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Phenol Removal from Aqueous Solutions Using Low-Cost Neem Seeds Activated Carbon as an Adsorbent

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Abstract

The potential of laboratory prepared Neem Seeds Activated Carbon (NSAC) as a natural adsorbent for toxic organic compound, such as Phenol, From Wastewater Was Investigated. Batch experiments were conducted to study the effects of pH, temperature, initial concentration, and dose of absorbents for their optimum values. Results indicated that the adsorption of Phenol Depended Significantly on All the Above-Mentioned Parameters. The experimental data were fitted to pseudo-first-order and pseudo second-order kinetics models. The diffusivity and mass transfer coefficients for phenol was also evaluated in the present work. Langmuir, Freundlich, Temkin and Redlich-Peterson isotherms were tested for their fitness to the experimental data. The maximum mass of phenol adsorbed was evaluated using Langmuir isotherm at optimum conditions and compared with that obtained for previously reported materials. Thermodynamic parameters including the Gibbs free energy, enthalpy, and entropy were also calculated. This study showed that NSAC may be explored as a new material for removing phenol from the waste water.

Keywords: Adsorption; Isotherm; Kinetics; Neem Seed Activated Carbon; Phenol Removal

Introduction

Phenol Commonly Is Widely Used in Several Industries, e.g., petrochemicals, plastics, pesticides, pharmaceuticals dyes and many others [1,2]. Phenol is a hazardous compound (U.S. EPA), therefore the various agencies of the world has set a maximum discharge limit of Phenol in to Wastewaters Stream. If it is released in effluent it can cause serious damage to the environment due to its high toxicity for aquatic organisms [3]. Thus, the elimination of Phenol Is Very Necessary for Environmental Protection. Several Techniques Have Been Developed to Remove Phenol from Wastewater like Chemical Oxidation, electrocoagulation, solvent extraction, membrane separation and adsorption [4]. Among all of these methods adsorptions has been preferred due to its low-cost and the high-quality of the treated effluents. Research interests into the production of alternative adsorbents to replace costly activated carbon and synthetic resins have intensified in recent years. Attention has been focused on various adsorbents, which have absorption capacities and are able to Remove Unwanted Phenols from Contaminated Water at Low-Cost. Recently, some nature and cheap adsorbents have been developed in the laboratory [5]. Adsorption onto agricultural waste material used recently as an economical and realistic method for removal of different pollutants has proved to be efficient at removing of phenol [6]. Since, not many studies have been reported in literature on the adsorption of phenol using Neem Seed Activated Carbon. In This Study, Neem Seeds Activated Carbon (NSAC) was investigated as a low-cost adsorbent for removing of phenol from aqueous solutions. Several experimental factors which affect the removal of phenol such as adsorbate-adsorbent contact time, initial solution pH, adsorbent dosage, adsorbate concentration and adsorption temperature were optimized. The equilibrium and kinetic data of the adsorption process were then analyzed to study the adsorption characteristics and mechanism of phenol onto the prepared activated carbon.

Materials and Methods

Activated Carbon Preparation from Neem Seeds

Among various materials available for the production of activated carbons, cost, high carbon content and easily availability are important criteria for their selection [7]. In the present work, a new adsorbent has been explored which good adsorption capacity as compare to other low cost activated carbon has derived from agro-waste. Neem Seeds (NS) were obtained from the campus of National Institute of Technology (NIT), Rourkela. Without any treatment excepting washing in tap water to remove dirt etc.,

NS was charred in muffle furnace at temperature of 700 K for 60 min and it was further treated with alkali (NaOH). The alkali (NaOH)-treated charred was filtered, washed with Distilled Water (DW) and then oven-dried at 95°C for 12 h, and stored for end use. Activated Carbon Thus Prepared Was Named as Neem Seed Activated Carbon (Nsac).

Characterization of The Prepared Activated Carbon

The specific surface area measurement of NSAC was carried out at Kunash Instruments Pvt. Ltd., Mumbai, by N_2 adsorption using a Micromeritics instrument (Tristar 3000) and by using the Brunauer-Emmett-Teller (BET) method, using the software of Micromeritics. Nitrogen was used as a cold bath (77.15 K). The physico-chemical characterizations (Table 1) of NSAC were done using standard methods [8-10]. The Point of zero charge of was determined as per the method presented by [11]. Surface groups (acidic and basic) present on the NSAC (Table 1) were determined using Boehm titration method [12].

Characteristics	Neem Seed Activated Carbon
Proximate analysis	
Moisture (%)	3.59
Volatile matter (%)	36.54
Ash (%)	3.09
Fixed Carbon (%)	56.28
Bulk density (kg/m^3)	0.7702
Dry density	0.7434
Porosity	0.1985
Specific gravity	0.9285
Void ratio	0.2488
Heating value (cal./g)	6094
Average particle size (μm)	531.96
Chemical analysis of Ash	
Insoluble (%)	70
SiO_2 (%)	0.32
Fe_2O_3 & Al_2O_3 (%)	4.89
CaO (%)	10.37
MgO (%)	0.86
Others	2.07
Ultimate Analysis of Adsorbents	
Carbon (%)	56.3
Hydrogen (%)	4.02
Nitrogen (%)	4.55
Sulfur (%)	0.81
EDX AnalysisCarbon	67.6
Nitrogen	-
Oxygen	26.34
Magnesium	0.34
Phosphorus	3.99
Sulfur	0.29
Potassium	0.62
Calcium surface Area of Pores (M^2/G)	
(i) BET	145
(ii) BJH (adsorption/ desorption)	107/70
BJH cumulative pore volume (cm^3/g)	0.1367
(i) Single Point Total	0.1287
(ii) BJH adsorption	0.1132
(iii) BJH desorption	
Average Pore Diameter (Å)	
(i) BET	21.7
(ii) BJH adsorption	30
(iii) BJH desorption	37
Boehm Titration	
Surface acidity (mmol/g)	5.93
Surface alkalinity (mmol/g)	2.66

Table 1: Physico-chemical characteristics of NSAC.

Preparation of Adsorbate Stock Solutions

The stock solutions of phenol concentration 1000 mg/L were prepared by dissolving appropriate amount of phenol in distilled water. Desired concentrations were prepared from the respective stock solutions, making fresh dilutions for each adsorption study. The C_o was ascertained before the start of each experimental run. The pH of each solution was adjusted to the required value with 0.1 M HCI and NaOH solutions before mixing the NSAC.

Analytical Measurements

The concentration of phenol in the aqueous solution was determined by using a UV-spectrophotometer. Absorbance values were recorded at the corresponding maximum absorbance wavelength λ_{max}. The calibration curve of the peak area versus phenol concentration was used for the determination of the unknown concentration of phenol from a sample. Wherever required, the sample was appropriately diluted to have the phenol concentration in the calibration range.

Adsorption Studies

For each experiment, 50 ml of phenol of known concentration and a known amount of the adsorbent were placed in a 100 ml airtight stoppered conical flask. This mixture was agitated in a temperature -controlled shaking water bath, at a constant speed (150 rpm) for all experimental runs. The percentage removal of phenol was calculated using the following relationship:

$$\text{Percentage removal } (\%) = 100\ \frac{(C_o - C_t)}{C_o} \qquad (1)$$

Where, C_o is the initial sorbate concentration (mg/l) and C_t is the equilibrium sorbate concentration (mg/l). The adsorption capacity of NSAC was calculated using the following equation:

$$q_e = \frac{(C_o - C_e)V}{m} \qquad (2)$$

Where, q_e (mg/g) is the amount of phenol sorbed by adsorbent, C_o and C_e (mg/l) are the initial and equilibrium liquid phase concentration of phenol solutions, respectively, V (l) is the initial volume of dye solution, m (g) is the weight of the NSAC. For the optimum conditions determination of the various parameters such as contact time, pH, initial dye concentration, adsorbent dose, temperatures were studied for the phenol. Using optimum conditions phenol removal capacity, equilibrium values and kinetic studies were performed for phenol.

Results and Discussion

Effect of Various Parameters

Effect of NSAC Concentrations

To find out the optimum dosage of NSAC, the NSAC concentrations were varied from 0.2 to 6 g/l at fixed initial phenol concentration of 100 mg/l (Figure 1). It was observed that on increasing the adsorbent dosage the uptake capacity of phenol decreases, while the %R increases because m is inversely proportional to the uptake capacity. The point where these two curves cut together is regarded as an optimum adsorbent dose which was found to be 1.2 g/l. Beyond this dosage, there is limited availability of adsorption sites and do not contribute much for further removal of phenol. Various authors have been reported similar finding for phenol adsorption onto activated carbon prepared from various adsorbents [13-15].

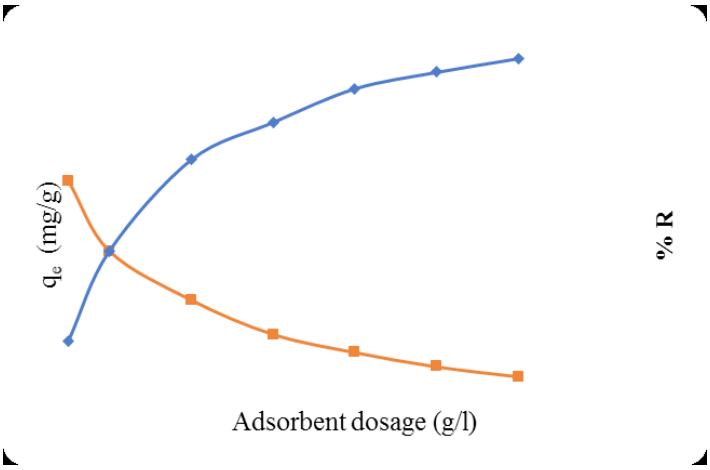

Figure 1: Effect of NSAC dosage for the adsorption of phenol (C_o =100 mg/l, initial pH=6, T =303 K, t =5 h).

Effect of pH

The pH of the phenol solution plays an important role in the whole adsorption process and especially on the adsorption capacity. The experiments were performed at various pH [2-12]. It was clear from (Figure 2) that as the pH varies the adsorption of phenol increases and reached to maximum (22 mg/g) at pH=8. Further, increase in pH reduces the uptake of phenol onto NSAC. This phenomenon can be explained based point of zero charge of the adsorbent. The pH, at which the surface charge of adsorbent is zero, is called the point of zero charge (PZC). The surface is positively charged at $pH<pH_{PZC}$ and negatively charged at $pH>pH_{PZC}$ [16, 17]. The PZC of NSAC is 7. Adsorption of positive ions is favored at $pH > pH_{PZC}$, whereas the adsorption of negative ions is favored at $pH < pH_{PZC}$. For $pH>pH_{PZC}$, high electrostatic attraction exists between the negatively charged surface of the NSAC and the phenolate ion ($C_6H_5OH_2^+$) while at higher pH, a negatively charged surface site on NSAC reduces the sorption of $C_6H_5O^-$ as a result of electrostatic repulsion [18-20]. Thus, maximum uptake of phenol occur at pH=8.

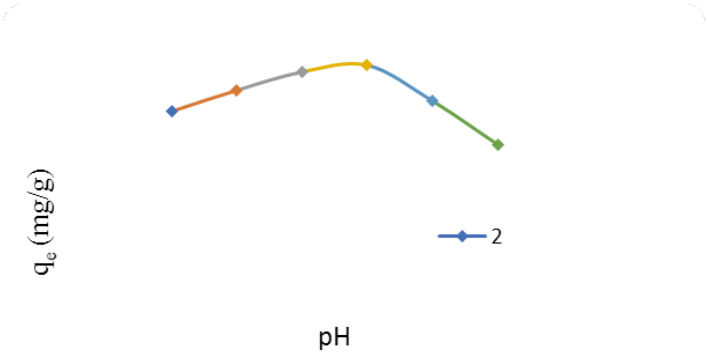

Figure 2: Effect of initial pH on the equilibrium uptake of phenol (C_o=100 mg/l, m=1.2 g/l for T = 303 K, t =5 h).

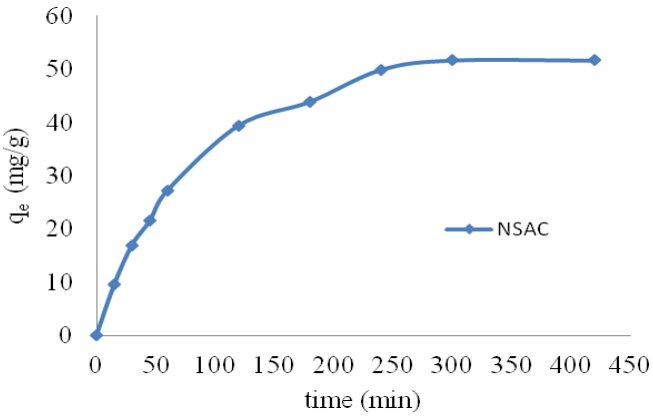

Figure 3: Effect of initial phenol concentration on the removal of phenol onto NSAC (C_o= 50-150 mg/l, m=1.2 g/l, pH=8, T = 303 K).

Effect of contact time and initial phenol concentrations

To find out the optimum contact time for maximum adsorption of phenol onto NSAC, experiments were done for varying time periods between 15 and 360 min at pH 8 by adding 1.2 g/l of adsorbent to C_o=50-100 mg/l phenol solution. In (Figure 3) the relationship between the phenol uptake (q_e, mg/g) and the initial concentration of phenol (C_o=50-150 mg/l) in the aqueous solutions after 6 hours of adsorption for NSAC is shown. From the it is clear that the amount of phenol uptake, q_e (mg/g), is increased with contact time at all initial phenol concentrations. Further, the amount of phenol adsorbed is increased with increase in initial phenol concentration. For the first 70 min, the phenol sorbed was found from ~9 to ~47 mg/g for an increase in C_o from 50 to 150 mg/l. (Figure 3) also depicts that phenol uptake is rapid for the first 70 min and thereafter it proceeds at a slower rate and finally attains saturation. These observations show that the C_o has no effect on equilibrium time. The higher sorption rate at the initial period (first 70 min) may be due to an increased number of vacant sites available at the initial stage, as a result there exist increased concentration gradients between adsorbate in solution and adsorbate in the adsorbent surface [21]. This increase in concentration gradient tends to increase in phenol sorption rate at the initial stages. As time precedes this concentration is reduced due to the accumulation of phenol in the vacant sites, leading to a decrease in sorption rate at later stages from 70 to 120 min. It can be seen, that the higher the initial concentration, the higher the adsorption ability, as is documented by values of q_t. For phenol C_o =50- 150 mg/l, time of 120 min was sufficient to achieve the equilibrium state. Hence, 120 min was taken as optimum contact time for phenol-NSAC system.

Adsorption kinetic study

The pseudo-first-order and pseudo-second-order models kinetic models (table 2) have been used in the present study to investigate the adsorption process of phenol onto NSAC. The details of all these kinetic models are presented elsewhere [22-24]. Pseudo-first and second-order equation have been solved by using non-linear technique and k_S and q_e were obtained. (Figure 4) shows a representative plot of q_t versus t (experimental and calculated) for adsorption of phenol onto NSAC for C_0 = 50-150 mg/l at m = 1.2 g/l, pH=8 and T=303 K. The best-fit values of h, q_e and k_S along with the correlation coefficients for the pseudo-first-order and pseudo-second-order models for the adsorbate-adsorbent system are given in (Table 2). In the present work, the applicability of the pseudo-first-order and pseudo-second-order models has been tested for the sorption of phenol onto NSAC. The best-fit model was selected based on the regression correlation coefficient, R^2 values. The corresponding non-linear regression correlation coefficient R^2 values are given in (Table 2). From (Table 2), it was observed that the R^2 values for the pseudo-first-order and pseudo-second-order models were found to be comparable at all initial phenol concentrations. The higher values of R^2 confirm that the sorption process follows a physio-chemical mechanism sorption behavior. This was later on also confirming by the thermodynamics of phenol adsorption onto NSAC.

Pseudo-first-order [40]:

Concentration (mg/l)	50 mg/l	75 mg/l	100 mg/l	150 mg/l
qe,exp (mg/g)	13.75	21.21	30.91	53
qe,calc (mg/g)	13.94	21.23	30.92	53
kf (min^{-1})	0.018	0.023	0.026	0
R^2	0.985	0.99	0.987	0.9
MPSD	13.36	9.78	10.81	12

Pseudo-second-order [45]**:**

Concentration (mg/l)	50 mg/l	75 mg/l	100 mg/l	150 mg/l
qe,exp (mg/g)	13.75	21.21	30.91	53
qe,calc (mg/g)	13.94	21.23	30.92	53
kf (min^{-1})	0.018	0.023	0.026	0
R^2	0.985	0.99	0.987	0.9
MPSD	13.36	9.78	10.81	12

Intra particle diffusion [41]**:**

kint1(mg/ g. $min^{1/2}$)	1.9862	2.1462	3.0338	3.8558
C1(mg/g)	1.1759	1.1598	0.3013	17.023
R^2	0.9873	0.9982	1	0.9821
kint2 (mg/ g. $min^{1/2}$)	-	0.0092	-	0.0064
C2 (mg/g)	-	21.044	30.9	53.54
R^2	-	0.8318	-	0.3844

Elovich [42,43]**:**

b (g/mg)	0.2806	0.5736	0.1594	7.5263
a (mg/g. min)	6.53*10-9	12.8	10.625	45.94
R^2	0.9171	0.9223	0.9159	0.9203

Bangham [44]:

α	0.78	0.57	0.5	0.3
k_o	0.4	1.073	1.662	5.3
R^2	0.98	0.997	0.997	1

Table 2: Kinetic parameters for the removal of phenol onto NSAC.

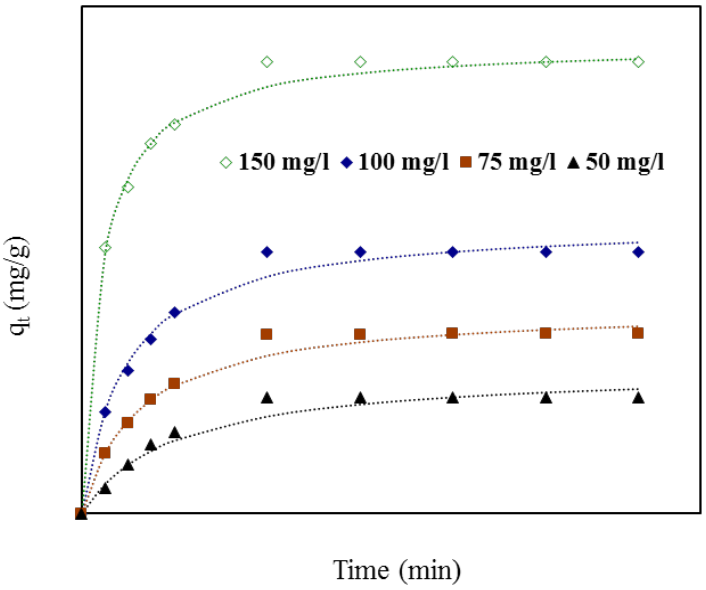

Figure 4: Effect of initial phenol concentration on the removal of phenol onto NSAC (C_o= 50-150 mg/l, m=1.2 g/l, pH=8, T = 303 K).

Adsorption diffusion study

In order to estimate weather, the sorption process is rate limiting step mean either pore diffusion or surface diffusion or external mass transfer means boundary layer diffusion. The kinetic data as obtained by conducting batch experiments have been tested by the model given by (25):

$$F(t) = 1 - \left(6/\delta^2\right)\exp\left(-B_t\right) \quad (3)$$

and

$$F(t) = \frac{q_t}{q_e} \quad (4)$$

Where q_t and q_e are the amount of phenol adsorb at any time t and equilibrium (mg/g). F (t) is fractional amount of phenol adsorb and Bt is a function of F (t).

Substituting eq. 3 in eq. 4, eq simplifies to:

$$B_t = -0.4977 - \ln(1 - F) \quad (5)$$

The fitting of data plot (linear lines) Bt versus t (min) for all phenol initial concentrations did not pass through the origin (Figure 5) indicating that the adsorption of phenol onto the NSAC was mainly due to external mass transport where particle diffusion (exterior surface of the adsorbent) was the rate limiting step [26].

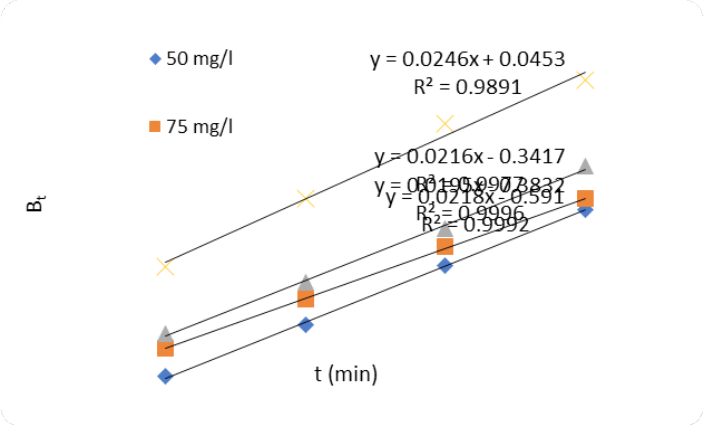

Figure 5: Boyd plot for the removal of phenol by NSAC (C_o =50-150 mg/l; t =5 h; W = 1.2 g/l; pH $_o$ = 8).

The Bt values were also used to calculate the effective diffusivity, De (cm^2/s) using the relation given by [27]:

$$B = \frac{\pi^2 D_e}{r^2} \quad (6)$$

Where, r represents the particle radius estimated by sieve analysis by assuming as spherical particles. The values of effective diffusion coefficient (D_e) for concentrations 50-150 mg/l calculated by Eq. (5). Average value of D_e are found to be 4.18 x 10^{-13} m^2/s for phenol adsorption onto NSAC.

A mass transfer phenomenon was studied with the help of following equation,

$$\ln\left[\frac{C_t}{C_o} - \frac{1}{1+mK}\right] = \ln\left[\frac{mK}{1+mK}\right] - \left[\frac{1+mK}{mK}\right] K_1 S_s t \quad (7)$$

$$S_s = \frac{6W}{d_p \rho_p (1-\varepsilon_p)} \quad (8)$$

Where and C_t are the initial phenol concentration (mg/L) and concentration at time of t of the adsorbate respectively; m (g/L) is the mass of adsorbent. K (L/g) is the Langmuir constant, $\hat{a}_1$ (cm/s) is the mass transfer coefficient and S_s (L/cm) is the outer surface of the adsorbent per unit volume. According to above equation, surface mass transfer is controlling when tends to zero. A plot of $\ln\left[(C_t/C_o) - (1/(1+mK))\right]$ versus t results in a straight line (Table 3). The value of $\hat{a}_1$ have been calculated from slope and intercept of the straight line. At C_o =100 mg/l, $\hat{a}_1$ values 3.44×10^{-7}, 2.74×10^{-7} and 2.34×10^{-7} cm/s were obtained at temperature 303, 313 and 323 K respectively, indicating that the transfer of phenol from bulk of the liquid to adsorbent surface is very rapid and the adsorbent is suitable for removal of phenol from aqueous solution. Similar finding related to determination of mass transfer coefficient has been reported earlier (28).

303K	0.7216	8.5491	0.9856	_
313K	0.6076	8.4662	0.9792	_
323K	0.4576	8.6719	0.9945	_
333K	0.3941	8.7019	0.9687	_
303K	1.983	0.0244	1.1434	0.9997
313K	1.293	0.0018	1.6369	0.9941
323K	14.19	1.8206	0.6749	0.9974
333K	121.43	20.1323	0.6311	0.9872

Table 3: Isotherm Parameters for the Removal of Phenol onto NSAC at different temperatures (C_o = 50-150 mg/l; t =5 h; m = 1.2 g/l; pH $_o$ = 8).

Adsorption isotherms studies

The adsorption isotherms show the relation between the concentration of adsorbate and its degree of adsorption onto adsorbent surface at constant temperature. Several isotherm models have been used to fit to the experimental data over the temperature range of 303-333K and evaluate the isotherm performance for phenol adsorption. These isotherm models included the Freundlich model [29-31], Langmuir model, Temkin model and Redlich-Peterson (R-P) adsorption isotherm model. The adsorption plots and the fitting model parameters with R^2 for the different models were individually shown in (Figure 6)) and (Table 4). Calculated constants of all the isotherms and their corresponding non-linear regression coefficients at various temperatures are presented in (Table 4). In terms of R^2 values, the applicability of the above four models for present experimental data approximately followed the order: Langmuir >R-P>Temkin>Freundlich. It was shown that the Langmuir equation had the best fit to the experimental data. The maximum adsorption capacity calculated by this function was ~39 to 41 mg/g over the temperature range as mentioned above. For comparison, the phenol adsorption capacities of reported adsorbents were given in. For comparison, the phenol adsorption capacities of reported adsorbents were given in (Table 4). From the Temkin isotherms, typical bonding energy range for the ion exchange mechanism was reported to be in the range of 8-16 kJ/ mol while the physic-sorption process was reported to have adsorption

energies less than −40 kJ/mol [32]. The value of b_T (8.46 to 8.70 kJ/mol) obtained in the present work indicated that the adsorption process seemed to be involved in the chemic-sorption and physic-sorption [33]. Further, it was noted that the *n* value is less than one for Freundlich model indicating a favourable adsorption process for phenol-NSAC system.

(mg/l)			303K	313K	323K	333K
50	-34.42	8.52	-18	-22.5	-15.12	-19.13
75	-13.42	13.7	-18	-17.8	-17.9	-18.06
100	-6.21	34.1	-17	-17.1	-17.18	-17.85
125	-3.57	61.1	-15	-16.2	-16.62	-16.86
150	-5.78	30.9	-15	-15.6	-15.9	16.22

Table 4: Thermodynamic parameter for phenol adsorption onto NSAC (C_o = 50-150 mg/l; t =5 h; m = 1.2 g/l; pH $_o$ = 8).

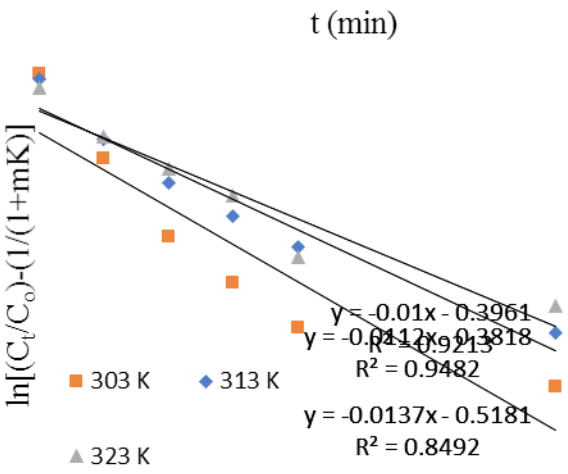

Figure 6: Mass transfer plot for adsorption of phenol-NSAC system (C_o =100 mg/l; t =5 h; W = 0.4 g/l; pH $_o$ = 8).

Effect of temperature

Adsorption experiments were carried out at various temperatures, i. e. 303, 313 and 323 K, keeping the phenol concentration constant (100 mg/l), NSAC dosage 1.2 g/l and pH 8. It was observed that uptake of phenol by NSAC decreased with increase in temperature.

Estimation of thermodynamic parameters

The free energy of adsorption (ΔG^o) can be related with the equilibrium constant K (L/mol) corresponding to the reciprocal of the Langmuir constant, by the following equation [34]

$$\Delta G^o = -RT \ln K \quad (9)$$

Where, R is the gas universal constant (8.314 J. mol/K) and T is the absolute temperature. Also, enthalpy (ΔH^o) and entropy (ΔS^o) changes can be estimated by the following equations, respectively [35]

$$\Delta H^o = R\left(\frac{T_1 T_2}{T_1 - T_2}\right) \ln \frac{K_2}{K_1} \quad (10)$$

$$\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T} \quad (11)$$

Where, K_1 and K_2 are the values of the equilibrium constant at temperatures T_1 and T_2, respectively.

Since, the Langmuir isotherm could be fitted to the experimental data, free energy of adsorption (ΔG^o), enthalpy (ΔH^o), and entropy (ΔS^o) changes were estimated by Eq. (9-11) for phenol-NSAC system. At various concentrations, the estimated values for ΔG^o were −15.30 to 18.32 kJ/mol at 303 K, -15.57 to -22.45 kJ/mol at 313 K, -15.12 to -17.90 kJ/mol at 323 K and -16.22 to -19.13 kJ/mol at 333 K which are rather low indicating that a spontaneous physiosorption process occurred [36,35]. The enthalpy changes (ΔH^o) and entropy of adsorption. Physical nature of adsorption [38]. As per the values presented in (Table 5), the present phenol-NSAC system is physco-chemic-sorption in nature. (ΔS^o) were -3.57 to -34.42 and 8.52 to 61.14 kJ/mol K, respectively. The positive entropy change (ΔS^o) value showed that randomness increased with the increase of species number at the solid/liquid interface during the adsorption of phenol on NSAC. The negative values of G° indicated that the adsorption process was exothermic and spontaneous in nature. The physical adsorption mechanism exist, if the ΔG^o values is <−10 kJ/mol [37]. The heat of adsorption values (ΔH^o) between 0 and -20 kJ/mol are frequently assumed as to indicate.

Adsorbents	adsorption capacities q (mg/g)		References
Sawdust based Activated carbon	2.82	Ads. Dosage=2 g/L, pH= 3.5	Mohanty et al. (2005)
Rice husk carbon	22	Ads. Dosage=15 g/L, pH= 2.7	Kennedy et al. (2007)
Baggase fly ash	12-13	Ads. Dosage=10 g/L, pH= 6.5	Srivastava et al. (2006)

Dried sewage sludge	16	Ads. Dosage=5 g/L, pH= 6.5	Thawornchaisit andPakulanon (2007)
Neutralized red mud	5.13	Ads. Dosage=1 g/L, pH= 6	Tor et al. (2006)
Modified attapulgite	1.4	Ads. Dosage=10 g/L, pH= 10	Huang et al. (2007)
Olive pomace	5-Apr	Ads. Dosage=10 g/L, pH= 9	Stasinakis et al. (2008)
macro alga	20	Ads. Dosage=6 g/L, pH= 6	Rathinam Aravindhan, 2009
Luffa cylindrical	10.37	Ads. Dosage=3 g/L, pH= 7	O. Abdelwahab, 2013
Chitin	12.7	Ads. Dosage=3 g/L, pH= 2	GiselePigatto, 2013
Chitin	21.5	Ads. Dosage=1 g/L, pH= 1	Arzu Y. Dursun, 2005
Neem seed activated carbon	~39-41	Ads. Dosage=1.2 g/L, pH= 8	Arzu Y. Dursun, 2005

Table 5: Recent reported adsorption capacities q (mg/g) of non-conventional low cost adsorbents for phenol.

Isosteric Heat of Adsorption

Apparent isosteric heat of adsorption ($\Delta H_{st,a}$) at constant surface coverage (by considering the range of q_e values obtained in each experiment) is calculated using (Figure7) Clausius-Clapeyron equation [39].

$$\frac{d \ln C_e}{dT} = \frac{-\Delta H_{st,a}}{RT^2} \qquad (12)$$

Or

$$\Delta H_{st,a} = R \frac{d \ln C_e}{d(1/T)}\bigg|_{q_e} \qquad (13)$$

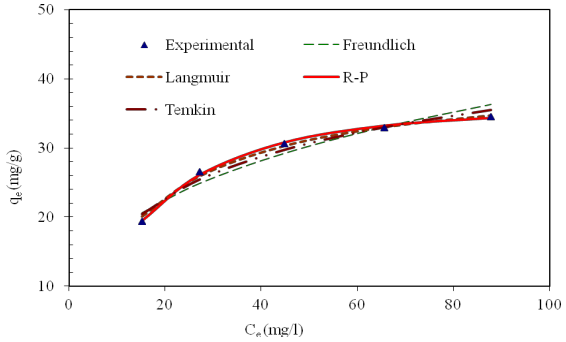

Figure 7: Equilibrium isotherm plot for the removal of phenol onto NSAC (C_o =50-150 mg/l; t =5 h; m = 1.2 g/l; pH_o = 8, T = 303 K).

For this purpose, the equilibrium concentration (C_e) at a constant equilibrium amount of adsorbed solute, q_e, is obtained from the adsorption isotherm data at different temperatures. $\Delta H_{st,a}$ Is calculated from the slope of the ln C_e versus $(1/T)$ plot for different q_e of phenol onto NSAC. The isosters corresponding to different equilibrium adsorption uptake of phenol by all the adsorbents is shown through (Figure 8).

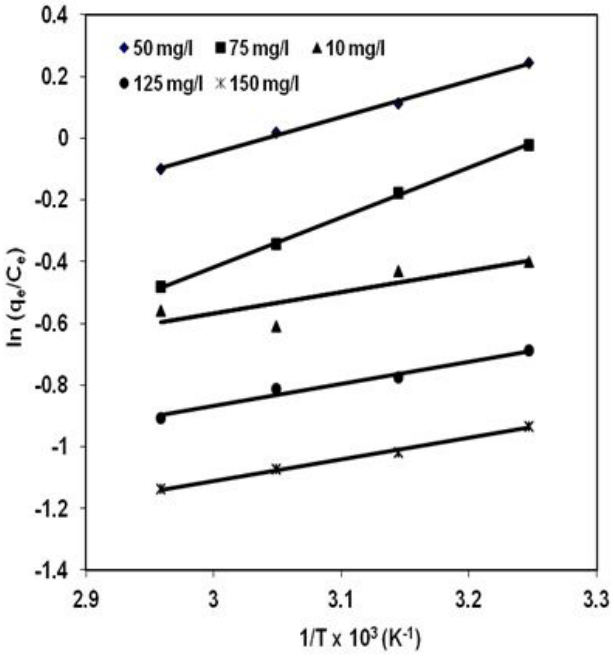

Figure 8: Van't Hoff plot for the adsorption of phenol onto NSAC. (C_o = 50-150 mg/l; t =5 h; m = 1.2 g/l; pH_o =8).

The variation of $\Delta H_{st,a}$ for the adsorption of phenol with the surface loading is presented in (Figure 9) which shows that the $\Delta H_{st,a}$ is increasing with increasing surface loading indicating that NSAC have homogeneous surface. The dependence of heat of adsorption with surface coverage is usually observed to display the adsorbent-adsorbate interaction. The negative values of isosteric heat of adsorption for the adsorbate-adsorbent system shows that the sorption of phenol is an exothermic process.

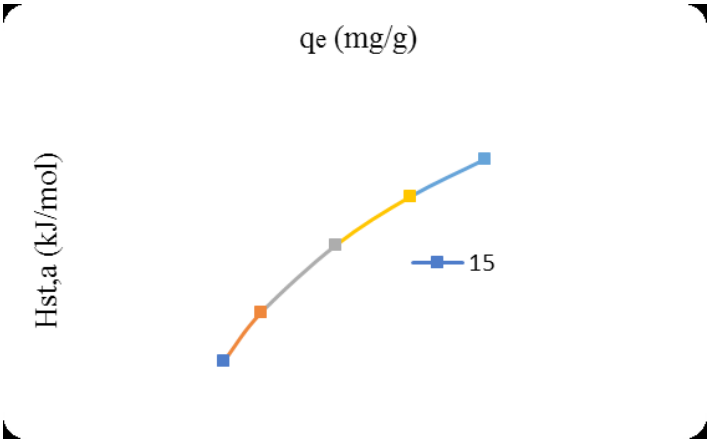

Figure 9: Variation of $\Delta H_{st,a}$ with respect to surface loading of phenol adsorption.

Conclusions

The following conclusions can be drawn from the present work

- The NSAC, an agrobased waste biomaterial can be efficiently used as an adsorbent for the removal of phenol from its aqueous solutions.
- The uptake of phenol adsorbed was found to maximum at optimum conditions: adsorbent dose= 1.2 g/l, pH= 8, and contact time=120 min at ambient temperature.
- The amount of phenol uptake (mg/g) was found to increase with increase in solution concentration and contact time and found to decrease with increase in adsorbent dosage.
- Equilibrium data fitted very well to the Langmuir isotherm model, confirming the monolayer sorption capacity of phenol onto NSAC with a monolayer sorption capacity of ~170 mg/g.
- A Boyd plot confirms the external mass transfer as the slowest step involved in the sorption process.
- Based on regression coefficients values of pseudo-first-order and pseudo-second order kinetics models, and thermodynamics of present phenol-NSAC system; the phenol sorption onto NSAC is physico-chemic-sorption in nature.
- The negative value of enthalpy of adsorption indicated that the adsorption of phenol onto NSAC was exothermic in nature

References

1. Dabrowski A, Podkoscielny P, Hubicki Z, Barczak M (2005) Adsorption of phenolic compounds by activated carbon-a critical review. Chemosphere 58: 1049-1070.
2. Guocheng LÜ, Jiao HAO, Liu LIU, Hongwen MA, Qinfang FANG, et al. (2011) The Adsorption of Phenol by Lignite Activated Carbon. Chinese Journal of Chemical Engineering 19: 380-385.
3. Srivastava VC, Prasad B, Mishra IM, Mall ID, Swamy MM, et al. (2008) Prediction of Breakthrough Curves for Sorptive Removal of Phenol by Bagasse Fly Ash Packed Bed. Ind. Eng. Chem. Res. 47:1603-1613.
4. Hameed BH, Tan IAW, Ahmad AL (2008) Adsorption isotherm, kinetic modeling and mechanism of 2, 4, 6 -trichlorophenol on coconut husk-based activated carbon. Chemical Engineering Journal 144: 235-244.
5. Su-Hsia Lin, Ruey-Shin Juang (2009) Adsorption of phenol and its derivatives from water using synthetic resins and low-cost natural adsorbents: A review. Journal of Environmental Management 90: 1336-1349.
6. Abdelwahab O, Amin NK (2013) Adsorption of phenol from aqueous solutions by Luffa cylindrica fibers. Kinetics, isotherm and thermodynamic studies. Egyptian Journal of Aquatic Research 39: 215–223.
7. Rodriguez-Reinoso F (1997) Activated carbon: Structure characterization preparation and applications. In: Marsh H, Heintz EA, Rodriguez-Reinoso F, (Eds.), Introduction to Carbon Technologies Chapter 2: 35.
8. ISI (1989) Activated carbon powdered and granular-methods of sampling and tests IS 877. New Delhi: Bureau of Indian Standards.
9. Eaton AD, Clesceri LS, Greenberg AE (2005) Standard methods for the examination of water and wastewater. (21st edition), Washington DC, USA: APHA.
10. A.I. Vogel., 1969. A text book of quantitative inorganic analysis. 3rd ed., London: ELBS.
11. Saeed A, Iqbal M, Holl WH (2009) Kinetics equilibrium and mechanism of Cd^{2+}removal from aqueous solution by mungbean husk. Journal of Hazardous Materials 168: 1467-1475.
12. Boehm (2002) Surface oxides on carbon and their analysis: a critical assessment. Carbon 40: 145-149.
13. Kilic M, Varol EAM, Putun AE (2011) Adsorptive removal of phenol from aqueous solution on activated carbon prepared from tobacco residues equilibrium, kinetics, and thermodynamics. Journal of Hazardous Materials 189: 397-403.
14. Tan IAW, Ahmad AL, Hameed BH (2009) Adsorption, is other mskinetics, thermodynamics and desorption studies of 2, 4, 6-trichlorophenol on oil palm empty fruit bunch-based activated carbon. Journal of Hazardous Materials 164: 473-482.
15. Dutta S, Basu JK, Ghar RN (2001) Studies on adsorption of p-nitrophenol on charred saw-dust. Separation and Purification Technology 2: 227-235.
16. Liu T, Li YH, Du Q, Sun J, Jiao Y, et al. (2012) Adsorption of methylene blue from aqueous solution by grapheme. Colloids Surfaces B 90: 197-203.
17. Yanhui L, Qiuju D, Tonghao L, Jianku S, Yuqin J, et al. (2012) Equilibrium, kinetic and thermodynamic studies on the adsorption of phenol onto grapheme. Materials Research Bulletin 47: 1898-1904.
18. Nadavala SK, Swayampakula K, Boddu VM, Abburi K (2009) Biosorption of phenol and o-chlorophenol from aqueous solutions on to chitosan calcium alginate blended beads. Journal of Hazardous Materials 162: 482-489.

19. Kumar NS, Min K (2011) Phenolic compounds biosorption onto *Schizophyllum commune* fungus: FTIR analysis, kinetics and adsorption isotherms modeling. Chemical Engineering Journal 168: 562-571.

20. Altenor S, Carene B, Emmanuel E, Lambert J, Ehrhardt JJ, et al. (2009) Adsorption studies of methylene blue and phenol onto vetiver roots activated carbon prepared by chemical activation. Journal of Hazardous Materials 165: 1029-1039.

21. Vadivelan V, Vasanth Kumar K (2005) Equilibrium kinetics mechanism and process design for the sorption of methylene blue onto rice husk. Journal of Colloid and Interface Science 286: 90-100.

22. Mall ID, Srivastava VC, Agarwal NK, Mishra IM (2005) Removal of Congo red from aqueous solution by bagasse fly ash and activated carbon: Kinetic study and equilibrium isotherm analyses. Chemosphere 61: 492-501.

23. Mall ID, Srivastava VC, Agarwal NK (2006) Removal of Orange-G and Methyl Violet dyes by adsorption onto bagasse fly ash - Kinetic study and equilibrium isotherm analyses. Dyes and Pigments 69: 210-223.

24. Srivastava VC, Swamy MM, Mall ID, Prasad B, Mishra IM, et al. (2006) Adsorptive removal of phenol by bagasse fly ash and activated carbon: Equilibrium kinetics and thermodynamics. Colloids and Surfaces A: Physicochemical and Engineering Aspects 272: 89-104.

25. Boyd GE, Adamson AE, Meyers LS (1947) The exchange of adsorption ions from aqueous solutions by organic zeolites II kinetics. Journal of the American chemical society 69: 2836-2848.

26. Kalavathy MH, Karthikeyan T, Rajgopal S, Miranda LR (2005) Kinetic and isotherm studies of Cu (II) adsorption onto H3PO4-activated rubber wood sawdust. Journal of Colloidal and Interface Science 292: 354-362.

27. Kumar KV, Ramamurthi V, Sivanesan S (2006) Biosorption of malachite green, a cationic dye onto Pithophora sp fresh water algae. Dyes and Pigments 69: 102-107.

28. Mondal MK, Singh S, Umareddy M, Dasgupta B (2010) Removal of Orange G From aqueous solution by hematite: Isotherm and mass transfer studies. Korean Journal of Chemical Engineering 27: 1811-1815.

29. Song X, Pan Y, Wu Q, Cheng Z, Ma W, et al. (2011) Phosphate removal from aqueous solutions by adsorption using ferric sludge. Desalination 280: 384-390.

30. Langmuir I (1916) The constitution and fundamental properties of solids and liquids.Chem A J Soc 38: 2221-2295.

31. Tempkin MI, Pyzhev V (1940) Kinetics of ammonia synthesis on promoted iron catalysts Acta Phys. Chim. USSR 12: 327-356.

32. Helfferich F (1962) Ion-Exchange, McGraw Hills, New York, USA.

33. Hu X, Wang J, Liu Y, Long F, Zeng X, et al. (2011) Adsorption of chromium (VI) by ethylenediamine modified cross-linked magnetic chitosan resin: isotherms kinetics and thermodynamics Journal of Hazard. Mater. 185: 306-314.

34. Parfitt GD, Rochester CH (1983) Adsorption from Solution at the Solid/Liquid Interface. Academic Press Orlando.

35. Jain AK, Gupta VK, Jain S (2004) Removal of chlorophenols using industrial wastes. Environ Sci Technol 38: 1195-1200.

36. Roig MG (2008) Sorption Processes in Kennedy JF, Cabral JMS. Recovery Processes for Biological Materials Wiley Chic ester 15: 369-414

37. Liu X, Zhang L (2015) Removal of phosphate anions using the modified chitosan beads: Adsorption kinetic isotherm and mechanism studies. Powder Technology 277: 112-119.

38. Singh S, Srivastava CV, Mall DI (2009) Fixed-bed study for adsorptive removal of furfural by activated carbon. Colloids and Surfaces A: Physicochem. Eng. Aspects 332: 50-56.

39. Young, DM, Crowell AD (1962) Physical Adsorption of Gases. Butterworths London.

40. Lagergren S (1898) Zur theories der sogenannten adsorption geloster stoffe. Kungliga Svenska Vetenskapsak ademines Handlingar 24: 1-39.

41. Weber WJ, Morris JC (1963) Kinetics of Adsorption on Carbon from Solution. Journal of Sanitary Engineering Division ASCE 89: 31-59.

42. Cheung CW, Porter JF, McKay G (2002) Sorption kinetics for the removal of copper and zinc from effluents using bone char. Separation and Purification. Technology 19: 55-64.

43. Onal Y (2006) Kinetics of adsorption of dyes from aqueous solution using activated carbon prepared from waste apricot. Journal of hazardous materials 137: 1719-1728.

44. Aharoni C, Sideman Hoffer SE (1979) Adsorption of phosphate ions by colloid ion-coated alumina. Journal of Chemical Technology and Biotechnology 29: 404-412.

45. Ho YS, McKay G (1999) Pseudo-second order model for sorption processes Process Biochemistry 34: 451-465.