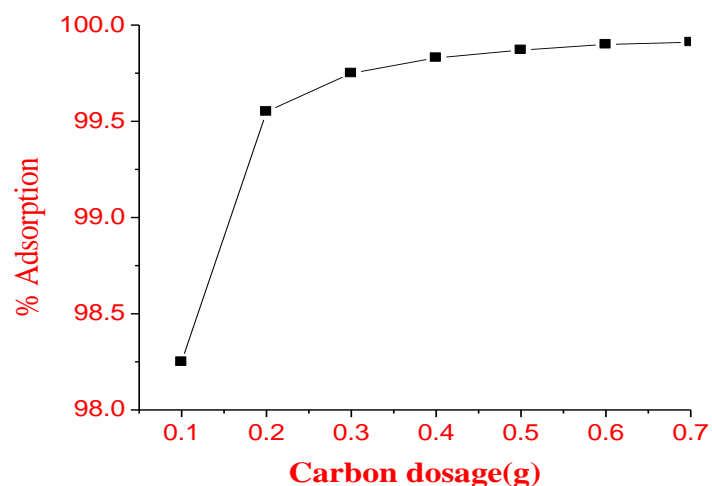


Figure 5: Effect of adsorbent dose on adsorption of 2-chlorophenol onto precarp of *Ricinus cominnus* (Initial concentration of 2-chlorophenol = 100 mg/L, pH= 6 contact time = 60 min agitation speed = 150 rpm and temperature of 30 °C).

4.6. Effect of temperature

The effect of temperature on the percent removal of 2-chlorophenol was studied at a constant initial 2-chlorophenol concentration of 100 mg/L, carbon dose of 0.2 gm and temperature range of 30 to 90 °C.

Fig 6 is a plot depicting the effect of temperature on percentage adsorption of 2-chlorophenol on RCAC. The percentage removal of 2-chlorophenol was optimum at 30 °C. The amount of 2-chlorophenol adsorbed decreased as temperature increased from 30 °C to 90 °C as follows CPCAC (24.84 – 15.08 mg/g). Hence the lower temperature is favorable for the adsorption of 2-chlorophenol. The decrease in adsorption with increase in temperature is partly due to the weakening of the attractive forces between the adsorbates and adsorbent. It could also be attributed to the enhancement of thermal energies of the adsorbate, thus making the force between adsorbent and adsorbate insufficient to retain the adsorbed molecules at the binding sites which indicate the adsorption process is exothermic. The rapid removal of 2-chlorophenol further indicates that physisorption involved in the adsorption of the adsorbates by the adsorbents. Therefore physical adsorption is very effective particularly at a temperature close to the critical temperature of a given gas. The overall high percentage of 2-chlorophenol

removal from solution could possibly be due to adsorption through ion exchange, hydrogen bonding, van-der Waal's forces as well as intraparticle diffusion^{68, 69}.

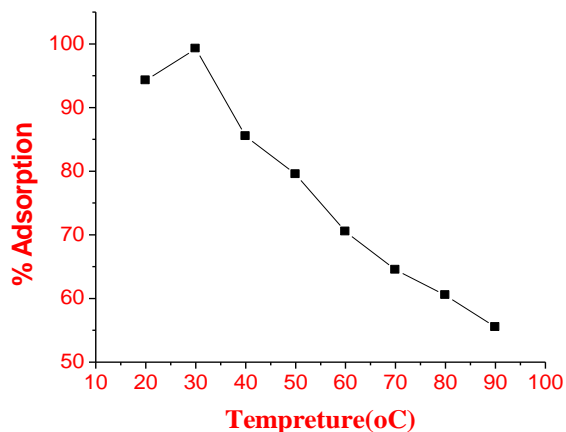


Figure 6: Effect of temperature on adsorption of 2-chlorophenol onto precarp of *Ricinus cominnus* (Initial concentration of 2-chlorophenol = 100 mg/L, pH= 6 contact time = 60 min agitation speed = 150 rpm and adsorbent dose 0.2 gm).

4.7. Adsorption Isotherm

Sorption equilibria provide fundamental physiochemical data for evaluating the applicability of sorption process as a unit operation. The equilibrium study has been conducted based on the commonly used monolayer and multi layer adsorption isotherm models of Langmuir and Freundlich. According to the plots of C_e/q_e versus C_e for Langmuir isotherms and $\log q_e$ versus $\log C_e$ for Freundlich, the experimental data was found to fit better to Freundlich model. The Langmuir adsorption isotherm is the best known of all isotherms describing sorption and it has been successfully applied to many sorption processes⁷². The Langmuir model been empirically most often used, contained the two parameters q_m and K_L , which reflect the two important characteristics of the sorption systems they are calculated from the intercept and the slope. The Freundlich isotherm was adopted to characterize the adsorption intensity of 2-chlorophenol by fitting the experimental data. The Freundlich isotherm model is based on the assumption that the adsorption occurs on heterogeneous surfaces with interaction between adsorbed molecules and suggests that adsorption energy has a non-uniform distribution over the adsorbent surface⁷³. The Freundlich equation does not consider all sites on the adsorbent

surface to be equal. Furthermore, it is assumed that, once the surface is covered, additional adsorbed species can still be accommodated.

Even though, the Langmuir and Freundlich constant q_m and K_F have different meanings, they led to the same conclusion about the correlation of the experimental data with the sorption model. The basic difference between K_F and q_m is that Langmuir isotherm assumes adsorption-free energy independent of both the surface coverage and the formation of monolayer whereas the solid surface reaches saturation, while the Freundlich isotherm does not predict saturation of the solid surface by the adsorbate, and thus, the surface covering being mathematically unlimited⁷⁴.

Therefore, result clearly show that the adsorption of 2-chlorophenol on RCAC fit very well with the Freundlich model. The fact that the Freundlich model is a good fit to the experimental adsorption data suggests physical adsorption as well as a heterogeneous distribution of active sites on the surface of adsorbent. The observed correlation coefficient for Freundlich and Langmuir isotherms were 0.996 and 0.921 respectively. The other Freundlich constant, n , is a measure of the deviation of the adsorption from linearity. The value of n at equilibrium was above unity, suggesting favorable adsorption. Furthermore, the dimensionless separation factors calculated 0.006. R_L value was between 0 and 1 indicating favorable adsorption.

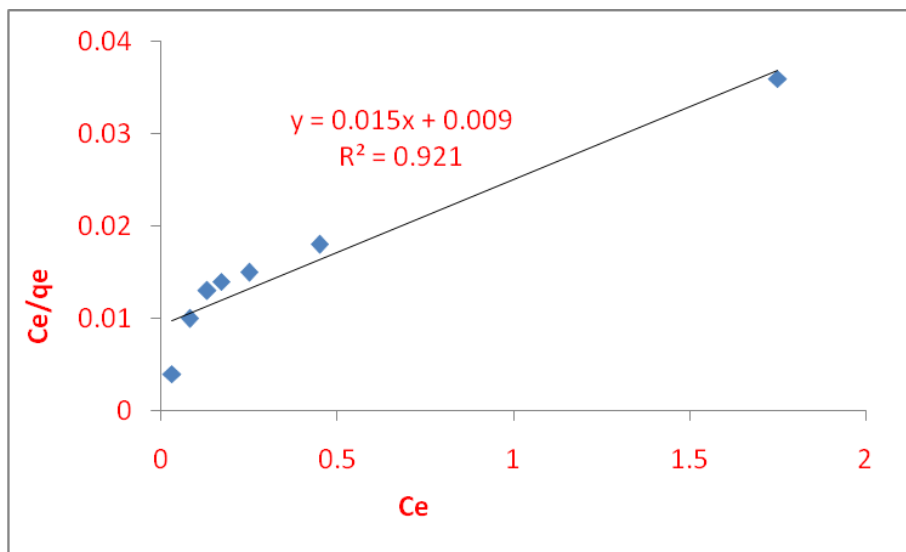


Figure 7: Langmuir plots for the sorption of 2-chlorophenol from solution by RCAC.

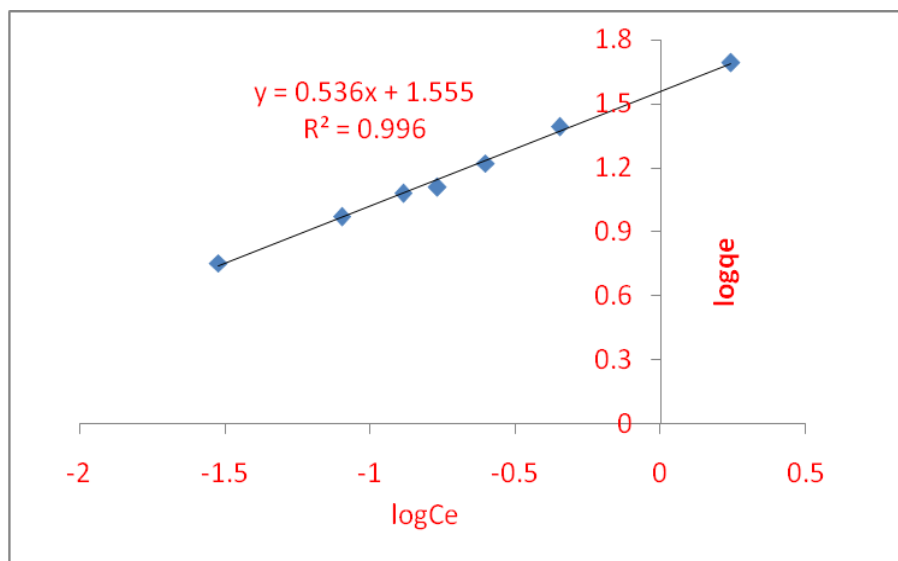


Figure 8: Freundlich plots for the sorption of 2-chlorophenol from solution by RCAC

Table 3: Results of isotherm models for the adsorption of 2-chlorophenol by RCAC at 303 K

Isotherm model	Parameters	Values
Langmuir	Maximum sorption capacity, q_m (mg/g)	66.7
	Adsorption/Desorption energy, K_L (dm ³ /g)	1.667
	Equilibrium parameter, R_L	0.006
	R^2	0.921
Freundlich	Intensity of adsorption, n (L/mg)	1.866
	Adsorption capacity, K_F (mg/g)	35.892
	R^2	0.996

4.8. Sorption kinetic studies

The amount of 2-chlorophenol adsorption increases with time and it remains constant after a contact time of about 60 min. (i.e. equilibrium time). The equilibrium time is independent of initial 2-chlorophenol concentration. The time profile of 2-chlorophenol uptake is a single, smooth and continuous curve leading to saturation, suggesting the possible multilayer coverage of 2-chlorophenol on the surface of the adsorbent. In order to examine the mechanism of adsorption process such as mass transfer and chemical reaction, a suitable kinetic model is needed to analyze the rate data. Many models such

as homogeneous surface diffusion model and heterogeneous diffusion model (also known as pore and diffusion model) have been extensively applied in batch reactors to describe the transport of adsorbate inside the adsorbent particles⁷⁵. The conformity between experimental data and the model predicted values was expressed by the correlation coefficient (r^2 , values close or equal to 1). A relatively high r^2 value indicates that the model successfully describes the kinetics of 2-chlorophenol adsorption. The time dependent experimental data in this study was analysed using five kinetic models, namely pseudo first order, pseudo second – order, Elovich, intra-particle and liquid – film diffusion models. Therefore, the pseudo –first order correlation coefficient value was found to be slightly higher than those of Elovich, Liquid-film, pseudo-second order and intraparticle values, indicating that the sorption follows better the pseudo-first order model.

Pseudo –first order

The values of q_e and K_1 for the pseudo-first-order kinetic model were determined from the intercepts and the slopes of the plots of $\log (q_e - q_t)$ versus time, respectively. The K_1 , R^2 and q_e values (experimental and calculated) are summarized in Table 4. R^2 value for the pseudo-first-order is 1. Besides, the experimental q_e value, very agree with the calculated values obtained from the linear plot. It suggests that the kinetic of 2-chlorophenol adsorption onto RCAC follow the pseudo first-order kinetic model.

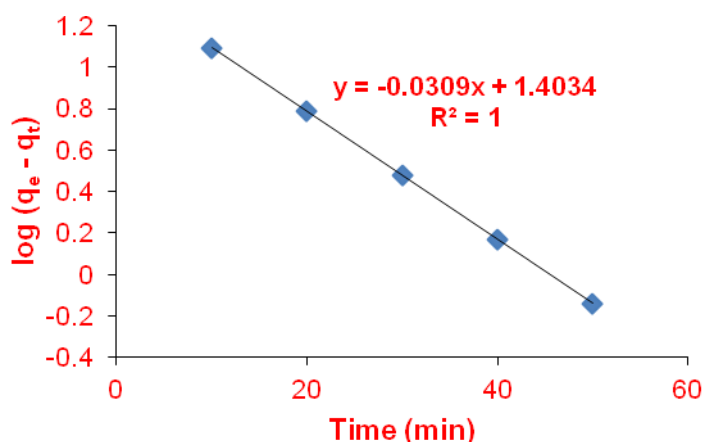


Figure 9: Pseudo-first order sorption kinetics of chlorophenol on RCAC

Pseudo second order

The pseudo-second-order plot of t/q_t versus time is a straight line as shown in Fig. 10. The K_2 and q_e values determined from the slopes and intercepts of the plot are presented in Table 4. This procedure is more likely to predict the behavior over the whole range of adsorption. The linear plot shows a wide variation agreement between the experimental and calculated q_e values (Table 4). The corresponding R^2 value for the pseudo-first-order kinetic model was greater than pseudo-second-order kinetic indicating the applicability of the pseudo-first-order kinetic model to describe the adsorption. The pseudo-second order model is based on the sorption capacity on the solid phase. Contrary to other well-established models, it predicts the behavior over the whole range of studies and it is in agreement with the chemisorptions mechanism being the rate controlling step⁷⁶. According to the other parameter like effect of temperature, thermodynamics parameter and Freundlich isotherm the adsorption of 2-chlorophenol onto AC is physisorption. Therefore Correlation coefficients of pseudo-first order and pseudo-second order 1 and 0.985 respectively. So, the correlation coefficient in this case was better than the pseudo-second order model correlation coefficient. The value of predicted equilibrium sorption capacity showed reasonably good agreement with the experimental equilibrium uptake value

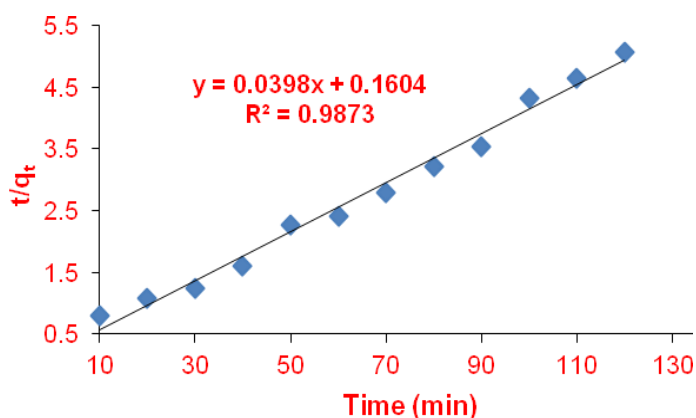


Figure 10: Pseudo-second order kinetics of chlorophenol sorption on RCAC

Elovich model

The Elovich kinetic model constants, α and β , as well as the coefficient of correlation, r , for the phenolic compound adsorption system using activated carbon are obtained using the linear form of the equation q_t vs $\ln t$. The value of the parameter indicates in Table 4. In all cases, the Elovich kinetic model exhibited higher coefficients of correlation, but lower than those obtained the pseudo-first order kinetic model and Freundlich isotherm equation. In spite of the good correlation coefficients, the values of maximum adsorption capacity determined using the linear transformation of the Elovich equation (Table 4) are much lower than the experimental adsorbed amounts at equilibrium corresponding to the plateaus of the adsorption isotherms. This means that the assumption of the exponential covering of adsorption sites that implies multilayer adsorption is not in agreement with the experiment in the studied contact time range. Therefore, the Elovich model is unable to describe the adsorption of 2-chlorophenol onto AC.

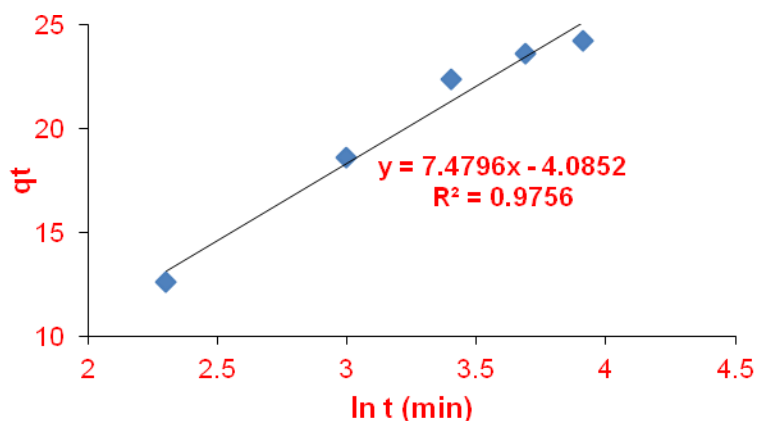


Figure 11: Elovich diffusion kinetics of chlorophenol sorption on RCAC

Intraparticle diffusion

To investigate the internal diffusion mechanism during the adsorption of 2-chlorophenol onto AC, the intra-particle diffusion eq. 9 in chapter two has been used, considering that adsorption is usually controlled by an external film resistance and/or mass transfer is controlled by internal or intra-particle diffusion⁷⁷. Intraparticle diffusion parameters calculated from the slopes of the q_t vs $t^{0.5}$ are presented in table 4. According to Weber and Morris⁷⁸, if the intra-particle diffusion is the rate-limiting step in the adsorption

process, the graph of q_t vs. $t^{0.5}$ should yield a straight line passing through the origin. McKay and Allen⁷⁹ suggested that three linear sections on the plot q_t vs $t^{0.5}$ can be identified. That means that two or three steps can occur. The first portion represents external surface adsorption or an instantaneous adsorption stage. The second portion is a gradual adsorption stage, where the intra-particle diffusion is the controlling factor. The third portion is a final equilibrium stage where the intra-particle diffusion starts to decelerate due to extremely low solute concentrations in the solution⁸⁰. Therefore, the intraparticle diffusion model the intercept (K_{id}) value indicates that the line was not passing through origin, there are some other process affect the adsorption.

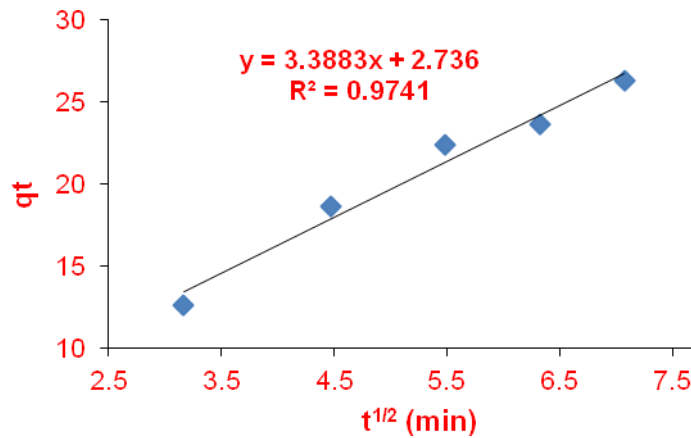


Figure 12: Intraparticle diffusion kinetics of 2-chlorophenol sorption on RCAC

Liquid film diffusion

The overall adsorption process may be controlled either by one or more steps, e.g. Liquid film diffusion is the linear driving force rate law. In liquid/solid adsorption systems the rate of solute accumulation in the solid phase is equal to that of solute transfer across the liquid film according to the mass balance law. Film diffusion and adsorption on the pore surface are considered to be fast process in a rapidly stirred batch adsorption process⁸¹. A linear plot of $-\ln(1 - F)$ versus t with zero intercept would suggest that the kinetics of the sorption process is controlled by diffusion through the liquid surrounding the solid sorbent. The significance of liquid film diffusion in rate determination of the sorption process indicated that the intercept values were less than

zero. The regression value 0.986 on activated carbon show the relevance of film diffusion as a rate determining factor in the sorption process.

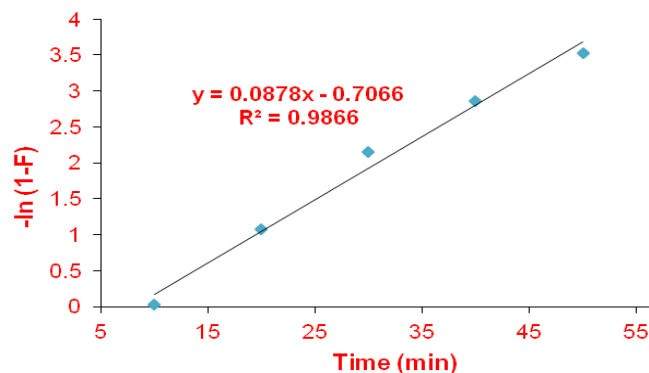


Figure 13: Liquid film diffusion kinetics of 2-chlorophenol sorption on RCAC

Table 4: Comparison of kinetic parameters for the adsorption of 2-chlorophenol onto RCAC at pH 6.

Kinetic models	Parameters	Values
Pseudo first order	Sorption capacity at equilibrium q_e (mg/g)	24.946
	Rate constant, K_1 (g/(mg/min))	6.91×10^{-2}
	R^2	1
Pseudo second order	Sorption capacity at equilibrium q_e (mg/g)	27.293
	Initial sorption rate, h_o (mg/g.min)	6.25
	Rate constant, K_2 (mg/g/min ^{1/2})	8.56×10^{-3}
	R^2	0.987
Elovich diffusion	\square (mg/g/min)	4.323
	\square (g/mg)	0.134
	R^2	0.975
Intraparticle diffusion	K_{id}	3.388
	Intercept	2.736
	R^2	0.974
Liquid film diffusion	K_{id}	8.7×10^{-2}
	Intercept	-0.706
	R^2	0.986

4.9. Thermodynamic analysis of experimental data

In order to qualify the present adsorptive removal process, thermodynamic factors including the Gibbs free energy change of adsorption, ΔG° (kJ/mol), the enthalpy

change of adsorption, H° (kJ/mol) and the entropy change of adsorption; S° (J/mol/K) . According to Eq. 15 in chapter two the values of enthalpy change (ΔH°) and entropy change (ΔS°) were calculated from the slope and intercept of the plot of $\ln K_o$ vs. $1/T$, Fig 14. The calculated values of thermodynamic parameters ΔG° , ΔH° and ΔS° for the adsorption of 2-chlorophenol onto RCAC are reported in Table 5.

Table 5: Thermodynamic parameters for the adsorption of 2-chlorophenol onto RCAC at pH 6.

Thermodynamic Parameters			
Temperature (K)	ΔG° (KJ/mol)	ΔS° (KJ/mol)	ΔH° (KJ/mol)
293	-7.298	0.565	-22.772
303	-12.326		

A negative value of the free energy (ΔG°) -7.298 and -12.326 kJ/mol at 293 and 303 K indicated the spontaneous nature of the adsorption process. It was also noted that the change in free energy, increases with increase temperature in which exhibits a decrease in adsorption with rise in temperature. Increase in value of ΔG° with increase in temperature suggests that lower temperature makes the adsorption easier. Generally, ΔG° values range from 0 to -20 kJ/mol for physical adsorption and -80 to -400 kJ/mol for chemical adsorptions⁸². In this study, the ΔG° values -7.298 and -12.326kJ/mol, indicating that adsorption is mainly physical. Again negative ΔH° value confirms that the sorption is exothermic in nature. The type of sorption can be explained in terms of the magnitude of ΔH° . This is the indication of physical adsorption mechanism, because it takes much less adsorption heat in contrast to chemical adsorption, and dispersion forces act a major role in the process. The heat evolved during physisorption generally lies in the range of 2.1-20.9 kJ mol⁻¹, while the heats of chemisorption fall into a range of 80-200 kJ mol⁻¹. Therefore, in the present study, the ΔH° value -22.772kJ/mol, indicating that the 2-chlorophenol sorption onto RCAC surface attributed to a physical adsorption process⁸³. A positive ΔS° value indicates that the organisation of the adsorbate at the solid/solution interface becomes more random⁸⁴. In this condition the adsorbed water molecules, which are displaced by the adsorbate species, gain more translational entropy is lost by adsorbate molecules, thus allowing the prevalence of randomness in the system. This is further supported by the positive value of ΔS° , which

suggested that the freedom of molecule is not too restricted in the adsorbent, confirming a physical adsorption. The ΔG° value increase in the temperature, the increase or enlargement of pore size and/or activation of the adsorbent surface.

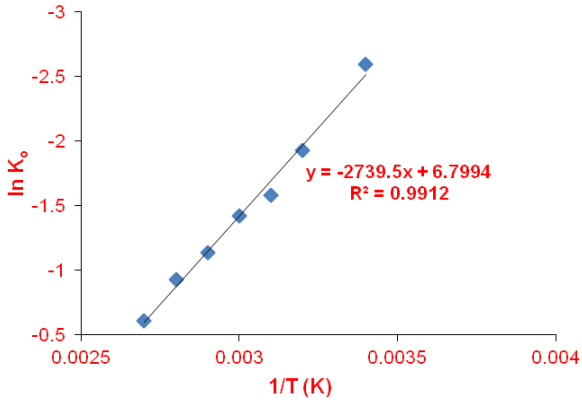


Figure 14: Linear plots of $\ln K_o$ versus $1/T$ for the sorption of 2-chlorophenol onto RCAC

Conclusion and Future prospective

This study investigated the adsorption of 2-chlorophenol from aqueous solution using activated carbon prepared from pericarp of *Ricinus communis* (RCAC) by chemical activation method. The experiment was carried out at initial pH of 6 of the solution to ensure true adsorption. The adsorption was found to be strongly influenced by pH, contact time and temperature. Based on the experimental findings of this work the enthalpy value for adsorption process, ΔH and the magnitude of Gibbs free energy change, ΔG were shown that the adsorption of 2-chlorophenol RCAC is a physical adsorption process. Equilibrium attained very quickly within 60 minute. Both Freundlich and Langmuir models were used to fit the data and estimate model parameters but the overall data is better fitted by Freundlich isotherm at the studied temperature range reflecting surface heterogeneity of RCAC. The kinetic studies conducted using time dependent experimental data in this study was analysed using five kinetic parameters, namely pseudo first order, pseudo second – order, Elovich, intra-particle and liquid–film diffusion models showed that the adsorption mechanism involves were but pseudo second – order, Elovich, intra-particle and liquid–film diffusion models not the fully operative mechanism in the adsorption of 2-chlorophenol by RCAC. The pseudo-first order kinetic model was found to be a better fit for the adsorption of 2-chlorophenol by RCAC. Thermodynamic studies predict that the adsorption is spontaneous and exothermic in nature at temperatures of 293 and 303 K. As negative values of standard change in Gibbs free energy (ΔG°), negative values of standard enthalpy change (ΔH°) and positive values of standard entropy change (ΔS°) are suggested. The result indicates that, the findings will be helpful up to a great extent for treating 2-chlorophenol contaminated effluents and at the same time it is environmentally friendly material which can be employed successfully for separation of 2-chlorophenol in industrial scale.

It can be concluded that RCAC is a good and cheap adsorbent with high potential for the adsorption of organic compounds from contaminated wastewater and could therefore serve as effective and efficient biomass for treating of wastewaters in terms of high adsorption capacity and it will help to enable people to use environmentally friendly and easily operational methods in developing countries as alternatives of advanced technologies. Further, the study initiates the community to due attention for treatment of chemicals disposed nearby the water.

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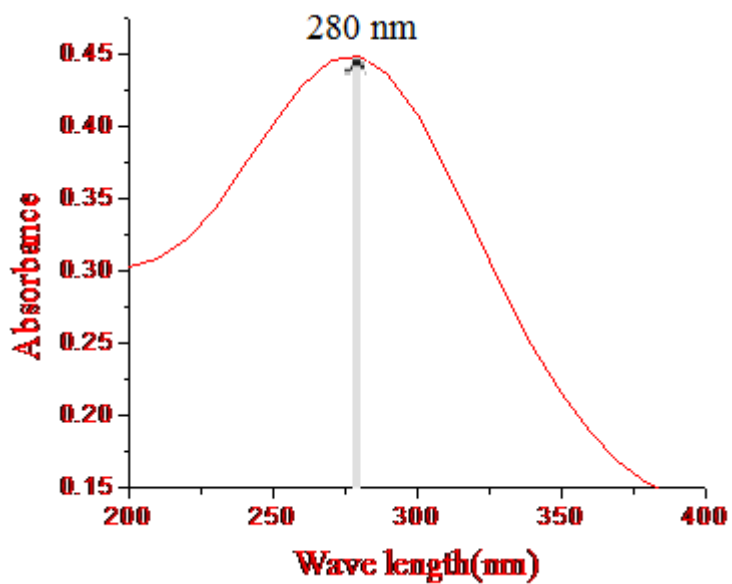
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Appendix



The absorbance of 2-chlorophenol (initial concentration = 100mg/L, wavelength between 200-400nm).