Kinetic, equilibrium and thermodynamic study of 2-chlorophenol adsorption onto Ricinus communis pericarp activated carbon from aqueous solutions

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ABSTRACT
This study reports on the adsorption of 2-chlorophenol from an aqueous solution using activated carbon prepared by H2SO4 activation of the pericarp of Ricinus communis (RCAC). The pericarp was carbonized and activated by treating with H2SO4 solution followed by heating in an oven at 105°C for 12 hrs. Batch adsorption experiments were carried out as a function of pH, contact time, initial concentration of the adsorbate, adsorbent dosage and temperature of the solution. Kinetic data were best fit to a pseudo-first-order rate equation for the adsorption of 2-chlorophenol on RCAC. Thermodynamic parameters ΔH°, ΔS° and ΔG° for the adsorption were also determined which shows that adsorption on the surface of RCAC was spontaneous in nature, and exothermic between temperatures of 20°C and 80°C. The equilibrium data better fit the Langmuir isotherm model for 2-chlorophenol adsorption on RCAC. IR spectrum for loaded and unloaded RCAC was obtained and found to be in good agreement.

1. Introduction
Water is mainly polluted with organic and inorganic sediments, radioactive materials and heavy metals (1). Industrial and domestic wastewater is responsible for causing damage 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. Several 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 (2). Therefore, the importance of water quality preservation and improvement is essential and is increasing continuously. The surface and ground waters at many places of the world are contaminated and not fit for drinking purpose (3).

2-Chlorophenol or ortho-chlorophenol, a derivative of phenol is an organic compound shown in (Figure 1) It is used as disinfectant (bactericide and fungicide) agents, various pesticides and preservatives. This particular compound has few applications, but is an intermediate in the polychlorination of phenol (4). It is in liquid form at room temperature.

The most important 2-chlorophenol water pollution sources are wastewaters from pesticide, paint, solvent, pharmaceutics, and paper and pulp industries as well as water disinfecting processes (5). The acute toxicity of 2-chlorophenol includes increased respiratory rate, vomiting and nausea (6). Chlorophenols also create complicated problems to water bodies such as bad odor and taste in drinking water, death of aquatic life and inhibition of normal activities of microbial population in wastewater treatment plants (7). There are 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 wastewater treatment involves physical and chemical processes. The different methods each 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 way (8).

Chemical methods involve coagulation combined with flotation and filtration, electro flotation, electro kinetic coagulation, conventional oxidation methods by oxidizing agents, irradiation and electrochemical processes. The high electrical energy demand and consumption of chemical reagents are common problems. Physical methods are membrane filtration and adsorption (9). Membrane filtration processes are nanofiltration, reverse osmosis, electrodialysis, etc. (10) 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 (11, 12).

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 difficult (13). The common adsorbents include activated carbon, molecular sieves, polymeric adsorbents and some other low-cost materials. Thermodynamic and kinetic studies are important aspects to know more details about adsorption performance and mechanisms. Except for adsorption capacity, kinetic performance of a given adsorbent is also of great significance for the pilot application (14). 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 (15, 16).

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 world (17).

It is also important here to emphasize that 2-chlorophenol removal has not been attempted by using activated carbon prepared from locally available materials. This work is an attempt to use R. communis, a locally available adsorbent to remove 2-chlorophenol contaminant from an aqueous solution and demonstrate that it can be used for wastewater treatment.

2. Result and discussion

2.1. Characterization of the adsorbent

Activated carbons are widely used as adsorbents due to their high adsorption capacity, high surface area, and microporous structure. Table 1 presents physicochemical characteristics of R. communis-activated carbon (RCAC) synthesized.

An FTIR spectrum of RCAC before and after adsorption shows that some peaks were shifted (Figure 2 and Table 2). In the spectrum of RCAC before adsorption of 2-chlorophenol, there is a strong peak at 3429 cm\(^{-1}\) representing the \(-\text{OH}\) stretching of the phenol group of cellulose and lignin, and the peak at 3004 cm\(^{-1}\) indicates the presence of -\text{CH}\(_2\) stretching of an aliphatic compound. The appearance of peaks at 1627 and 1387 cm\(^{-1}\) indicates the presence of C-O stretching of an aldehyde group and the C–C stretching of a phenol group, respectively. The peaks at 1270, 1030 and 624 cm\(^{-1}\) might be due to C–O stretching of the phenolic group, the ester group of cellulose and long chain

![Figure 1. Structural representation of 2-chlorophenol.](image1)

![Figure 2. FT-IR spectra of RCAC before and after adsorption of 2-chlorophenol.](image2)

**Table 1.** Physicochemical characteristics of RCAC.

| Parameters                  | Value |
|-----------------------------|-------|
| pH                          | 7.1   |
| Conductivity (\(\mu\)S/cm)  | 0.688 |
| % Moisture Content           | 17.5  |
| % Volatile Content           | 16.2  |
| % Ash Content                | 19.75 |
| Bulk density (g/cm\(^3\))    | 0.241 |
| Pore volume (cm\(^3\))      | 1.053 |
| % Porosity                   | 94.75 |
| Specific gravity             | 2.766 |
| Particle size (\(\mu\)m)     | 150   |
| % Fixed Carbon               | 46.55 |
| % yield                      | 48.9  |
band of lignin, respectively (18). The FTIR spectrum after adsorption, shown in Figure 1(b), indicates that the peaks due to the RCAC functional groups are slightly affected in their position and intensity. These changes observed in the spectrum indicate the possible involvement of those functional groups on the surface of RCAC in the adsorption process.

2.2. Effect of initial 2-chlorophenol concentration

The influence of initial concentration on the removal of 2-chlorophenol by RCAC was studied at initial 2-chlorophenol concentration of 40–200 mg/L with a constant dose of adsorbent 0.2 g per 50 mL solution and the result is presented in Figure 3. It is observed that the percentage adsorption of 2-chlorophenol is more than 97.65% achieved at all 2-chlorophenol concentrations. It was also observed that the percentage of 2-chlorophenol adsorption decreases with increasing 2-chlorophenol concentrations. At high 2-chlorophenol concentrations, the available sites for adsorption become fewer. This behavior is connected with the competitive diffusion process of 2-chlorophenol through the micro channel and pores. This competition locks the inlet of channel on the surface and prevents the 2-chlorophenol from passing deeply inside the activated carbon, that is the adsorption occurs on the surface only. Hence, it can be conclude that increasing 2-chlorophenol concentration in an aqueous solution favors energetically less sites decreasing the removal of 2-chlorophenol.

2.3. Effect of contact time

In order to find out the time for equilibrium adsorption, the contact time for 2-chlorophenol on the RCAC was varied from 20 to 120 min at a fixed 2-chlorophenol concentration of 100 mg/L, a dosage of adsorbent of 0.2 g per 50 mL solution, agitation speed 150 rpm, temperature 30°C and pH of 6, (Figure 4). It was found that at the initial stage, the adsorption curve rises sharply with time, indicating that the rate of adsorption of 2-chlorophenol is quite high, and that there are plenty of readily accessible sites (19). The adsorption reaches a maximum, 99.87% with capacity 24.97 mg/g at 60 min that remain unchanged with further elapse of time. Hence, the optimum contact time was selected as 60 min for further experiments.

Table 2. The FT-IR Spectral Characteristics of RCAC before and after adsorption of chlorophenol.

| S. No | Absorption bands(cm⁻¹) | Functional groups | Before adsorption | After adsorption | difference | difference |
|-------|-------------------------|-------------------|-------------------|------------------|-----------|-----------|
| 1.    | 3429                    |                   |                   | 3435             | 6         | OH stretching |
| 2.    | 3004                    |                   |                   | 2931             | 73        | CH₂ stretching |
| 3.    | 1627                    |                   |                   | 1624             | 3         | CO₂ asymmetric stretching |
| 4.    | 1387                    |                   |                   | 1388             | 1         | In plane C-H rocking |
| 5.    | 1270                    |                   |                   | 1207             | 63        | COOR, ester stretching |
| 6.    | 1029                    |                   |                   | 1030             | 1         | C-O stretching |
| 7.    | 624                     |                   |                   | 538              | 86        | Long chain band |

Figure 3. Effect of initial 2-chlorophenol concentration on adsorption of 2-chlorophenol onto RCAC (adsorbent dose = 0.2 g per 50 mL solution, pH = 6, contact time = 60 min, agitation speed = 150 rpm and temperature of 30°C).

Figure 4. Effect of contact time on adsorption of 2-chlorophenol onto RCAC (Initial concentration of 2-chlorophenol = 100 mg/L, pH = 6 adsorbent dose = 0.2 g per 50 mL solution, agitation speed = 150 rpm and temperature of 30°C).
2.4. Effect of pH

pH of the solution affects the surface charge of the adsorbents, ionization, rate of adsorption and dissociation of functional groups. The effect of pH on the adsorption of 2-chlorophenol was studied by varying pH from 2 to 12 and is plotted in Figure 5. The relative amount of phenolic compounds adsorbed was significantly affected by pH. The maximum uptake of adsorbate was the highest at pH of 6.0, with the adsorption capacity of 24.69 mg/g of RCAC and 98.75% of adsorption. A significant decline in removal efficiency was observed with further increase in pH above 6.0, which may be attributed to formation of phenolate anions ($\text{CO}_2\text{O}^-$).

The pKa of 2-chlorophenol is 8.3, thus at optimum conditions of pH 6 the neutral species predominates, and appears to be more readily adsorbed on the negatively charged surface of the carbon. The donor–acceptor complex mechanism for adsorption was reported earlier for the adsorption of 2-chlorophenol on activated carbon (20). In this mechanism, carbonyl oxygen on the carbon surface acts as the electron donor, whereas the aromatic ring of the phenol acts as the electron acceptor. When the pH of a solution goes higher than the pKa, 2-chlorophenol chiefly exists as negatively charged 2-chlorophenolate anion, whereas 2-chlorophenol exists as neutral molecule at pH less than the pKa. Hence, the pH behavior indicates that 2-chlorophenol effectively adsorbed on to the adsorbent as molecules but not as 2-chlorophenolate anions. From the experimental results pH 6 was selected as an optimum pH.

2.5. Adsorbent dosage

The effect of adsorbent dosage for 2-chlorophenol uptake was studied on RCAC and is shown in Figure 6. It is observed that the adsorption of 2-chlorophenol increased from 98.25% to 99.91% with increasing doses of the activated carbon (0.1–0.7 g per 50 mL solution) at a fixed 2-chlorophenol concentration of 100 mg/L, contact time 60 minute, agitation speed 150 rpm, temperature 30°C and pH 6. This can be attributed to an increased adsorbent surface area and availability of more adsorption sites resulting from the increased adsorbent dosage (22, 23). With the rise in adsorbent dosage, the adsorption capacity decreases from 49.14 to 7.14 mg 2-chlorophenol/g RCAC. The percent adsorption of 2-chlorophenol increases more rapidly, from 98.25% to 99.83% with an increase in the adsorbent dose from 0.1 to 0.4 g per 50 mL solution. Above this dose (0.4 g RCAC per 50 mL solution) the percent adsorption of 2-chlorophenol increases much more slowly almost attains equilibrium.

2.6. Effect of temperature

The effect of temperature on the percent adsorption of 2-chlorophenol was studied at a constant initial 2-chlorophenol concentration of 100 mg/L, carbon dose of 0.2 g per 50 mL solution, and temperature range of 20°C to 90°C. (Figure 7) depicts the effect of temperature on percent adsorption of 2-chlorophenol on RCAC. The amount of 2-chlorophenol adsorbed decreases as temperature increases from 30°C to 90°C. Hence the lower temperature is favorable for the adsorption of 2-chlorophenol (24). The rapid
adsorption of 2-chlorophenol further indicates that both physisorption and chemisorption processes may be involved in the adsorption of the adsorbate by the adsorbents. This effect further explained recalling that the molecules of 2-chlorophenol adsorbed on the surface have greater vibrational energy when the temperature is increased. Therefore, more molecules have enough energy to overcome the adsorptive forces and remain in the solution (25).

2.7. Adsorption isotherm

Adsorption equilibria provide fundamental physiochemical data for evaluating the applicability of the adsorption process as a unit operation. In the present investigation, the equilibrium data were analyzed using Langmuir (26) and Freundlich (27) isotherm models.

2.7.1. Langmuir adsorption isotherm

The Langmuir adsorption isotherm is the best known and most used of all isotherms describing adsorption and it has been successfully applied to many adsorption processes (28). The Langmuir model was applied to the data;

\[
\frac{C_e}{q_e} = \frac{1}{q_mK_L} + \frac{C_e}{q_m},
\]

where \(C_e\) is the equilibrium concentration of adsorbate in solution (mg/L), \(q_e\) is the amount of adsorbate adsorbed at equilibrium (mg adsorbate/g adsorbent), \(q_m\) (mg adsorbate/g adsorbent) adsorption capacity of the adsorbent and \(K_L\) is the adsorption coefficient (adsorbate concentration in the solution, L/g). The values of \(q_m\) and \(K_L\) are obtained as slope and intercept from the plot of \(C_e/q_e\) against \(C_e\) (Figure 8).

The favorable nature of adsorption was expressed in terms of dimensionless equilibrium parameters (29)

\[
R_L = \frac{1}{1 + K_L C_0},
\]

where \(K_L\) is the Langmuir constant and \(C_0\) is the initial concentration of the adsorbate in the solution. The values of \(R_L\) indicate the type of isotherm to be irreversible \((R_L = 0)\), favourable \((0 < R_L < 1)\), linear \((R_L = 1)\) or unfavorable \((R_L > 1)\). The dimensionless \(R_L\) value was calculated to be 0.0078, which is less than one indicating favourable adsorption.

2.7.2. Freundlich isotherm model

The experimental equilibrium data were also analyzed using the Freundlich isotherm model. The linearized form of the Freundlich equation is:

\[
\log q_e = \log C_e + K_F n \log C_e,
\]

where \(q_e\) is the adsorption density (mg adsorbate/g adsorbent), \(C_e\) is the concentration of the adsorbate in the solution at equilibrium (mg adsorbate/L solution), and \(K_F\) and \(n\) are the Freundlich constants. Figure 9 shows the plot of \(\log q_e\) against \(\log C_e\) with intercept \(K_F\) and \(n\) slope.

The exponent \(n\) is an index of the diversity of free energies associated with the adsorption of the solute by multiple components of a heterogeneous adsorbent. When \(n = 1\), the isotherm is linear, when \(n < 1\), the isotherm is concave and adsorbate is bound with weaker and weaker free energies, and when \(n > 1\), the isotherm is convex and more adsorbate presence on the adsorbent enhances the free energies of further adsorption (30).
is proceeding. In order to evaluate the kinetic parameters, pseudo-first-order (32) and pseudo-second-order (33) models were implemented to analyze the experimental data. Many models such as the homogenous surface diffusion model and the 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 particles.

2.8.1. Pseudo-first order
The linearized form of the pseudo-first-order equation is generally expressed as follows:

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

where \(q_e\) is the amount of 2-chlorophenol adsorbed at equilibrium (mg adsorbate/g adsorbent), \(q_t\) is the amount of 2-chlorophenol adsorbed at time \(t\) (mg adsorbate/g adsorbent), \(k_1\) 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 \(t\) (Figure 10(a)) gives a linear relationship from which the pseudo-first-order rate constant \(k_1\) and equilibrium adsorption capacity \(q_e\) were calculated from the slope and intercept respectively, and are given in Table 4.

2.8.2. Pseudo-second order
The linearized form of the kinetic rate expression for a pseudo-second-order model was applied to the experimental data using (34):

$$\frac{t}{q_t} = \frac{1}{h_0} + \frac{1}{q_e} t,$$

$$h_0 = k_2 q_e^2,$$

where \(q_t\) is the amount of 2-chlorophenol molecules on the activated carbon surface (mg adsorbate/g adsorbent) at time \(t\), \(q_e\) is the amount (mg adsorbate/g adsorbent) of 2-chlorophenol adsorbed at equilibrium, the initial adsorption rate, \(h_0\) (mg/g/min), and \(k_2\) is the pseudo-second-order rate constant (g adsorbent/mg adsorbate/min). The slope and intercept of \(t/(q_t)\) vs. \(t\) plot gives \(h_0\) and \(k_2\) which are shown in Figure 10(b) and Table 4.

2.8.3. Elovich model
The linearized form of the Elovich equation is mainly applicable for chemisorption kinetics. The equation is often valid for systems in which the adsorbing surface is heterogeneous (35). The Elovich model is generally expressed as (36)

$$\frac{dq_t}{dt} = ae^{-\beta h}.$$
Figure 10. Adsorption kinetic models for 2-chlorophenol adsorption on RCAC: (a) Pseudo-first order; (b) Pseudo-second order; (c) Elovich diffusion; (d) Intra-particle diffusion and (e) Liquid film diffusion.
Integrating the equation for the boundary conditions gives

\[ q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln(t), \]

where \( \alpha \) is the initial adsorption rate (mg/min) and \( \beta \) is related to the extent of surface coverage and the activation energy for chemisorption (g adsorbent/mg adsorbate). A plot of \( q_t \) versus \( \ln t \) (Figure 10(c)) should give a linear trace with a slope of \( \frac{1}{\beta} \) and an intercept of \( \frac{1}{\beta} \ln(\alpha \beta) \). The values for \( \alpha \) and \( \beta \) are given in Table 4.

2.8.4. Intra-particle diffusion

Intra-particle diffusion model was applied to investigate the adsorption rate limiting step (22). According to this expression:

\[ q_t = k_{id} t^{1/2} + C, \]

where \( k_{id} \) is the intra-particle diffusion rate constant (mg/g/min\(^{1/2}\)) and \( C \) (mg/g) is a constant that gives information about the thickness of the boundary layer, that is, the larger the value of \( C \) the greater the boundary layer effect is. If a plot of \( q_t \) versus \( t^{1/2} \) (Figure 10(d)) gives a straight line, then the adsorption 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 adsorption process (37) (Table 4).

2.8.5. Liquid film diffusion

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

\[ \ln(1 - F) = -k_{id}t, \]

where \( F \) is the fractional attainment of equilibrium \( F = q_e/q_t \) and \( k_{id} \) is the adsorption rate constant. A linear plot of \( \ln(1 - F) \) versus \( t \) with zero intercept would suggest that the kinetics of the adsorption process is controlled by diffusion through the liquid surrounding the solid sorbent (Figure 10(e)). Values for \( k_{id} \) the intercept are given in Table 4.

The kinetics of 2-chlorophenol adsorption on activated carbon were studied for evaluating the adsorption kinetics. The pseudo-first-order model, the pseudo-second-order model, Elovich model, intra-particle diffusion and liquid film diffusion models were used to fit the experimental data by using the linear regression analysis. Because of the high correlation coefficients the pseudo-first-order kinetics data value \( (R^2 = 1) \) is greater than that of pseudo-second-order value \( (R^2 = 0.987) \).

The experimental \( q_e \) value was closer to the calculated \( q_e \) value obtained from pseudo-first-order kinetic plot \( (R^2 = 1) \) compared to the pseudo-second-order kinetic plot \( (R^2 = 0.987) \). Therefore, the adsorption kinetics can well be approximated more favorably by pseudo-first-order kinetic model for 2-chlorophenol adsorption onto RCAC. The correlation coefficient for the Elovich kinetic model obtained was low. This suggests that this adsorption model is not an acceptable one for this system. In the intra-particle diffusion model the intercept, \( k_{id} \) value indicates that the line was not passing through the origin, and there are some other processes affecting the adsorption.

The significance of liquid film diffusion in rate determination of the adsorption process indicated that the intercept values were less than zero. The regression value of 0.986 on activated carbon shows the relevance of film diffusion as a rate determining factor in the adsorption process. According to linear regression analysis method, it was observed that the values of the correlation coefficients were slightly high (>0.974). This shows that the results fit these five models very well. However, the pseudo-first-order correlation coefficient value was found to be slightly higher than those of Elovich, liquid film, pseudo-second-order and intra-particle values, indicating that the adsorption follows better the pseudo-first-order model.

Table 4 shows that the results fit any of these five models very well. However, the pseudo-first-order correlation coefficient values were found to be slightly higher than those of Elovich, Liquid film, pseudo-second-order and intra-particle values, indicating that the adsorption follows better the pseudo-first-order model.

2.8.6. Thermodynamic analysis of experimental data

The thermodynamic parameters that help us to understand the nature of the adsorption of 2-chlorophenol on adsorbents are the standard change in Gibbs free energy \( (\Delta G^o) \), the standard change in entropy \( (\Delta S^o) \) and the standard change in enthalpy \( (\Delta H^o) \). These can be determined using the following equation:

\[ -\Delta G^o = RT \ln K_o. \]

where \( K_o \) the distribution coefficient of the adsorbent is equal to \( q_e/C_e \), \( T \) (K) is the solution temperature.
and $R$ is the universal gas constant (8.314 J/mol K). $\Delta H^o$ can be calculated from the slope and $\Delta S^o$ can be calculated from the slope and intercept of the linear plot of $\ln K_o$ versus $1/T$ (Figure 11 and Table 5),

$$\ln K_o = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}. \quad (12)$$

The reaction is spontaneous, as $\Delta G^o$ values are negative at all temperatures. The increase in the value of $\Delta G^o$ with the increase in temperature till 303 K suggests that lower temperature makes the adsorption easier. Generally, $\Delta G^o$ values range from 0 to $-20$ kJ/mol for physical adsorption and $-80$ to $-400$ kJ/mol for chemical adsorptions (38). In this study, $\Delta G^o$ values vary between $-6.323$ and $-2.726$ kJ/mol which indicates physical adsorption. This decrease in $\Delta G^o$ value suggests that 2-chlorophenol adsorption is lowered at higher temperature which is also found in temperature effect discussion. 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$^{-1}$. Hence, negative $\Delta H^o$ value of $-22.772$ kJ/mol confirms that the 2-chlorophenol adsorption onto RCAC is best attributed to a physical adsorption process (39). A positive $\Delta S^o$ value of $56.526$ kJ mol$^{-1}$ indicates that the association of the adsorbate at the solid–solution interface becomes more random; the existence of the molecules in solution is less random than that on surface (40).

### 2.9. Comparison of 2-chlorophenol adsorption with different adsorbents

The adsorption capacity of the adsorbents for the adsorption of 2-chlorophenol is compared with those of others reported in the literature and presented in Table 6. Results of our investigation revealed that RCAC has comparable adsorption capacity.

### 3. Conclusion

This study investigated the adsorption of 2-chlorophenol from an aqueous solution using activated carbon prepared from pericarp of *R. communis* by the chemical activation method. The adsorption was found to be

![Figure 11. Van’t Hoff plot for thermodynamic study of 2-chlorophenol adsorption onto RCAC.](image-url)
strongly influenced by pH, contact time and temperature. The adsorption is pH dependent, with the adsorption capacity maximum at pH 6. Equilibrium was attained very quickly, at 60 min. Langmuir and Freundlich isotherm models were tested and model parameters were estimated. The overall data are better fitted for Langmuir isotherm at the studied temperature range, reflecting surface mono layerity. The pseudo-first-order kinetic model was found to be the best fit for the adsorption of 2-chlorophenol by RCAC. Thermodynamic studies predict that the adsorption is feasible, spontaneous and exothermic in nature.

4. Materials and methods

4.1. Materials

The materials used in this work are sulfuric acid (H$_2$SO$_4$), sodium hydroxide (NaOH), 2-chlorophenol (Sigma-Aldrich) and sodium bicarbonate. All the chemicals were of analytical reagent grade. The instruments used were pH meter, thermostat water bath, Centrifuge, FT-IR spectrophotometer (Spectrum 65, Perkin Elmer) and UV-Visible spectrophotometer (T80 UV/VIS double beam).

4.2. Preparation of activated carbon

Castor bean (*R. communis*) pericarp for the preparation of activated carbon was collected from local seller (vendor) N/Wollo in Gobalafto woreda north to Addis Ababa. The chemical activation process of obtained sample was performed by taking 5 g of raw material by pouring 50% sulfuric acid (2N) at ratio of 1:2 (w/v) with constant stirring. The charred material was heated in hot air oven at 105°C for 12 h. The raw material was washed with redistilled water and then soaked in 10% sodium bicarbonate solution overnight to remove the residual acid from the pores of activated carbon. The charred material was again washed with distilled water, until the pH of the adsorbent reached 7 ± 0.2 then it was dried in a hot air oven at 105°C for 12 h. Finally the RCAC powdered and sieved to obtain the particle size of 150 μm (47). The sieved adsorbent was stored in an airtight container for further experiments.

4.3. Preparation of stock solutions

The test solutions were prepared by diluting a stock solution of 2-chlorophenol to the desired concentrations. A stock solution of chlorophenol was obtained by dissolving 1.0 g of chlorophenol (obtained from Sigma-Aldrich) in distilled water and was diluted to 1000 mL. Several dilutions of stock solution were made to obtain specific concentrations required for the adsorption study. 0.2 g each of activated carbon was weighed and introduced into 18 (250 ml) conical flasks. 50 ml of 100 mg/L solution of 2-chlorophenol 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$_2$HPO$_4$ and KH$_2$PO$_4$ for pH 6.0 and pH 8.0 and NH$_3$ and NH$_4$Cl for pH 10 and 12. The flasks were tightly covered and shaken for 1 h at 150 rpm. The suspensions were filtered through filter paper, centrifuged for 5 min and analyzed.

4.4. Adsorption study

Adsorption experiments were carried out by shaking 0.2 g of adsorbent with 50 mL of adsorbate solution of known concentration in a 250 mL conical flask placed in a thermostat water bath provided with a shaking mechanism. The solution–adsorbent mixtures were stirred at 150 rpm and at the end of a predetermined time interval the reaction mixtures were filtered and the filtrate was analyzed for 2-chlorophenol concentration using UV/Vis spectrophotometer by measuring the absorbance at the wavelength of maximum absorption of (280 nm). The removal kinetics of the adsorbate was investigated by filtering the samples after the desired contact time and the filtrate was analyzed for the remaining adsorbate concentration. The same procedure has been used to study the effect of contact time (20–120 min), initial 2-chlorophenol concentrations (40–200 mg/L), adsorbent dosage (0.1–0.7 g per 50 mL solution), pH (2–12), and temperature (20–90°C).

All experiments were carried out in 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
The percent adsorption (%) were computed as follows:

\[
q_t = \frac{(C_0 - C_f)V}{M},
\]

where \(C_t\) (mg/L) is the liquid phase concentrations of 2-chlorophenol at any time, \(C_0\) (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 (%) were computed as follows:

\[
q_e = \frac{(C_0 - C_e)V}{M},
\]

\[
\% \text{ Adsorption} = \left(\frac{C_0 - C_e}{C_0}\right) \times 100.
\]

where \(C_o\) and \(C_e\) are the initial and final equilibrium concentrations of 2-chlorophenol (mg/L), respectively.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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