

Removal of Phenol from Aqueous Solution using Activated Carbon from Coconut Coir

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Abstract: The research intended to find out the adsorption efficiency of activated carbon from coconut coir for removal of phenol from the wastewater. The surface characterization of adsorbent was studied through SEM and BET analyzers. The results indicated that the adsorbent had a honey-combed microstructure with high surface area. The removal percentage of phenol from wastewater was examined in batch experiments with variation of pH (4-9), contact time (50-300 min), adsorbent dose (0.1-0.4 gm/L), phenol concentration (50-140 mg/L) and temperature (30-50⁰C). The adsorption results indicated that percentage of phenol removal reached maximum (>95%) at pH of 6, time of 250 min, dose of 0.2 gm/L, phenol concentration of 50 mg/L and temperature of 30⁰C. The optimized values of adsorption experiments were used for testing of various kinetic, thermodynamic and isotherm models. It was observed that the pseudo-second-order model was better than the pseudo-first-order model. The Elovich model and the Boyd model indicated that the process supported chemisorption. The Reichenberg model suggested that the adsorption involved film diffusion and the Fick's model indicated that the film and intraparticle diffusions took 100 min and 150 min respectively. The Furusawa and Smith model indicated that phenol moved faster from bulk to solid stage and the Dubinin–Radushkevich model indicated that the process was explained by physical adsorption. However, the correlation coefficient was found to be only 0.81559. The Langmuir, Freundlich, and Temkin models indicated that they were all supportive of equilibrium data. The isothermal study indicated that the process was exothermic, non-random and spontaneous. The authors concluded that the activated carbon prepared from coconut coir could be used as a cheap and efficient adsorbent for removal of phenol from wastewater.

Keywords: Adsorption, Phenol, Activated carbon from coconut coir, Wastewater, Isotherms, Scale-up design

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I. INTRODUCTION

Phenols are considered as environmental pollutants because of their toxicity and also included in the list of priority pollutants (Dutta et al., 1992). The phenols can cause vomiting, anorexia, fainting, headache and can damage liver and kidney (Swertson et al., 1996). The Environmental Protection Agency (EPA), USA and the Ministry of Environment, Forest and Climate Change (MOEFCC), India have set the phenol content in the surface discharge up to the maximum extent of 1 mg/L. The World Health Organization (WHO) has limited the phenol content of the potable water up to the maximum extent of 0.001 mg/L.

The phenol and composites of phenol usually get introduced in the environment when the industrial effluents from petroleum refineries and coal tar, plastic, disinfectant, rubber proofing, steel, paper, paints, pharmaceutical plants are discharged into surface water. Some amounts of phenols are also released into the surface water when the domestic wastewater and agricultural run-off get mixed with the surface water. The content of phenols in such industrial, domestic and agricultural wastewaters may vary from 1 to 6800 mg/L.

The phenol removal techniques are classified into three categories viz. biological, chemical and physical (Hao et al., 2000). The biological degradation methods are not preferred as they are sensitive to temperature. The chemical methods are also not preferred as they release further toxic compounds. The physical adsorption methods are found to be very useful and are therefore widely used in the industry (Darwish et al., 1996). Many researchers are in the hunt for cheap and readily available natural adsorbents (Roostaei et al., 2004). Some of the important criteria for choosing the best adsorbents are the surface area, pore sizes, structural characteristics, adsorption capability, simple regeneration and numerous uses (Banat et al., 2000).

In this research work, the activated carbon prepared from the coconut coir is applied as the natural adsorbent to remove phenol. The coconut coir is usually found as a residue during the processing of raw coconuts and is dumped in rural areas for the uses as fuel (Conrad et al., 2007). It usually contains lignin (16-45%), hemi cellulose (24-47%) and pectin (2%) and other impurities (Han et al., 1996).

Although some studies are already available with activated carbon from coconut coir for phenol removal, however, this research work emphasizes for treatment of wastewater with a moderate range of initial phenol concentrations usually observed in petroleum refineries and many other allied industries.

II. MATERIALS AND METHODS

2.1 Adsorbent Preparation

The adsorbent activated carbon from coconut coir is an offshoot of coconut and is mostly used as fuels in the rural areas or thrown out as waste because of its abundance. For the research work, the coconut coir was arranged from the sub-urban area near Kolkata, India. It was washed carefully in distilled water and was sun-dried for seven days. Then it was processed for activation at 800°C for one hour. This activated carbon was rewashed in distilled water and was dried at 100°C for one day. This was then crushed to powder in a grinder with the sizes from 300 to 350 µm and sieved through -44 +52 mesh. The morphology and surface characterization of activated carbon from coconut coir were studied through the Scanning Electron Microscopy (SEM) analyser [Model S415A, Hitachi, Japan] and the Brunauer-Emmett-Teller (BET) analyzer [Model Quanta chrome, NOVA 1000e, USA].

2.2 Adsorbate Preparation

Initially, 1000 ml of aqueous phenol solution was prepared by mixing 1.0 gm of phenol (Merck, Germany) in distilled water. The strength of this solution was 1000 mg/L (1000 ppm). The variations of phenol concentration were carried out by dilution with distilled water and their concentrations during the adsorption process were measured using spectrophotometer (DR 5000 Hach Co. Germany) with the addition of 4-Amino antipyrine. The pH was calculated using a pH meter (Model Multi 304i, Hach Co., Germany).

2.3 Adsorption Batch Studies

The aqueous phenol solution (100 ml) was taken inside 250 ml stopper conical flasks. Dilution adding distilled water was made as per the desired phenol concentration ranging 50-140 mg/L. The pH was maintained at 4-9 by using NaOH and HCl. The necessary amount of activated carbon from coconut coir from 0.1 to 0.4 gm/L was mixed. The solution was then shaken as per pre-determined time ranging from 50 to 300 min in the electrically thermostatic shaker with 120 strokes per minute. The experiments were performed at temperatures 30°C, 40°C, and 50°C, respectively. At the end of specific contact time, the residue was filtered out while filtrate was examined for residual phenol concentration in the spectrophotometer (APHA 1998). All the experiments were run thrice to check reproducibility, and the average was used for better accuracy. The percentage of phenol removal was derived from Equation (1).

$$\% \text{ removal of phenol} = \frac{(C_0 - C_t)}{C_0} \times 100\% \quad (1)$$

Here C_0 and C_t are phenol concentrations in the beginning and at any given time (mg/L). The quantity of phenol adsorbed per unit quantity of activated carbon from coconut coir was derived from Equation (2).

$$q_t = \frac{(C_0 - C_t)}{m_s} \quad (2)$$

Here q_t was phenol quantity adsorbed per unit weight of activated carbon from coconut coir at any given time (mg/gm), and m_s was the amount of activated carbon from coconut coir added in gram (gm/L). The experiments were carried out with the various operating conditions, e.g., initial pH(4-9), contact time (50-300 min), adsorbent dose (0.1-0.4 gm/L), phenol concentration (50-140 mg/L) and temperature (30-50°C).

III. RESULTS AND DISCUSSIONS

3.1 Adsorbent Characterization

The surface morphology of the activated carbon from coconut coir was investigated through a Scanning Electron Microscope (SEM). The result as shown in Fig. 1 showed that the surface was porous with large pore sizes.

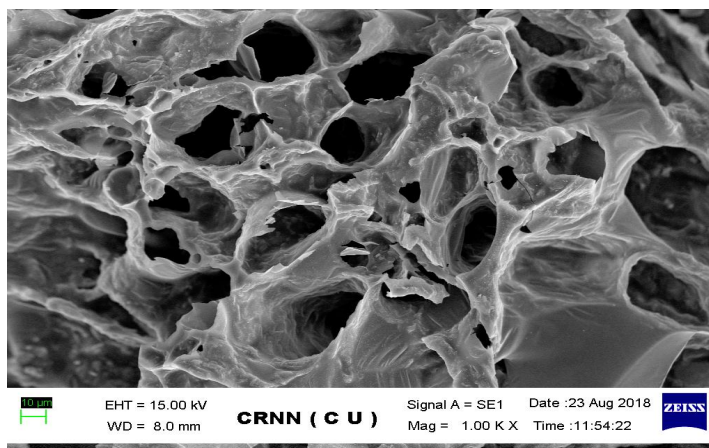


Fig. 1: The SEM topography of activated carbon from coconut coir

The surface area of activated carbon from coconut coir was evaluated by BET analyzer, along with the distribution of its pore sizes. The results indicated that the adsorbent had a honey-combed microstructure with high surface area. The bulk density and the surface area were estimated to be 0.31 gm/cm^3 and $830 \text{ m}^2/\text{gm}$ respectively (Chaudhuri et al. 2011). The physical properties of activated carbon from coconut coir are given in Table 1.

Table 1: Physical properties of activated carbon from coconut coir

Bulk density, gm/cm^3	0.31
BET surface area, m^2/gm	830
Micropore area, m^2/gm	502
Micropore volume, ml/gm	0.21
Average pore diameter, \AA	19
Ash content, %	12.6

In this research work, the point of zero charge (pH_{pzc}) was measured using the salt adding method (Singha et al., 2012) and was found to be 5.5.

3.2 Variation of pH

The pH is assumed to be a significant factor since pH affects the adsorption process (Lalruaitluanga et al., 2010). The study was therefore made with the variation of initial pH from 4 to 9 but keeping the other process variables constant, i.e., at phenol concentration of 50 mg/L , at the adsorbent dose of 0.2 gm/L , at adsorption time of 250 min and the constant temperature of 30°C . The experiment was repeated similarly with the change of phenol concentration ranging between 50 and 140 mg/L . The plot of removal of phenol percentage against different pH in Fig. 2 showed that the value increased with the rise of pH from 4 to 6.

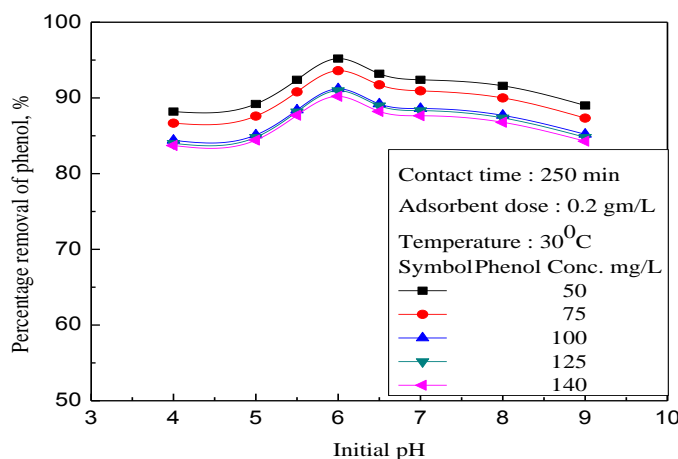


Fig. 2: The effect of initial pH on the removal efficiency of phenol

However, with the further rise in pH the removal efficiency decreased significantly. This observation was found irrespective of the initial phenol concentration. Therefore it supported the general concept that the adsorption of phenol is superior at $pH > pH_{pzc}$. This phenomenon could be attributed to the amphoteric properties of the activated carbon from coconut coir against the variation of pH. At low pH values, phenol removal was fewer because of the existence of the H^+ ions preventing ionization of phenol, whereas, in high pH values, phenol removal was higher because of presence of the OH^- ions preventing uptake of phenolate ions (Mahavi et al. 2004).

3.3 Variation of Contact Time

The experiment was performed with variation of the contact time from 50 to 300 min at a constant pH of 6, at a constant phenol concentration of 50 mg/L, at the adsorbent dosage of 0.2 gm/L and at the constant temperature of $30^{\circ}C$ and was repeated in the similar way with change of phenol concentration ranging between 50 and 140 mg/L. The plot of percentage removal of phenol versus adsorption time in Fig. 3 indicated that the efficiency was quite high in the beginning and then the equilibrium reached at 250 min.

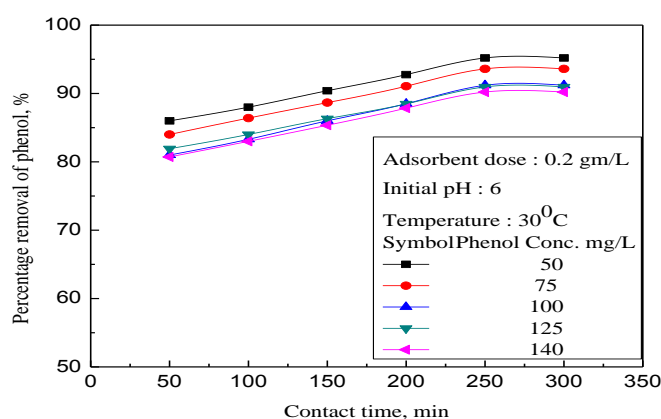


Fig. 3: The effect of contact time on the removal efficiency of phenol

The faster adsorption at an initial period could be endorsed to the augmented quantity of the unfilled sites on activated carbon from coconut coir existing at the original phase (Uddin et al., 2007). It might be assigned that a tendency to reach equilibrium after a specific time occurred due to three consecutive mass transfer steps. The first one was film diffusion which meant that solute migrated through the solution. The second one was pore diffusion which implied that the solute moved from surface to interior and lastly the solute was adsorbed within the interior.

3.4 Variation of Adsorbent Dose

The experiment was carried out with the variation of adsorbent dose from 0.1 to 0.4 gm/L at pH of 6 and constant phenol concentration of 50 mg/L, and at constant temperature of $30^{\circ}C$ for 250 min and was repeated in the similar way varying phenol concentration ranging from 50 to 140 mg/L. The plot of removal percentage of phenol versus adsorbent dose in Fig. 4 represented the equilibrium condition with the adsorption dose of 0.2 gm/L.

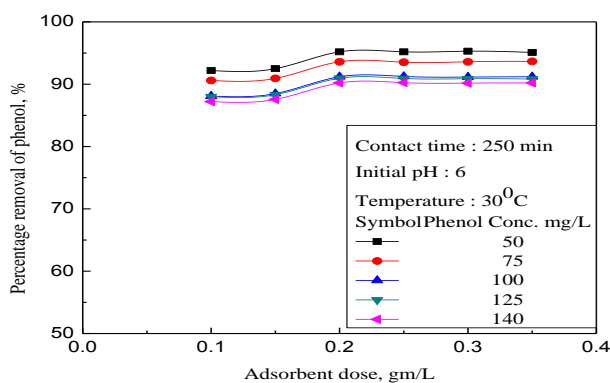


Fig. 4: The effect of adsorbent dose on the removal efficiency of phenol

The phenomenon suggested that the removal efficiency increased rapidly at first due to additional adsorption sites and then remained steady due to reaching saturation.

3.5 Variation of Temperature

The experiment was carried out with the variation of temperature from 30 to 50°C at a constant pH of 6, at constant initial phenol concentration of 50 mg/L and at adsorbent dosage of 0.2 gm/L for 250 min and was repeated in the similar way with change of phenol concentration ranging from 50 to 140 mg/L. The plot of removal percentage of phenol versus temperature in Fig. 5 represented that percentage reduced with the increase in temperature ranging from 30 to 50°C, representing lower chemical interaction of the adsorbate with surface functionality of activated carbon from coconut coir.

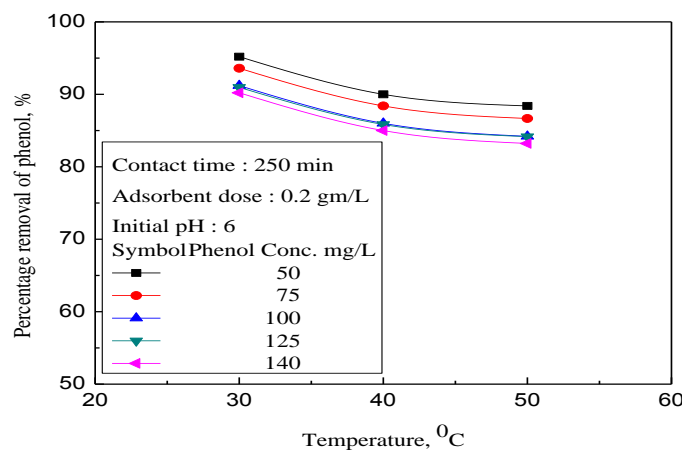


Fig. 5: The effect of temperature on the removal efficiency of phenol

Since phenol adsorption was exothermic, the extent of adsorption decreased with the rise in temperature.

3.6 Variation of Initial Phenol Concentration

In our investigation, we had experimented with a variation of phenol concentration ranging from 50 to 140 mg/L and for each experiment the removal percentage of phenol were studied at constant pH of 6, constant time of 250 min, at the constant adsorbent quantity of 0.2 gm/L and constant temperature of 30°C. It was evident from the Fig. 6 that at constant pH value of 6, constant time of 250 min, the constant dosage of 0.2 gm/L and the constant temperature of 30°C, the adsorption efficiency decreased with the rising of initial phenol concentration.

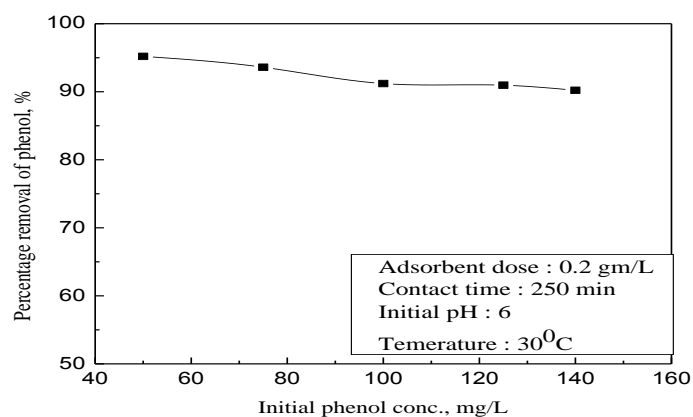


Fig. 6: The effect of phenol concentration on the removal efficiency of phenol

At higher phenol concentration the total adsorption sites were inadequate because of the gathering of phenol particles on the adsorbent surface, thus causing in the reduction of removal percentage of phenol (Ekpete et al., 2010).

3.7 Kinetic Study

The kinetic study is essential to designate the adsorption mechanism on the adsorbent surface. The analysis of experimental data about the kinetic models facilitates to evaluate the adsorption rate and to predict the information about adsorbent / adsorbate interaction, i.e., physisorption or chemisorption. In this research work, six different kinetic models were tested viz., pseudo-first-order, pseudo-second-order, Elovich, Boyd, Reichenberg, and Fick models.

3.7.1 Pseudo-First-Order Model

This model is designed by Lagergren (1898) and is expressed in the Equation (3).

$$\log(q_e - q_t) = \log q_e - \frac{K_{ad}t}{2.303} \quad (3)$$

Here q_e and q_t denote quantity for phenol adsorbed (mg/gm) during equilibrium and at any specific time t , and K_{ad} is the pseudo-first-order kinetic constant (min^{-1}). This model supports that the adsorption process is physisorption and the adsorbent particles are homogeneous (Singha et al. 2012).

The graph of $\log(q_e - q_t)$ versus t as shown in Fig. 7 indicated that the curve was almost linear and the correlation coefficient (r^2) and K_{ad} were found to be 0.94706 and $0.00857 (\text{min}^{-1})$ respectively.

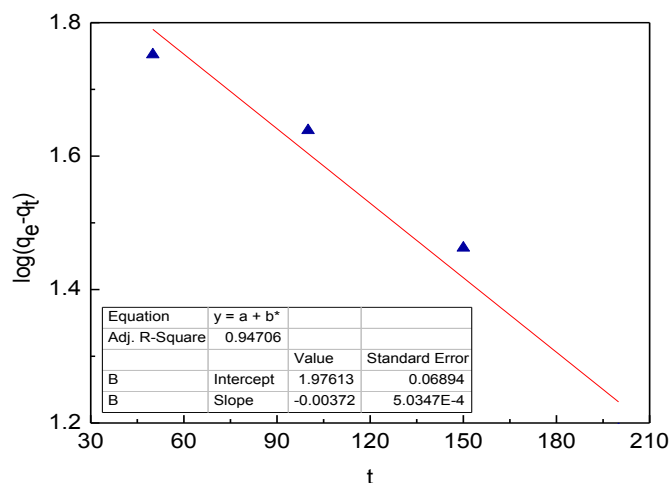


Fig. 7: The linear plot of the pseudo-first-order kinetic model

3.7.2 Pseudo-Second-Order Model

This model is stated in Equation (4).

$$\frac{t}{q_t} = \frac{1}{K'q_e^2} + \frac{1}{q_e}t \quad (4)$$

Here q_e and q_t denote the quantity of phenol adsorbed (mg/gm) during equilibrium and for any specific time t , and K' is pseudo-second-order kinetic constant (gm/mg min). This model supports that the adsorption process is chemisorption and adsorbent particles are heterogeneous (Chaudhary et al. 2014).

From the graph of $\frac{t}{q_t}$ versus t as shown in Fig. 8, it was seen that the curve was almost linear with the correlation coefficient (r^2) as 0.99919 and K' thus calculated from the slope was found to be $0.00016 \text{ gm/mg min}$.

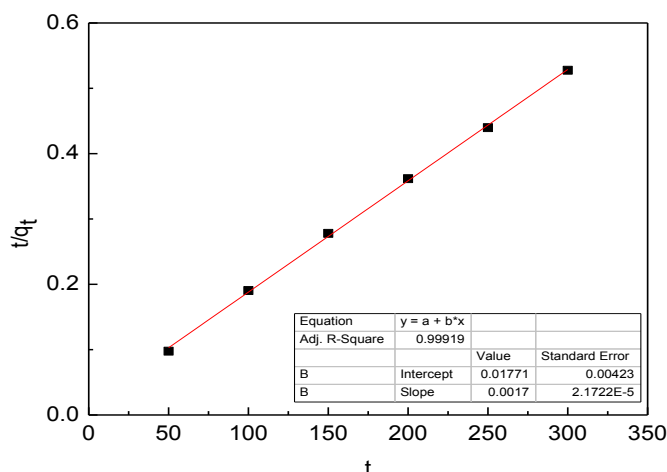


Fig. 8: The linear plot of the pseudo-second-order kinetic model

The Table 2 showed the calculated values of q_e as per the data obtained from pseudo-first-order and pseudo-second-order kinetic constants and suggested that there was good conformity between the experimental and the calculated q_e values for second one, and hence pseudo-second-order model was more relevant. This confirmed that the adsorbent particles were heterogeneous and the adsorption process was chemical.

Table 2: Kinetic parameters of Pseudo first-order and pseudo-second-order models

C_o (mg/L)	$q_{e, exp}$ (mg/gm)	Lagergen first order			Pseudo-second order		
		K_{ad} (1/min)	$q_{e, cal}$ (mg/gm)	r^2	K' (gm/mg min)	$q_{e, cal}$ (mg/gm)	r^2
125	568.50	0.00856	94.65	0.94706	0.00016	588.24	0.99919

3.7.3 Elovich Model

This model is usually applicable to chemisorptions and is expressed in the Equation (5).

$$q_t = \frac{1}{b_1} \ln(a_1 b_1) + \frac{1}{b_1} \ln(t + t_0) \quad (5)$$

Here q_t denotes the quantity of phenol adsorbed (mg/gm) at any given time, and a_1 , b_1 and $t_0 (= \frac{1}{a_1 b_1})$ are

Elovich constants. The graph q_t against $\ln t$ showed the high correlation coefficient of 0.94114, and therefore it indicated that the process of the adsorption was chemical (Ho et al, 2002).

3.7.4 Boyd model

The Boyd et al. (1947) model states the diffusion rates in adsorption process as shown in the Equation (6).

$$F(t) = 1 - \frac{6}{\pi^2} \sum_{n_1=1}^{\infty} \frac{1}{n_1^2} \exp\left(-\frac{D_e t \pi^2 n_1^2}{R_a^2}\right) \quad (6)$$

Assuming the adsorbent as spherical, the Vermeulen approximates it as in Equation (7).

$$\ln\left[\frac{1}{1 - F^2(t)}\right] = \frac{\pi^2}{R_a^2} D_e t \quad (7)$$

Here $F(t)$ denotes the ratio of phenol adsorbed per unit quantity of adsorbent at specific time t and at the equilibrium time, R_a is the radius of activated carbon from coconut coir particles (m), and D_e is the adsorbate's effective diffusion coefficient (m^2/sec). The graph of $\ln\left[\frac{1}{1-F^2(t)}\right]$ with t was best fitted to a straight line with the correlation coefficient of 0.94397 with a gradient of $\frac{\pi^2}{R_a^2} D_e t$. The value of diffusion coefficient (D_e) was calculated as $5.563 \times 10^{-10} \text{ m}^2/\text{sec}$. Since the value of D_e was in the range of 10^{-9} – $10^{-17} \text{ m}^2/\text{sec}$, it supported for chemisorptions system (Srivastava et al., 2009).

3.7.5 Reichenberg Model

This model (Reichenberg 1953) is usually applicable to film diffusion inside micropores and is expressed in the Equation (8).

$$F(t) = \left(1 - \frac{6}{\pi^2}\right) e^{-B_t} \quad (8)$$

The above Equation is rewritten as in the Equation (9).

$$B_t = -0.4977 \ln[1 - F(t)] \quad (9)$$

Here $F(t)$ is a ratio of phenol adsorbed per unit of activated carbon from coconut coir at specific time t and at the equilibrium time, and B_t denotes time-related constant. The graph of B_t vs. t indicated a higher correlation coefficient (r^2) of 0.94706 which signified that the adsorption was film diffusion.

3.7.6 Fick Model

The Equation (10) developed by Adolf Fick describes the diffusion of phenol on activated carbon from coconut coir surface by film or intraparticle.

$$\frac{q_t}{q_\alpha} = \frac{6}{R_a} \sqrt{\frac{D_e t}{\pi}} \quad (10)$$

Here q_α (assumed as q_e) is the quantity of phenol (in mg) per gram of activated carbon from coconut coir at equilibrium, R_a is the radius of activated carbon from coconut coir particles (m), and D_e is the adsorbate's effective diffusion coefficient (m^2/sec). The graph of $\frac{q_t}{q_\alpha}$ and \sqrt{t} that the first linear portion indicated film

diffusion which remained for first 100 min, the second linear portion indicated intraparticle diffusion which remained for next 150 min and the last linear portion indicated adsorption-desorption equilibrium which occurred at 250 min. Therefore the ratio of film diffusion and intraparticle diffusion in batch adsorption experiment was 1:1.5.

The results of the above four statistical kinetic models given in Table 3 showed good conformity for all the models due to high correlation coefficients.

Table 3: Various kinetic model parameters

<i>Kinetic model</i>	<i>Model equation</i>	<i>Correlation coefficient (r^2)</i>	<i>Result</i>
<i>Elovich model</i>	$q_t = \frac{1}{b} \ln(a_1 b) + \frac{1}{b} \ln(t + t_0)$	0.94114	<i>Adsorption is chemical</i>
<i>Boyd model</i>	$\ln\left[\frac{1}{1-F^2(t)}\right] = \frac{\pi^2}{R_a^2} D_e t$	0.94397	<i>Supports for chemisorption</i>

Reichenberg model	$B_t = -0.4977 \ln[1 - F(t)]$	0.94706	Adsorption is of film diffusion.
Fick model	$\frac{q_t}{q_a} = \frac{6}{R_a} \sqrt{\frac{D_e t}{\pi}}$	0.98956	The film diffusion and the intraparticle diffusion take about 100 min and 150 min respectively

3.8 Isothermal Study

When any adsorption process reaches its equilibrium, the adsorption isotherms are tested to evaluate the distribution of adsorbate molecules between the liquid and the solid phases, which in turn provide information about the heterogeneity and homogeneity of the adsorbent surface (Almeida et al., 2009). The analysis of the experimental isotherm results is also very essential since it can be applied for design purposes. Various isotherm models are available in the literature to test experimental isotherm values, from which Langmuir, Freundlich and Temkin models were used in this research work.

3.8.1 Langmuir Isotherm

This model is given in Equation (11).

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}} \quad (11)$$

Here, C_e denotes phenol concentration during equilibrium (mg/L), q_e is quantity of adsorbate (mg) adsorbed per adsorbent quantity (gm) at the equilibrium, q_{max} (mg/gm) and b denote Langmuir constants linked to maximum adsorption (mg of adsorbate per gm of adsorbent) and free energy during adsorption (L/mg). From the graph of $\frac{C_e}{q_e}$ and C_e shown in Fig. 9, values of the Langmuir constants q_{max} and b were derived (Langmuir, 1918) and shown in Table 4.

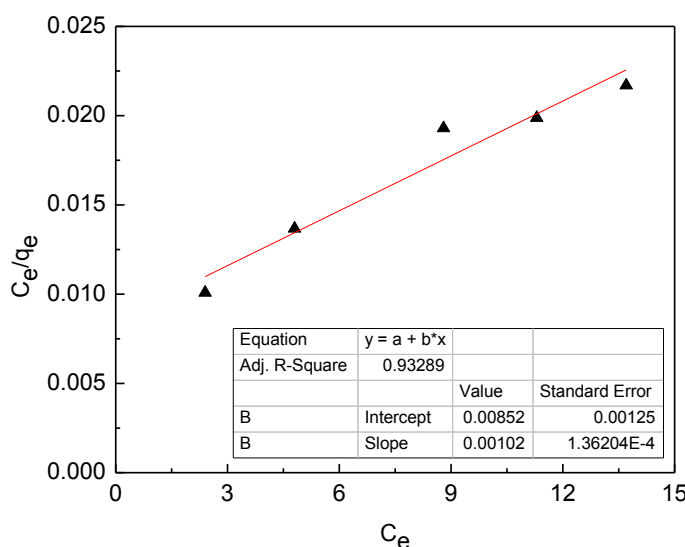


Fig. 9: The linear plot of the Langmuir isotherm model

The importance of q_{max} signified that this quantity of phenol adsorbed per unit weight of activated carbon from coconut coir (gm) formed a complete monolayer and the importance of b signified that the deep bonding of phenol took place for activated carbon from coconut coir (Aksu et al., 2001). The important characteristic of the Langmuir isotherm was that it was used to evaluate R_L , the constant separation factor (dimensionless), as in Equation (12).

$$R_L = \frac{1}{1 + bC_0} \tag{12}$$

Here, b denotes Langmuir constant related to free energy during adsorption (L/mg), and C_0 denotes phenol concentration at the beginning (mg/L). Using the value of b , the values of R_L were calculated as 0.143, 0.100, 0.077, 0.063 and 0.056 at the phenol concentration of 50, 75, 100, 125 and 140 mg/L respectively. Since the values of R_L lied within 0 and 1, the Langmuir isotherm was favorable within experimental range (Hall et al., 1966).

3.8.2 Freundlich Isotherm

This model is specified in Equation (13).

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{13}$$

Here, C_e is phenol concentration during equilibrium (mg/L), q_e denotes the quantity of adsorbate (mg) adsorbed per quantity of activated carbon from coconut coir (gm) at equilibrium, and K_f and n denote Freundlich constants associated to the capacity of adsorption and strength of the adsorption in the adsorption process. From the graph of $\log q_e$ and $\log C_e$, given in Fig. 10, the Freundlich constants K_f and $\frac{1}{n}$ were derived (Freundlich, 1906) and shown in Table 4.

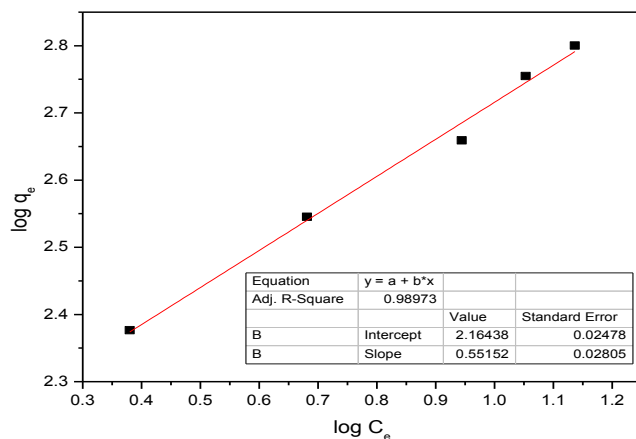


Fig. 10: The linear plot of the Freundlich isotherm model

The magnitude of Freundlich constant K_f represented easy removal of phenol from the wastewater. The value of n which represented the intensity of adsorption followed the limit ($0 < \frac{1}{n} < 1$) and therefore signified that surface of activated carbon from coconut coir was heterogeneous (Aksu et al., 2001).

3.8.3 Temkin Isotherm

This model is expressed in Equation (14).

$$q_e = B_1 \ln K_T + B_1 \ln C_e \tag{14}$$

Here, C_e is phenol concentration during equilibrium condition (mg/L), q_e denotes the quantity of adsorbate (mg) adsorbed per gram of the adsorbent at equilibrium, and K_T and B_1 are Temkin constants connected to equilibrium binding (L/gm) and heat of adsorption (J/mol) respectively. From the graph q_e against $\ln C_e$, given in Fig. 11, the Temkin constants B_1 and K_T were derived and shown in Table 4. The magnitudes of B_1 and K_T signified that adsorption process was chemical.

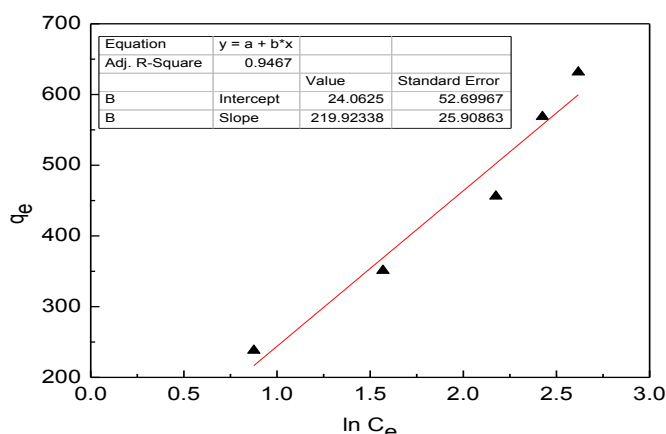


Fig. 11: The linear plot of the Temkin isotherm model

Table 4 indicated that all three isotherm models were applicable because of the high correlation coefficients (r^2) values. However, the Freundlich isotherm was best support among all. The monolayer adsorption capacity (q_{max}) from Langmuir isotherm model was assessed as 980.39 mg/gm.

Table 4: Various isotherm model parameters

Langmuir isotherm			Freundlich isotherm			Temkin isotherm		
q_{max} (mg/gm)	b (L/mg)	r^2	K_f (mg/gm)	n	r^2	K_T (L/gm)	B_1 (J/mol)	r^2
980.39	0.1197	0.93289	146.009	1.813	0.98973	1.116	219.923	0.94670

3.9 Analytical Study

For any adsorption process, it is essential to find out the extent of transfer of the adsorbate from the bulk stage to the surface of solid adsorbent and to predict whether the process is physical or chemical. Several analytical models have been published in the literature, of which Furusawa and Smith model and Dubinin–Radushkevich model were used in this research work.

3.9.1 Furusawa and Smith Model

This model for analyzing the effect of external mass transfer on adsorption rate is explained by Equation (15).

$$\ln\left(\frac{C_t}{C_0} - \frac{1}{1 + MK_{bq}}\right) = \ln\left(\frac{MK_{bq}}{1 + MK_{bq}}\right) - \left(\frac{1 + MK_{bq}}{MK_{bq}}\right)\beta S_s t \quad (15)$$

Here, C_0 and C_t are phenol concentration (mg/L) in the beginning, and at specific time t , M is the mass of activated carbon from coconut coir per unit volume (gm/L), β is mass transfer coefficient (cm/sec), S_s is the external surface area per unit volume (m^{-1}), and K_{bq} is a mass transfer constant (L/gm). The value of K_{bq} was evaluated by multiplication of b with q_{max} , where b meant Langmuir constants connected to free energy of adsorption (L/mg) and q_{max} meant maximum adsorption capability (mg/gm), and both b and q_{max} were derived

from Langmuir Adsorption Isotherm Model). The graph of $\ln\left(\frac{C_t}{C_0} - \frac{1}{1 + MK_{bq}}\right)$ against t formed the linear

line with the correlation coefficient of 0.95807 with the gradient of $\left(\frac{1 + MK_{bq}}{MK_{bq}}\right)\beta S_s$ in linear fitting. The

value of the mass transfer coefficient (β) of 3.168×10^{-11} which was calculated using the value of the slope indicated that phenol moved faster from bulk to the solid stage (Choy et al., 2004).

3.9.2 Dubinin–Radushkevich model

This model for calculation of adsorption energy is given in Equation (16).

$$\ln C_{ads} = \ln X_m - \lambda \varepsilon^2 \quad (16)$$

Here C_{ads} is the quantity of phenol adsorbed onto activated carbon from coconut coir surface (mol/gm), X_m is maximum adsorption capacity (mol/gm), λ is a constant for adsorption energy (mol²/kJ²), and ε is the Polanyi potential (kJ/mole). The Polanyi potential ε is computed using Equation (17)

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right). \quad (17)$$

Here R stands for ideal gas constant (0.008314kJ/mol.K), T denotes temperature (K), and C_e is phenol concentration during equilibrium condition (mg/L). The linear fitting of the graph for $\ln C_{ads}$ with ε^2 gave a line with the correlation coefficient (r^2) of 0.81559. The low value of correlation coefficient suggested that the experimental data did not as such support this model. From this graph, the values of λ and X_m were derived as 1.17056 (mol²/kJ²) and 2.170×10^{-3} (mol/gm) respectively. The adsorption energy was further computed using λ as in Equation (18).

$$E = \frac{1}{\sqrt{2\lambda}} \quad (18)$$

Here E is mean adsorption energy (kJ/mol) to adsorb one mole of phenol from its solution. Since the value of E as calculated here was 0.6536 kJ/mole and was below 8, hence the adsorption was physical.

3.10 Thermodynamic Study

The thermodynamic study is done to assess the viability of adsorption, evaluating the values of change of Gibbs free energy, enthalpy, and entropy. While the Gibbs free energy change indicates whether the process is spontaneous or not, the enthalpy change suggests whether the adsorption is endothermic or exothermic and the change of entropy points out whether adsorption process is physical or chemical. The Gibbs free energy, entropy, and enthalpy are expressed in Equations (19) and (20) respectively.

$$\Delta G^0 = -RT \ln K_c \quad (19)$$

$$\ln K_c = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (20)$$

Here, ΔG^0 is Gibbs free energy (kJ/mole), R stands for ideal gas constant 0.008314kJ/mole K, K_c indicates equilibrium constant, ΔH^0 is Enthalpy (kJ/mole), and ΔS^0 is Entropy (kJ/mole K). For activated carbon from coconut coir, using the value of K_c in the Equation (19), the values of ΔG^0 , for three different temperatures at 30^oC, 40^oC, and 50^oC were calculated. Using the Equation (20), the graph of $\ln K_c$ was plotted against $1/T$ to calculate the values of ΔH^0 and ΔS^0 . The values of ΔG^0 , ΔH^0 , and ΔS^0 thus calculated are shown in Table 5.

Table 5: Values of ΔG^0 , ΔH^0 and ΔS^0

$T (^{\circ}K)$	ΔG^0 (kJ/mole)	ΔH^0 (kJ/mole)	ΔS^0 (kJ/mole K)
298	-9.99556		
303	-8.94686	-26.684	-0.056
308	-8.90507		

Here the negative magnitude of ΔG^0 implied that the process was spontaneous, whereas negative magnitudes of ΔH^0 and ΔS^0 specified that adsorption involved exothermic and non-random at the interface of solid-liquid. The lower values of ΔG^0 at the higher temperature range (30-50^oC) were supportive with experimental results which showed that removal percentage of phenol reduced with the rise in the temperature. The exothermic pattern of the adsorption process because of negative value of ΔH^0 was supportive with the experimental results which showed that removal percentage of phenol decreased with rise in temperature.

IV. SCALE-UP DESIGN

The batch adsorption process is usually designed by considering adsorption isotherm (Naiya et al, 2009). It is assumed that when phenol is mixed with W mass of activated carbon from coconut coir, the initial

phenol concentration is decreased from C_0 to C_t in solution volume V at any specific time wherein the phenol quantity for each gram of the activated carbon from coconut coir is altered from q_0 to q_t .

When $t = 0$, $q_0 = 0$, mass balance Equation is expressed as Equation (21).

$$V(C_0 - C_t) = W(q_t - q_0) = Wq_t \quad (21)$$

At equilibrium $C_t = C_e$ and $q_t = q_e$, the Equation (20) is modified as Equation (22).

$$\frac{W}{V} = \frac{(C_0 - C_t)}{q_t} = \frac{(C_0 - C_t)}{q_e} \quad (22)$$

From the testing of the isotherm models, it was seen that Langmuir, Freundlich and Temkin models were applicable because of high correlation coefficients. Using the best supportive Freundlich model, the Equation (22) is modified as Equation (23).

$$\frac{W}{V} = \frac{(C_0 - C_t)}{q_e} = \frac{(C_0 - C_t)}{K_f - C_e^{1/n}} \quad (23)$$

Using the Equation (23), the weight of the activated carbon from coconut coir (gm) required for phenol concentration of 125 mg/L for a different volume of aqueous phenol solution (wastewater or effluent) from 2 L to 10 L was evaluated and is given in Table 6.

Table 6: Weight of adsorbent (gm) for a different volume of phenol solution (L)

Volume of effluent (L)	80% Adsorption	60% Adsorption	40% Adsorption	20% Adsorption
2	1.41	1.05	0.70	0.35
4	2.81	2.11	1.41	0.70
6	4.22	3.16	2.11	1.05
8	5.63	4.22	2.81	1.41
10	7.03	5.27	3.52	1.76

V. CONCLUSION

The efficiency of activated carbon from coconut coir to adsorb phenol from wastewater was assessed in this research work. The adsorbent activated carbon from coconut coir was at first characterized by using SEM and BET analyzers. The adsorption efficiencies were studied with the change of pH, phenol concentration, contact time, adsorbent dose and temperatures. The authors found that the equilibrium conditions were achieved at pH of 6, the adsorbent dosage of 0.2 gm and contact time of 250 min and at these equilibrium conditions the efficiency reduced with the rise of the phenol concentration (50-140 mg/L) and with the rise of temperature (30-50°C). Various models had also been applied to this work. The pseudo-second-order kinetic model was better in comparison to pseudo-first-order. The Elovich model indicated that the adsorption process was chemical while Reichenberg model signified that film diffusion regulated the process. The Furusawa and Smith model for mass transfer analysis suggested that adsorbate movement from solution to solid occurred reasonably fast, while the Boyd model with the value of diffusion coefficient of $5.563 \times 10^{-10} \text{ m}^2/\text{sec}$ suggested that the process was chemical. The Fick's equation described that duration of the film diffusion was around 100 min followed by the intraparticle diffusion for the next 150 min and finally the adsorption-desorption equilibrium prevailed at 250 min. The adsorption energy calculation indicated that the process was explained by physical adsorption. However, the correlation coefficient was found to be only 0.81559. The test of isotherm models indicated that adsorption equilibrium data fitted very well for the Langmuir, the Freundlich, and the Temkin models. However, Freundlich isotherm was most supportive. The Gibb's free energy suggested that the process occurred spontaneously while enthalpy and entropy pointed out that process was exothermic and non-random. Thus this study concludes that the activated carbon from the coconut coir is a low-cost and proper adsorbent for phenol removal from wastewater. Since this study is carried out for the moderate range of initial phenol concentration in the wastewater, the results suggest that this research work is suitably applicable in petroleum refineries and many other allied industries.

CONFLICT OF INTEREST

The authors have no conflicts of interest to disclose.

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