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Removal of Phenol from Wastewater Using Chemically Treated Coconut Stalk: (*Cocos nucifera*)

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Abstract

In the present work, the potential of coconut stalk, an agricultural material reused as adsorbent for the phenol removal from wastewater was investigated. The influence of different experimental parameters on the adsorption was investigated. The experimental data were analysed by the various isotherm models. The data were found to follow Freundlich model showing that the process was physical adsorption. The kinetic data were tested by different kinetic equations. The kinetic data obeyed pseudo-first-order kinetic equation. The adsorption capacity of the adsorbent was found to be 38.24 mg/g.

Keywords: Coconut stalk, phenol, kinetic, equilibrium, adsorption capacity.

Introduction

Phenol and its derivative compounds are one of the organic pollutants that are toxic to human beings and to the environment and are designated as priority pollutants[1]. The wastewater released from different industries like petroleum refineries, petrochemical, textile, leather, coal conversion, wood preserving industry, phenolic resin, paint manufacturing, ferrous industry, rubber and pulp and paper industries contains an array of pollutants. Phenol is considered to be one of the key pollutants found in these wastewaters, since it is having wide variety of commercial applications[2]. The phenol will have harmful effect on both human beings and environment in various ways[3]. The European Union laid a ceiling concentration of maximum 0.5 µg/l of total phenol in drinking water[4].

A number of treatment methods like biodegradation, biosorption, membrane separation, pervaporation, extraction, distillation and adsorption using activated carbons prepared had been reviewed by Girish and Murty[5] to remove phenolic compounds. Activated carbon is used for the phenol removal from wastewater by adsorption[6]. But the drawback with the activated adsorbent is costly and it has to be produced from starting material which is expensive. This has urged a flourishing research interest for the activated carbon production from various agricultural by-products for wastewater treatment[7].

Girish and Murty[8] reviewed the various agricultural by-products utilized for activated carbon production. These by products were found to be cheap, renewable, easily available and effective alternative materials for the adsorption process. A number of raw materials have been used as adsorbents for the phenol removal from wastewater. These include rubber seed coat[9], tamarindusindica[10], beet pulp[11], coir pith[12], rice husk ash[13] and jute fibre[14].

The present work explores the suitability of coconut stalk based chemically treated carbon for the phenol removal from aqueous solutions. The investigation of effect of variables like pH, dosage and temperature on adsorption was studied. To verify the various adsorption isotherm, kinetic models for the process and the adsorption capacity.

Material and Methods

Adsorbent preparation: Coconut leaves stalk (*Cocos nucifera*) were collected from South Travancore region. The material was initially cleaned to remove all the dirt matter and dried at 50^0C for 24 hours. It was grinded and sieved to fine size particles. The proximate analysis of the raw carbon sample was carried out. The adsorbent was prepared by treating the raw carbon with different chemicals like 2M sulphuric acid, 2M phosphoric acid and 2M hydrochloric acid. Initially the powder was mixed with the various chemicals overnight and was dried in an oven at 80^0C for 5 hours[15]. Then excess water was added to remove excess of chemical and washing is carried out till a clear solution was obtained and pH was stabilised. The removal capacity of phenol, particle size and surface area for all the chemically treated carbons was studied. Then depending on the initial experimental results, adsorbent treated with HCl was considered for further experiments.

Characterization of adsorbent: The moisture content was found by heating the carbon sample in an oven heated at 110^0C for 60 minutes. The left carbon residue was heated in a muffle furnace at 750^0C for about 8 h and at 900^0C for 10 minutes to estimate the ash content and volatile matter respectively. The adsorbent particle size was evaluated by Particle size analyser (CILAS 1064, France). The determination of surface area and pore volume were found using BET apparatus (Smart Instruments, Mumbai). The functional groups of carbon surface were estimated by Fourier transform infrared (FTIR) spectroscopy instrument (Shimadzu, Japan).

Adsorbate: The analytical grade Phenol was obtained from Merck India Ltd. The stock solution prepared by dissolving the calculated quantity of phenol in distilled water. The solutions of required initial concentration 25 to 150 mg/L were prepared by diluting from the original stock solution. Hydrochloric acid, Sulphuric acid and Orthophosphoric acid purchased from SD Fine Chemicals, India, AR grade were used for the chemical treatment of carbon.

Adsorption Experiments: The variation of experimental conditions like pH, adsorbent dose, contact time and temperature on the adsorption were studied for the phenol removal from aqueous solution. The solution pH was varied from 2 to 12 by the addition of either 0.1 M NaOH or 0.1 M HCl to the solution and the carbon dosage varied from 0.25 to 4.5 gfor the initial experiments. After optimizing the above parameters, the isotherm and dynamic studies were performed.

The equilibrium experiments were conducted in 250 mL conical flasks containing 200mL of different concentrations (25, 50, 75, 100, 125 and 150mg/L) of phenol under the optimum conditions. The flasks were agitated in a thermo shaker at 130rpm speed and 298 K for 6 h till equilibrium was established. After the equilibrium time, the phenol concentration were analysed using double beam U-V spectrophotometer (UV-1700, Shimadzu, Japan) by measuring the absorbance at a wavelength of 270 nm. All the experiments were conducted in duplicates.

The phenol adsorbed per gram of carbon (qe) was determined using the expression:

$$qe = \frac{(Co - Ce) * V}{W} \quad (1)$$

where qe is the equilibrium adsorption capacity (mg/g), V is the volume of phenol solution (L),C_0 is the phenol initial concentration (mg/L), Ce is the phenol equilibrium concentration (mg/L), and M(g) is the mass of the carbon powder taken.

The percentage removal of the phenol is given by

$$\%\text{Removal} = \frac{(C_o - C_e)}{C_o} * 100 \quad (2)$$

The dynamic studies performed were similar to those of equilibrium experiments except that the samples were collected regularly and the phenol concentration was estimated. The adsorption capacity at time t, q_t, is given by:

$$q_t = \frac{(C_o - C_t) * V}{W} \quad (3)$$

Results and Discussion

Characterisation of the adsorbent: The proximate analysis of the raw carbon obtained showed volatile matter, moisture content, ash and fixed carbon content to be 37%, 5.1%, 7.2% and 50.7% respectively. The particle size, surface area and removal capacity of various chemically treated carbons are examined and shown in table 1. From the obtained results, the carbon treated with was taken for further studies. The FTIR spectra of adsorbent treated with HCl before and after phenol adsorption are shown in figure 1. From the spectra it was shown that the peak at 3394 cm^{-1} is because of O-H stretching in phenol, the peak at 2854 cm^{-1} is assigned to O-H of carboxylic group, the peak at 1266 cm^{-1} indicates the C-O bond of carboxylic acid, the band at 879 cm^{-1} is because of C-H bond of aromatic group. The band at 1627 cm^{-1} is because of C=C aromatic ring stretching[16] and the band at 1033 cm^{-1} is because of stretching vibration of C-O of carboxyl group[16]. From the figure it was observed that the peaks of C-O bond of carboxylic acid and C=C aromatic changed from 1266 cm^{-1} and 1627 cm^{-1} to 1218 cm^{-1} and 1589 cm^{-1} respectively.

Table-1
The table showing the various properties of chemically treated carbons

		Carbons (treated with chemicals)		
	Untreated	**H_3PO_4**	**H_2SO_4**	**HCl**
Specific surface area m^2/g	109.62	215.43	185.20	348.13
Pore volume, m^3/g	0.1086	0.2211	0.1856	0.2717
Particle size, µm	30.55	16.95	13.25	11.09
% Phenol removal	70.26	82.3	86.8	92.4

Influence of pH: The pHalters the ionization of the phenol molecule[17]. Phenol is having a low dissociation tendency with pKa value of 9.8. When pH of the solution is more than pKa, then phenol dissociates into phenolate ions and there is repulsion forces between phenolate ions and negatively charged carbon surface. This will lead to decrease in adsorption. At pH of the solution less than the pKa value, unionized phenol gets attracted to the positively charged carbon surface and thus the adsorption increases. As can be seed from the figure 2, the decrease in removal upto pH 7 was gradual, thereafter it decreases abruptly. Therefore the optimum value of pH was found to be 7.5. The same nature of results were observed in work[18].

Effect of adsorbent dosage: The influence of carbon dose on phenol removal was investigated by conducting the experiments at adsorbent dosages of 0.25 to 4.5 g. Figure 3 show the influence of carbon dosage on the phenol removal. It was found that the phenol removal increased by increasing adsorbent dosage. After the equilibrium, it was found that53.9 to 90.4% removal was obtained for carbon dosage of 0.25 to 1.5 g/l respectively. It was found that the phenol removal increased due to the enhancement of the sorption surface and increase in the number of adsorption sites[19]. It was found that the optimum carbon dosage was 1.5 g/l respectively. Similar results were obtained in work[20].

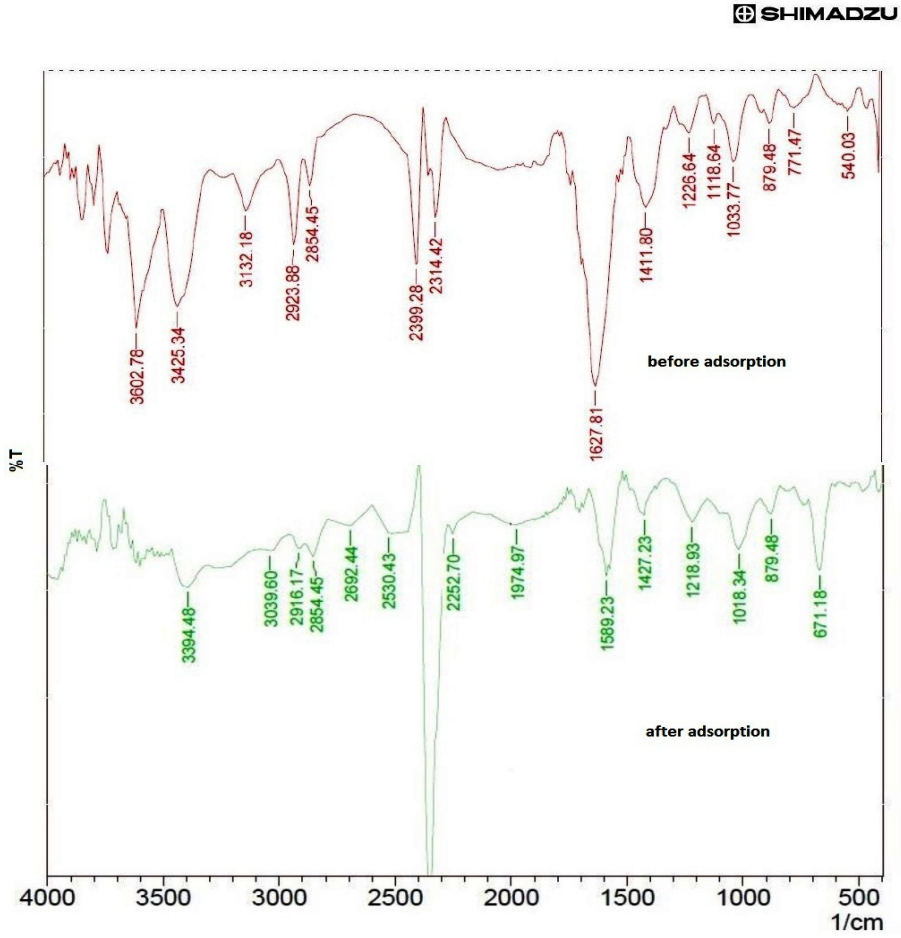

Figure-1
The FTIR of coconut stalk before and after adsorption

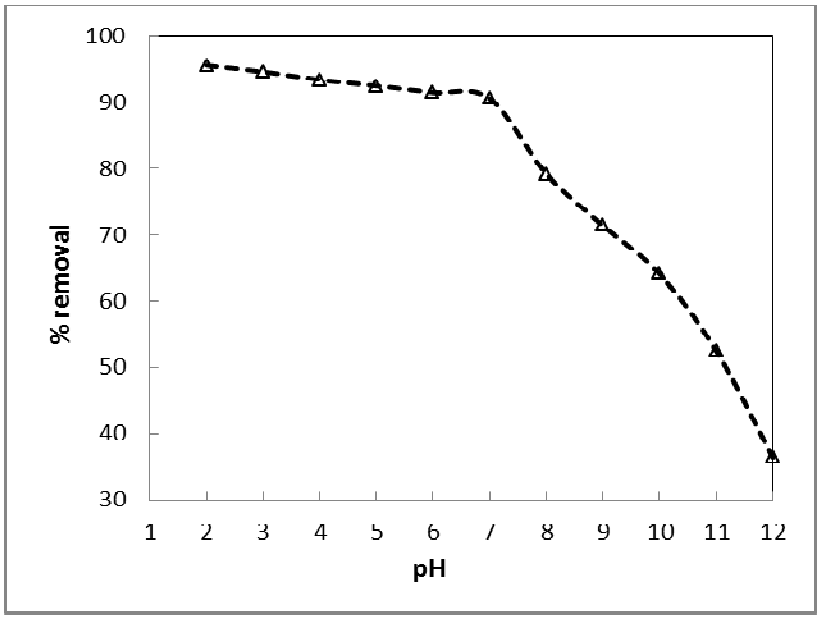

Figure-2
Plot of pH v/s % removal of phenol

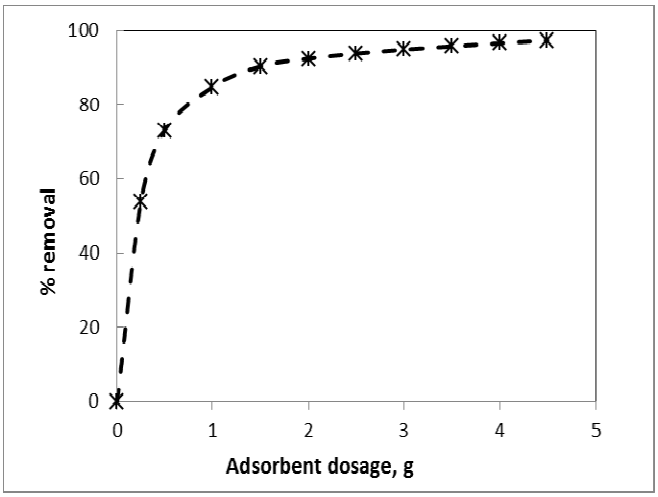

Figure-3
Plot of adsorbent dosage v/s percent removal of phenol

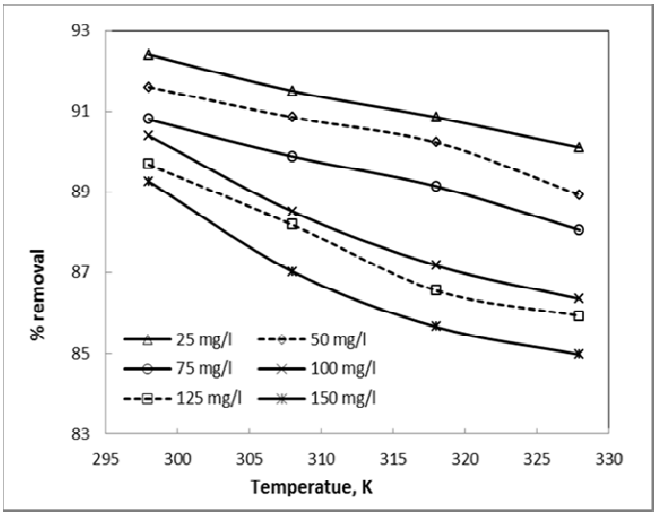

Figure-4
Plot of temperature v/s % removal of phenol

The effect of temperature: The influence of temperature on the phenol removal at various concentrations, onto adsorbent treated with HCl were investigated and shown in figure 4. The experiments were conducted at different temperatures of 298,308, 318 and 328 K. It is observed from the figure 4, that the % removal of phenol decreased by increasing temperature from 298 to 328K. This may be because of decreased active sites on the surface showing that adsorption between phenol and HCl treated carbon follows an exothermic process. Further experiments were carried out at 298 K.

Isotherm Studies: The experimental data was investigated with the various isotherm models. The Langmuir isotherm[21]is proposed for adsorption on the surface having a fixed number of uniform sites in a single layer. The model explains adsorption occurring uniformly on the adsorbent and distribution of energy takes place uniformly on the surface.

The Langmuir isotherm is given by:

$$\frac{C_e}{q_e} = \frac{1}{Q_0\, b} + \frac{C_e}{Q_0} \quad (4)$$

Where Ce is the adsorbate concentration at equilibrium, qe is the adsorption capacity at equilibrium, Q_o and b are isotherm constants.The values of qm and $b$are calculated from the plot of Ce/qe versus Ce (Figure 5).The experimental data were proposed to Langmuir isotherm and the isotherm constants with the regression coefficient values are represented in table 2.

The important parameter of the Langmuir model is the dimensionless constant called the separation factor, R_L, given by:

$$R_L = \frac{1}{(1+b\,C_0)} \quad (5)$$

where b is the Langmuir constantand the values of R_L shows the type of isotherm[22]. The adsorption is irreversible for $R_L = 0$, favourable for $0 < R_L < 1$, linear for $R_L = 1$ and unfavourable for $R_L > 1$.The values of R_L were varying from 0.170039 to 0.551419906 which shows favourable adsorption.

The Freundlich isotherm explains that adsorption occurs on heterogeneous surfaces and interaction occurs between adsorbate molecules. It also explains that the energy of adsorption decreases exponentially with the adsorption process[23].

The Freundlich equation is given by

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (6)$$

where q_e is amount adsorbed at equilibrium (mg /g), C_e is adsorbate equilibrium concentration (mg/ L), K_F is the isotherm constant (mg/ g)(L/mg)$^{1/n}$ and 1/n is dimensionless constant. The linear plot of $\ln qe$ against $\ln Ce$ (Figure 6) gives the values of n and K_F. The determined values of K_F, n and the regression coefficient for Freundlich model are represented in table 2.

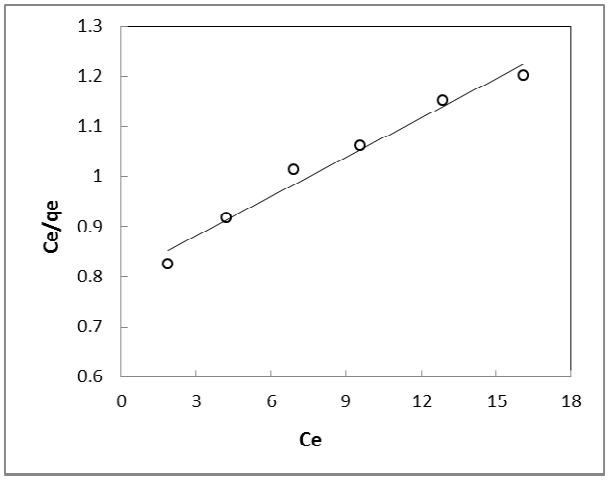

Figure-5
Linearized form of Langmuir isotherm

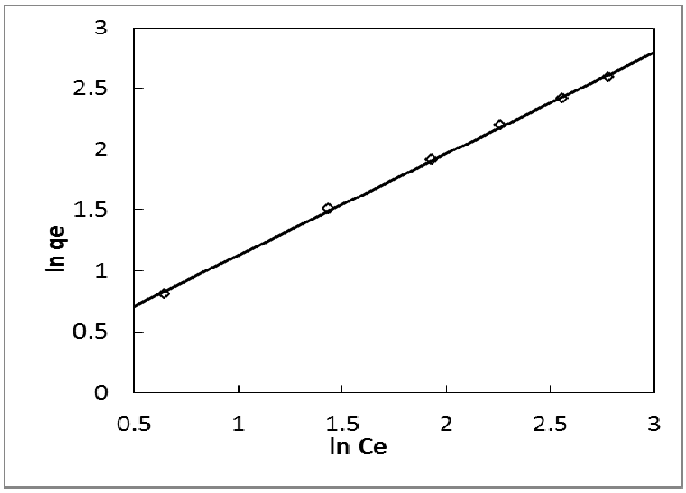

Figure-6
The linear plot of Freundlich isotherm

The Temkin isotherm[24]was investigated to study the energy distribution pattern in the adsorbent layers and also the interactions between adsorbate.

The Temkin isotherm is given by

$$\ln q_e = B \ln A + B \ln C_e \quad (7)$$

where A and B are isotherm constants. The linear plot of Temkin isotherm plot is shown in figure 7 and the corresponding isotherm parameters are given in table 2. From table 2, it shows that the experimental data follows Freundlichisotherm model with R^2 = 0.99881than the Langmuir isotherm with R^2 = 0.97132 and Temkin isotherm with R^2 = 0.93544. It also suggests that adsorption occurs on heterogeneous sites in multilayers on the adsorbent with random distribution of energy level. The values of different isotherm constants are shown in table 2. Thecomparison of different adsorbents and coconut stalk adsorbent with their capacities are represented in table 3. From table 3, it can be concluded that coconut stalk material is an effective adsorbent for removing phenol from wastewater.

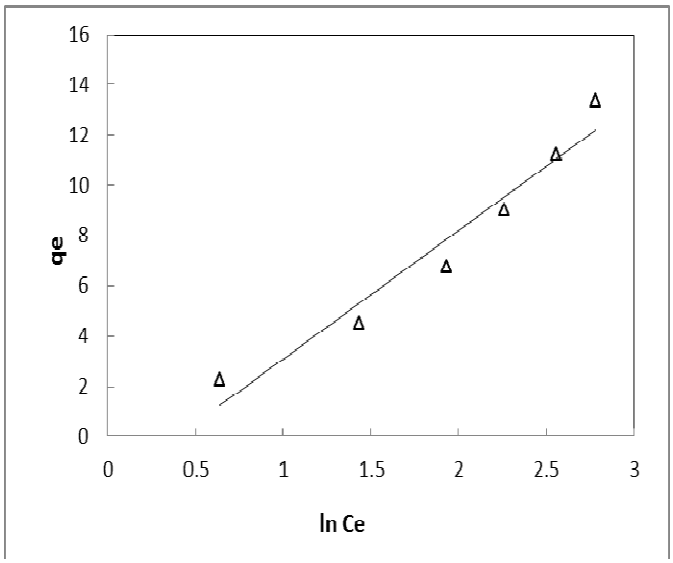

Figure-7
Linearized plot of Temkin isotherm

Kinetics of the adsorption: The dynamic studies have been conducted to explain the adsorption mechanism. From the different kinetic models, it was concluded that the adsorption depends on the chemical nature of material, experimental conditions and the mass transfer process. Therefore, the various kinetic models were tested to explain the adsorption mechanism process and the rate-determining step.

Table-2
The various isotherm constants for adsorption

Langmuir isotherm			Freundlich isotherm			Temkin isotherm		
qm (mg/g)	b (L/mg)	R^2	KF (mg/g)/ (l/mg) $^{(1/n)}$	n	R^2	B	A(L/mg)	R^2
38.24	0.03254	0.97132	1.3499	1.20231	0.9981	0.6705	5.12807	0.93544

Table-3
The monolayer adsorption capacity of various adsorbents

Adsorbent	q_m (mg/g)	Reference
rubber seed coat	56	9
tamarindusindica	80	10
beet pulp	89.5	11
coir pith	48.31	12
rice husk ash	14.382	13
jute fibre	181	14
coconut stalk	38.24	Present work

The Lagergrenpseudo-first-order kinetic model[25] is given by

$$\log (q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303} t \quad (8)$$

where qt is the adsorption capacity at any time (mg/g) and k_{ad} is the rate constant,(min^{-1}) for the pseudo-first- order model. The rate constantk_{ad} and adsorption capacity qe were obtained from the linear plots of log (qe-qt) versus t (as shown in figure 8) The values ofK_{ad} and the regression coefficient are represented in table 4. It was observed that the regression coefficient values for the pseudo-first-order kinetic model were high. It was also found that the theoretical values agreed closely with the experimental values supporting the pseudo-first-order kinetic model which shows reversible physical adsorption[25]. Similar nature of result was reported by works[26, 27].

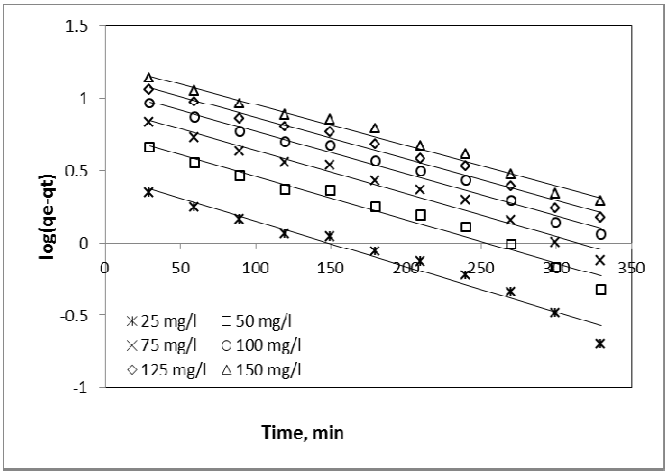

Figure-8
The plot showing the pseudo-first-order kinetic model

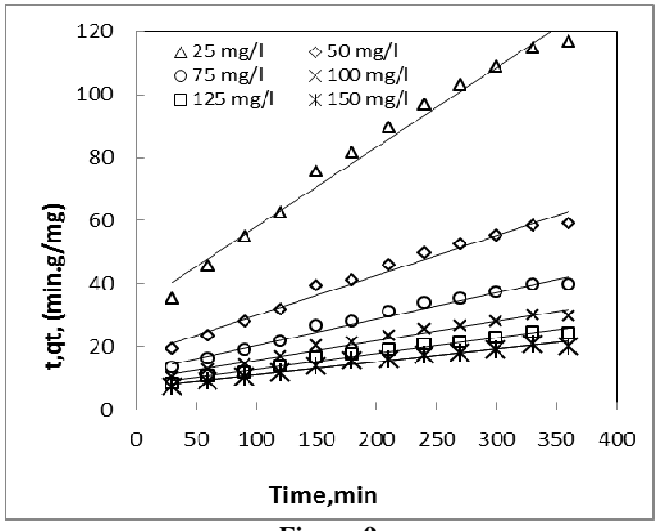

Figure-9
The plot showing pseudo-second-order model

The pseudo-second-order kinetic model is given by Ho[28]

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (9)$$

where h is the adsorption rate (mg/g.min) and k is the rate constant for the pseudo-second-order model (g/ mg. min). The values of q_e and k are obtained from the linear plot of t /q_t versus t, shown in figure 9. The experimental and theoretical q_e values, along with regression coefficients are represented in table 4. It can be observed from Table 4, that for the adsorbent, the R^2 values were relatively low and the experimental and theoretical values of adsorption capacity deviated to a large extent. Thus showing a poor fit of experimental result to the second order model.

The diffusion mechanism can be understood by investigating the Weber and Morris model[29]

$$q_t = k_p t^{1/2} + C \quad (10)$$

where, Cis the boundary layer thickness and k_p is the intraparticle diffusion rate constant. The values of C and k_p are obtained from the slope and intercept of the plot of q_t versust$^{1/2}$ which is shown in figure 10. The values of intra particle diffusion constant k_p are shown in table 5. If the qt versus $t^{1/2}$ plot passes through the origin, then intr aparticle diffusion will be the rate determining step. From the figure. 10, it signifies that the intraparticle diffusion is not the rate determining step.

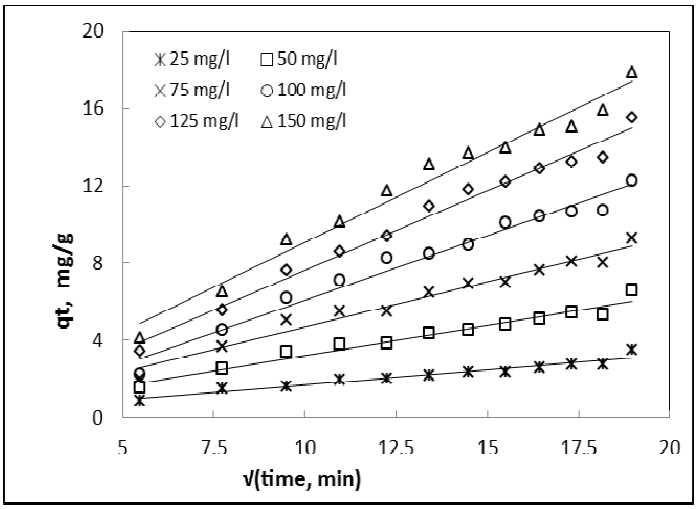

Figure-10
The linear plot of intraparticle diffusion model

Conclusion

In the current study, showed that chemically treated adsorbent produced from coconut stalk was an prospective adsorbent for phenol removal from aqueous solution. The characterisation of the adsorbent carried out signifies the efficacy of the adsorbent. It was investigated that the removal capacity was found to vary with adsorbent dosage, initial concentration, pH and temperature. The equilibrium data followed the Freundlich isotherm and the kinetic data obeyed pseudo-first-order model. The plots for intra particle diffusion model do not pass through the origin, signifying that more than one step affects the adsorption. The equilibrium adsorption capacity was 38.24 mg/g.

Table-4
The constants of pseudo-first-order and pseudo-second-order kinetic models

	Pseudo first order kinetic				**Pseudo second order kinetic**			
conc, mg/L	**Qe,exp,(mg/g)**	**K_1* 10^{-3}(min^{-1})**	**Qe,cal (mg/g)**	**R^2**	**Qe,cal (mg/g)**	**K_2* 10^{-4} (g/mg.min)**	**h (mg/g.min)**	**R^2**
25	3.08	7.254	2.9475	0.96376	3.953	7.7055	0.03046	0.9806
50	6.1066	6.932	5.7806	0.96862	7.9365	9.108	0.05737	0.97778
75	9.08	6.8399	8.6678	0.97303	11.9517	5.74	0.0821	0.97724
100	12.053	6.72	11.593	0.97927	16.12	4.002	0.1040	0.97562
125	14.946	6.632	14.459	0.98094	20.24	3.04	0.1246	0.97398
150	17.852	6.471	17.374	0.98259	24.48	2.38	0.14267	0.96964

Table-5
The values of constants of intraparticle diffusion model

	Intraparticle diffusion		
Conc (mg/L)	**Ki (mg/g $min^{0.5}$)**	**c**	**R^2**
25	0.15719	0.11232	0.94101
50	0.31359	0.09475	0.95553
100	0.46889	0.01276	0.96678
150	0.66741	-0.5847	0.97126
200	0.82909	-0.5736	0.98238
250	0.92884	-0.2171	0.97531

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