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Removal of catechol from aqueous solutions by adsorption using low cost activated carbon prepared from *Eichhornia crassipes*

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ABSTRACT

The adsorptive removal of catechol employing *Eichhornia crassipes* (water hyacinth) for preparation of activated carbon was executed. Response surface methodology (RSM) was used for the optimization of the process variables for preparation of adsorbent and removal of catechol. Weight ratio of activating agent to water hyacinth (1.0–1.5 ml/g), temperature (400°C–500°C) and time of carbonization (50–100 min) were selected as the dependent parameters during optimization of carbonizing condition and percentage removal of prepared sample was the response. The optimized parameters for the carbonization was found at 400°C for 53 min having a weight ratio of activating agent to water hyacinth taken at 1.04:1. Furthermore, the conditions for removal of catechol using charred water hyacinth (CWH) were optimized. For this, the initial concentration of catechol (25–100 mg/L), weight of CWH (0.5–1.5 g/L), pH (4–10) and temperature (30–40°C) were considered as independent parameters and percentage removal of catechol as the response. The maximum removal of 82% catechol was attained at an initial concentration of 100 mg/L under the optimized parameters of pH 4 at 35°C at the weight of CWH 1.5 g which can be harnessed for adsorption mediated wastewater treatment. The adsorption follows pseudo second order kinetics and it was seen that this technique could be used effectively for large scale adsorption processes.

Keywords: Adsorption; Catechol; Response surface methodology; Kinetics, Langmuir isotherm, Freundlich isotherm

1. Introduction

Catechol is an important chemical most commonly used as the basic raw material for the preparation of photographic films, insecticides polymerization inhibitors, lubricating oils, anti-oxidants and pharmaceuticals. [1–4]. Catechol, which is a refractory compound having mild affinity for transition metals, is released along with the industrial effluents water which is drained from bituminous shale and effluent from coal-tar chemical production [5]. These industrial effluents, which are toxic even at low concentration are often discharged into aquatic bodies cause harm to various life forms.

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Catechol is a phenolic compound which is more toxic in comparison to phenol and resorcinol [6,7]. International agency for research on cancer (IARC) has recognized that catechol impart the carcinogenic impacts to humans [8]. Catechol has been classified as priority contaminants by EPA, USA owing to recalcitrance, toxicity and its believed carcinogenicity [9,10]. Nevertheless, catechols are toxic organic pollutants which are present in the environment owing to their extensive use as biocides in industries and in agricultural sector. Higher concentrations of substituted catechols results in the uncoupling of NADH that results in the generation of hydrogen peroxide [11]. Moreover, reactions with catechols severely cause numerous irreparable damages to several biomolecules such as DNA, proteins and membranes [12]. Hence, abatement of catechol present in the wastewater is a concern which requires urgent attention. Researchers over the years have developed various technologies to remove catechol from their aqueous solution. This comprises of technologies like adsorptive micellar flocculation, destructive oxidation, biotechnlogical methods, membrane technology and adsorption on to organic as well as inorganic compounds. Adsorption process carried over the surface of activated carbon is considered as the most useful strategy among all the techniques owing to its several attributes such as being economical, faster, efficient and eco-benign [13]. Adsorption process edges over other processes as it is a sludge free process which provide efficient removal of toxic contaminants from their aqueous solutions. To carry out adsorption and separation processes industrially, activated carbons are extensively used because of its appreciable efficiency for adsorption of the organic pollutants from industrial effluents. Conversely there are certain loopholes associated to its use as they are usually expensive, and leading to the operational incumbencies during activated carbon regeneration, pore blocking and hygroscopic nature [14].

Water hyacinth has been evaluated for the preparation of activated carbon due to its wide capability to survive and grow in the heavily polluted water and accumulate high capacity of metal ions [15]. Water hyacinth is chiefly considered as obnoxious weed whose disposal from the aquatic bodies pose a major challenge. The preparation of activated carbon from water hyacinth will turn it into a valuable product and provide feasible solution for its disposal and adsorption of toxic organic pollutants from the industrial effluents. Moreover, fast and extensive growth of water hyacinth makes it easily and abundantly available for its use as raw material for adsorbent preparation. This will promote sustainable development through the application of readily available, low cost replacement to the expensive commercial adsorbents present in the market [16]. Water hyacinth has widely been recognized as the potential adsorbent for the removal of various harmful pollutants particularly in various dyes [17–22].

The main aim of this investigation is to valorize the water hyacinth for the synthesis of activated carbon and investigating adsorption of catechol from aqueous solution onto the prepared activated carbon. The detail adsorption behavior was carried out by the fitting the experimental data in the isotherm equations and kinetic models.

2. Materials and methods

2.1. Catechol and water hyacinth

Ortho-phosphoric acid (of 85% purity) and catechol, which was of analytical grade, was received from Merck, Mumbai, India. By dissolving required amount of catechol in distilled water without any pH adjustment, the stock solution of catechol was prepared. Water hyacinth was collected from the nearby local lakes and ponds of Durgapur district, West Bengal (India).

2.2. Design of experiments

The process was optimized using response surface methodology taking into account that the response under interest is influenced by various variable inputs [23,24]. The process optimization is mainly performed by three key steps viz., carrying out the statistically designed experiments, evaluating the coefficients obtained from the mathematical model and finally interpreting the responses along with predicting the suitability of the model [25].

2.3 Preparation of activated carbon and optimization of catechol removal applying charred water hyacinth (CWH) by RSM

Water hyacinth was thoroughly cleaned with running water followed by drying in the sunlight for 2 to 3 consecutive days. Subsequently, the dried water hyacinth was chopped and fractioned into pieces of size 2–3 cm in size and was finely ground by a mixer and grinder. The ground particles were sieved and particle size < 90 µm were collected followed by impregnation with suitable proportion of the ortho-phosphoric acid used as an activating agent.

Optimization of important process variables for carbonization of water hyacinth included weight ratio of finely grounded activating agent to water hyacinth (1.0–1.5 ml/g), temperature for the carbonization (400°C–500°C) and time period (50–100 min) 20 statistically designed were carried out with various combination of independent variables, as suggested by the design expert software. RSM provides a quantified relation between the independent variables on which the process behaviour depends and the process output or behaviour as shown in Eq. (1).

$$Y = f\left(x_1, x_2, x_3 \ldots x_n\right) \tag{1}$$

where Y is system behavior or system response because of the various independent parameter x_1, x_2, x_3 etc. The independent variables are known as factors [26].

The process of carbonization was carried out in a muffle furnace running under an elevated temperature maintained for a specified time period. The carbonized water hyacinth was washed until the neutral pH was attained. The charred material so obtained was dried overnight under ambient conditions to obtain the charred water hyacinth (CWH) activated carbon powder. The percentage removal of catechol obtained after each run was analyzed and the response obtained was correlated with three independent parameters using an empirical second degree polynomial equation [Eq. (2)] such as

$$Y = \beta_o + \sum_{i=1}^{n} \beta_i x_i + \left(\sum_{i=1}^{n} \beta_{ii} x_i \right)^2 + \sum_{j=i+1}^{n} \sum_{j=j+1}^{n} \beta_{ii} x_i x_j + \epsilon \quad (2)$$

where β_o is the constant coefficient, β_i is the linear coefficient, β_{ij} is the interaction coefficients, β_{ii} is the quadratic coefficients.

2.4. *Response surface methodology (RSM) for the optimization of catechol removal using CWH*

The interactive impact of several process parameters to remove the catechol using CWH was assessed using RSM. The maximum (+1) and minimum (−1) level of these process variables were varied under the selected range such as initial concentration of catechol (50–100 mg/L), weight of CWH (0.5–1.5 g/L), pH (4–10) and temperature (30°C–40°C), respectively. The statistical experimental were performed as suggested by the Design Expert software along with the values of responses.

2.5. *Scanning electron microscope (SEM) and Fourier Transform Infra-Red (FTIR)*

The surface morphology of the CWH before and after performing the catechol adsorption was investigated by SEM and FTIR analysis. The samples were spread onto the carbon tape and gold coated for imaging by SEM (Perkin, Elmer USA). For FTIR (Bruker Tensor spectrophotometer, Vertex Series, Opus, USA) spectroscopy, the samples were finely ground and mixed well with KBr to prepare the pellets before analysis .The spectra were analyzed in the range of 4000-400 cm^{-1} averaging 20 scans in the absorbance mode.

2.6. *Kinetic study*

The kinetics of the adsorption were studied to understand the underlying mechanism of adsorbate (catechol) uptake CWH as adsorbent and determination of the various kinetic parameters that are of great importance in the designing of a continuous reactor like Fluidized bed reactor and Packed bed reactor. For this, catechol solutions of different concentrations were prepared after dilution with appropriate content of distilled water from the stock solution. Different concentrations of CWH was added to the catechol solution in a batch reactor. The solution was continuously stirred to minimize the mass transfer resistance to facilitate adsorption. Samples were periodically taken out and filtered under vacuum to separate adsorbent for carrying out further analysis. Process parameters were set at optimized condition as indicated by RSM - pH 4 and weight of adsorbent 1.5 g/L with initial concentration of catechol varying from 25 to 100 mg/L. The concentration of residual catechol after each treatment period was determined spectrophotometrically at OD_{275nm} employing UV–Visible Spectrophotometer (Agilent Model Cary 7000) and 4-aminoantipyrene method [6,27].

2.7. *Equilibrium study*

For equilibrium study various initial concentration of catechol (25 mg/L–100 mg/L) was chosen. 0.5 g of CWH was added to each flask and placed in a BOD incubator for overnight with shaking conditions. Equilibrium studies were carried out at two different temperatures (28°C and 35°C). Before analysis, the samples were centrifuged to obtain the clear supernatant for residual catechol analysis. Langmuir, Freundlich and Temkin adsorption isotherm model were studied.

4. Results and discussion

4.1. *Optimization of carbonization process and synthesis of charred water hyacinth (CWH)*

Three operating parameters – weight ratio of activating agent to the amount of water hyacinth, temperature and time required for carbonization were optimized by RSM using Design Expert software taking removing power of charred sample as response. Table 1 illustrates the removal capacity of every sample of CWH achieved at defined experimental conditions as indicated by the software. For regression analysis, as per the suggestion of the software, with no transformation and quadratic model was used for fitting the data. Equation in terms of coded factors is shown below

$$\begin{aligned} R_1 = 46.27 + 0.6 \times A - 185 \times B - 1.88 \times C + 3.76 \times A \\ \times B + 6.67 \times A \times C + 1.22 \times B \times C \end{aligned} \quad (3)$$

where R_1 = Percentage removal of catechol, A = weight ratio of activating agent to water hyacinth, B = carbonization temperature (°C), C = carbonization time (min).

Table 1
Experiments suggested for preparation of charred water hyacinth and their corresponding response

Run	Time (min)	Temperature (°C)	Weight ratio (ml/g)	Removing power (%)
1	117.04	450.00	2.00	46.25
2	75.00	450.00	2.00	45.56
3	32.96	450.00	2.00	50.00
4	100.00	500.00	1.00	31.54
5	100.00	500.00	3.00	56.32
6	100.00	400.00	3.00	47.30
7	75.00	365.91	2.00	52.56
8	75.00	450.00	2.00	45.62
9	100.00	400.00	1.00	39.91
10	50.00	500.00	1.00	48.47
11	75.00	450.00	3.68	43.75
12	75.00	450.00	2.00	45.44
13	75.00	534.09	2.00	42.61
14	75.00	450.00	2.00	47.52
15	75.00	450.00	2.00	46.35
16	50.00	400.00	1.00	59.36
17	50.00	500.00	3.00	44.21
18	50.00	400.00	3.00	42.44
19	75.00	450.00	0.32	45.39
20	75.00	450.00	2.00	44.75

From ANOVA, the adjoined influence of weight ratio of activating agent to water hyacinth and carbonization temperature was observed to be significant. The response surface plot validating the cumulative effect of these two factors on the removal efficiency is depicted in Fig. 1 which illustrates that temperature has appreciable impact on the success of carbonization. Removal efficiency of the adsorbent was observed to be maximum at 400°C under constant value of weight ratio. Charred sample enhances the removal rate from 40% to 55% when the temperature declined from 500°C to 400°C under the particular weight ratio of 1 and 3 respectively. Removal power of charred sample significantly increased from 40% to 55% at 400°C when the weight ratio reached 1.00. With the decline in the temperature and weight ratio, the removal efficiency goes on increasing and vice-versa. Both time and temperature impart significant direct influence on carbonization. The fitting of models were analyzed after the determination of coefficients (R^2) and adjusted R^2 (adj R^2) values. The estimated values of R^2 (0.915) and R^2_{adj} (0.876) evidenced appreciable correlation between the actual and predicted responses. It is further concluded that all the three factors have cumulative influence on the carbonization process. The maximum adsorption was attained at the optimized proportion of weight ratio, temperature and time are 1.04:1 at 400°C for 50 min, respectively.

4.2. Optimization of conditions for the removal of catechol using charred water hyacinth

Four input parameters – the initial concentration of catechol, weight of CWH, pH and temperature were varied and sample experiments were performed as specified by the Design Expert software. At each of the experimental condition, the percentage removal of catechol were determined and the results have been summarized in Table 2. As suggested by the software, quadratic model was employed for fitting the response and no transformation was required. The regression equation [Eq. (4)] which represents the catechol uptake by the adsorbent is presented in terms of coded factors below.

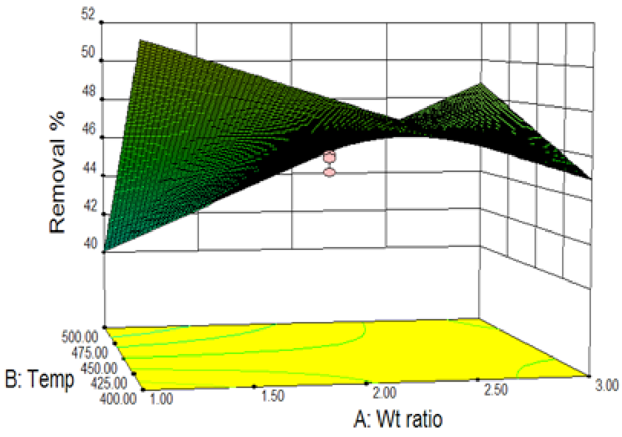

Fig. 1. Combined effect of temperature of carbonization & weight ratio on removing power for preparation of CWH.

Table 2
Experiments suggested by RSM at different values of parameters for removal of catechol and their corresponding response

Run	Initial concentration of Catechol (mg/L)	Weight of CWH (g)	pH	Temperature (°C)	Percentage removal of Catechol
1	50.00	1.50	10.00	30.00	70.21
2	100.00	0.50	4.00	40.00	73.00
3	50.00	0.50	4.00	30.00	79.80
4	100.00	1.50	4.00	30.00	84.10
5	100.00	0.50	10.00	30.00	54.60
6	50.00	1.50	4.00	40.00	88.80
7	75.00	1.00	7.00	35.00	72.40
8	75.00	1.00	1.00	35.00	91.50
9	75.00	1.00	7.00	35.00	71.45
10	50.00	0.50	10.00	40.00	59.64
11	50.00	0.50	10.00	30.00	60.40
12	100.00	1.50	10.00	40.00	63.50
13	50.00	1.50	4.00	30.00	89.10
14	125.00	1.00	7.00	35.00	65.00
15	75.00	1.00	7.00	35.00	79.34
16	75.00	1.00	7.00	35.00	79.34
17	100.00	1.50	10.00	30.00	63.90
18	50.00	0.50	4.00	40.00	80.00
19	75.00	1.00	7.00	35.00	71.70
20	75.00	1.00	7.00	25.00	72.50
21	100.00	0.50	4.00	30.00	77.80
22	75.00	1.00	7.00	45.00	74.15
23	75.00	1.00	7.00	35.00	84.56
24	75.00	2.00	7.00	35.00	81.67
25	75.00	0.02	7.00	35.00	62.10
26	25.00	1.00	7.00	35.00	77.40
27	100.00	1.50	4.00	40.00	83.35
28	50.00	1.50	10.00	40.00	70.20
29	75.00	1.00	13.00	35.00	52.80
30	100.00	0.50	10.00	40.00	54.10

$$\begin{aligned} R_1 = {} & 72.95 - 2.86 \times A + 4.71 \times B - 9.87 \times C - 0.17 \times D - 0.19 \\ & \times A \times B - 0.31 \times A \times C - 0.35 \times A \times D + 0.27 \times B \times C \\ & + 0.28 \times B \times D + 0.25 \times C \times D \end{aligned} \tag{4}$$

where R_1 = percentage removal of catechol, A = catechol conc. (mg/L), B = weight of CWH (g/L), C = pH, D = temperature (°C)

ANOVA illustrated that weight of CWH and pH has profound impact on the removal of catechol. The interaction between the weight of CWH and pH has significant effect on the process of adsorption. Hence, response surface plots depicting the effects due to interactions between these two parameters were investigated in depth.

Fig. 2a, b demonstrate that the percentage removal of catechol moves on increasing when the pH decreases and the adsorbent weight increases. Catechol adsorption onto CWH

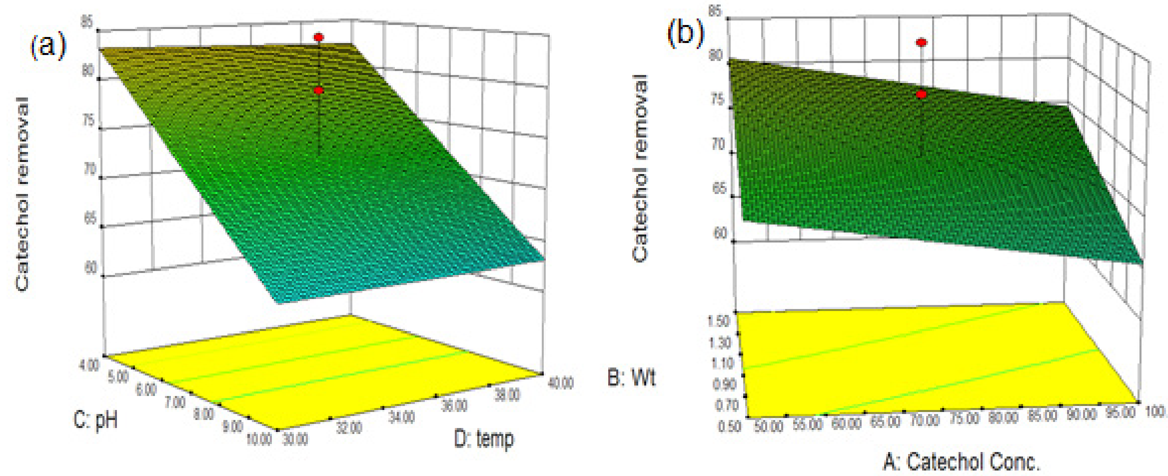

Fig. 2. Combined effect of (a) initial concentration and weight of CWH on percentage removal of catechol (b) effect of pH and temperature on percentage removal of catechol.

increases as pH of the solution increases and attains a maximum of 81% at pH 4 at 35°C. The variation of removal of Catechol with pH is demonstrated in Fig. 3. The pH of the solution effects the charge on the surface of the adsorbents due to the dissociation of functional groups that are present on the active sites of the adsorbent leading to the migration of charged contaminants towards the adsorption sites which influence catechol adsorption [28]. The response surface plots illustrating the cumulative impact of temperature and initial concentration indicates that the percentage removal of catechol varied from 76% to 68% when the temperature changes from 30°C to 40°C. A similar trend was seen when the cumulative impact of temperature along with weight on percentage removal of catechol was studied. Response surfaces depicting cumulative effect of pH and temperature on removal rate of catechol was studied. With the increase in temperature from 30°C to 40°C and the pH from 4 and 10 the removal efficiency declined from 81% to 61%. This suggests that pH has paramount impact on the removal of catechol.

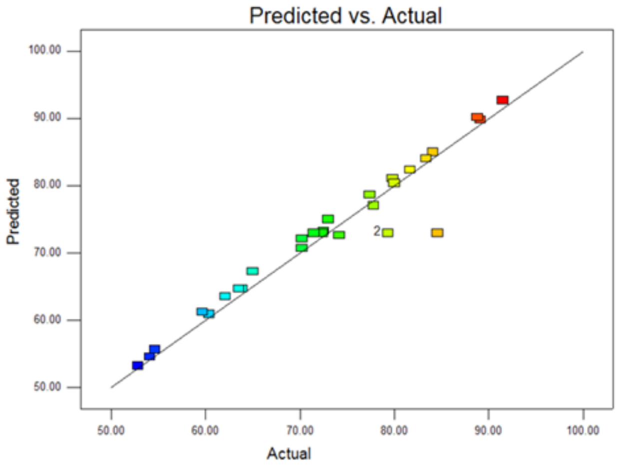

Fig. 3. Plot of actual response versus predicted response for removal of catechol.

The theoretical model was solved by the software to predict the response while the actual response was determined by experimental analysis. The values of coefficients viz., R^2 and R^2_{adj} were estimated to be 0.9528 and 0.9088 respectively. The optimized conditions were achieved when 100 mg/L of catechol was treated with 1.5 g of CWH at pH 4 and 35°C of temperature. Under this condition a maximum of 82% catechol removal was achieved.

Fig. 3 showed the correlation between the actual and predicted responses. For each of the experimental run, actual values were evaluated by the conducting the experiments while the predicted values were determined from the model equation. The experimental value of catechol removal (82%) matches appreciably well with the theoretical percentage removal of catechol (88.4%) under the same condition. The adsorption kinetics explains the adsorbate uptake over the activated carbon and control of the equilibrium time. The kinetic models such as pseudo-first order and pseudo-second order were applied to study the kinetics of the adsorption process.

4.3. Variation of catechol removal with the three independent parameters

The adsorptive intake of catechol onto CWH is largely dependent on pH of the catechol solution, the time of reaction and the adsorbent dose. Fig. 4 shows the variation of removal of catechol with time. While all the parameters influencing catechol removal were kept constant as the optimum condition, the time was varied and initial catechol concentration was kept at at 25, 50, 75 and 100 mg/L. The study reveals that the catechol degradation increases with time till 55 min, after which it is fairly constant. It is seen that the trend is more or less similar for different initial concentration of catechol solution. At that equilibrium point (t = 55 min), the quantity of catechol desorbed was similar with the catechol quantity being adsorbed on the surface of CWH. The equilibrium time displayed the significance in the maximum adsorptive uptake of the catechol

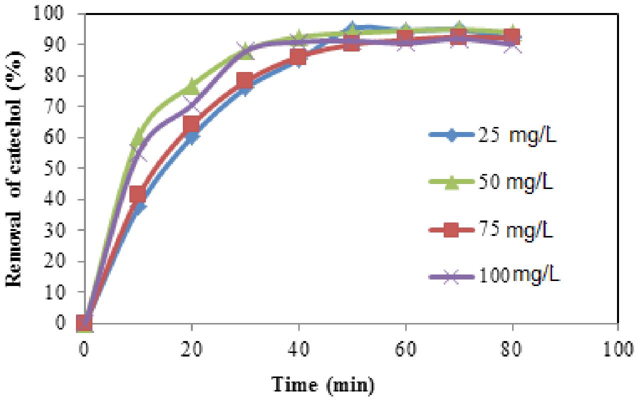

Fig. 4. Time course of percentage removal of catechol with initial concentration of catechol.

under the operating conditions. The catechol adsorption was rapid during the initial phases of the contact period, and henceforth turned gradually slow on reaching the equilibrium. This might be due to the phenomenon that numerous unoccupied sites were available for the adsorption during the early phase and time interval, the left over unfilled sites were challenging to be occupied owing to the action of repulsive forces acting between the solute molecules adsorbed on the surface of activated carbon. At maximum of 95% removal was achieved at equilibrium when the solution was reacted with 1.5 g CWH, pH 4 and temperature 35°C.

In Fig. 5 the percentage removal of catechol was plotted with time with varying adsorbent concentration to evaluate the impact of adsorbent quantity on the adsorptive uptake of catechol. The initial concentration of catechol in the solution (100 mg/L), pH of the system (4) and temperature (35°C) were kept constant. Higher concentration of adsorbent improves the removal rate compared to the lesser quantity. This might be due to the fact that more quantity of adsorbent facilitates more surface area availability as adsorption is basically a surface phenomenon. This is mainly due to the greater surface area and hence the presence of more active adsorption sites [29]. When 100 mg/L of catechol solution was treated with 1 g CWH, a maximum of 95.5% removal was measured at 35°C and equilibrium time of 55 min.

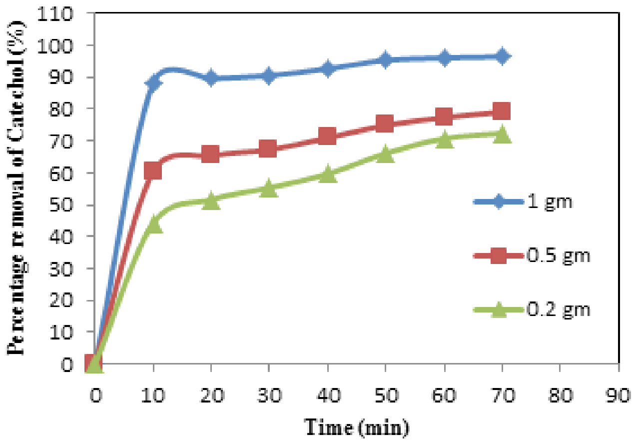

Fig. 5. Time course of percentage removal of catechol with weight of CWH.

Fig. 6 depicted the influence of pH on the adsorptive removal of catechol by the activated carbon derived from CWH. The adsorptive removal of catechol goes on decreasing with the increment in the pH from 4 to 11. The highest catechol removal (85.2%) was observed at pH 4 at 100 mg/L of initial concentration of catechol after 12 min of reaction. Catechol is a weakly acidic in nature having the pH value below its pKa of catechol. This results in predominating the dispersion interactions as catechol was dissociated [30]. The higher quantity of unionized species of organic compounds weakens the repulsion between the activated carbon surface and the catechol molecules. This results in increasing the electrostatic attraction between the catechol moieties and the available adsorption sites. Furthermore, the competition between the OH^- ions and other ionic molecules of catechol might occur which diminished the removal of catechol. At low pH, the dominating protonated phenolic compounds appeared more absorbable compared to the ionized forms. These results are in agreement with the trend shown during the adsorption of catechol on the activated carbon derived from coconut shell-based [31] and activated clay [32].

4.4. Kinetic study

A detailed kinetic investigation was performed under varying range of initial concentration of catechol (25–100 mg/L) while CWH dosage and pH was maintained as mentioned in the optimum condition. The determination of kinetic parameters will facilitate the designing of continuous adsorption unit and help us to design units which would enhance the underlying mechanism of the adsorption process. The removal of the catechol from aqueous solution by adsorption was analyzed at various time periods.

4.4.1. Pseudo-first-order kinetic model

The pseudo-first-order kinetic model has been extensively used to investigate the associated adsorption kinet-

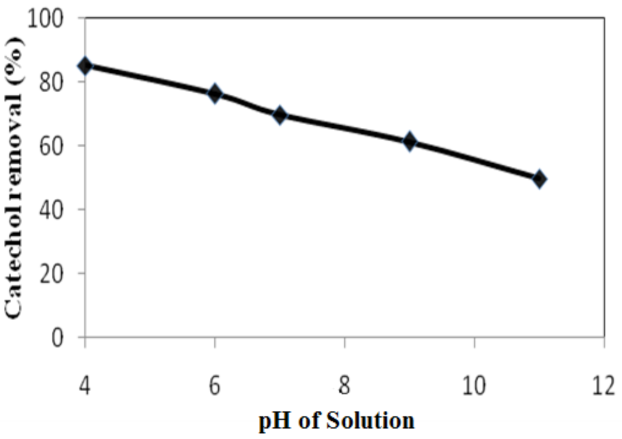

Fig. 6. Effect of solution pH on catechol removal at 35°C.

ics. Eq. (4) for pseudo-first-order model is shown below which was given by Langergren and Svenska [33] as:

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{5}$$

where q_e and q_t (mg/g) are defined as the amounts of adsorbate adsorbed at equilibrium and at any time, t (min) respectively and k_1 (min^{-1}) is defined as the adsorption rate constant.

The plot of ln ($q_e - q_t$) versus t depicts a straight line having the slope of k_1 and ln q_e as the intercept. Table 3 listed the values of k_1 and correlation coefficient (R^2) derived from the plots for catechol uptake onto the surface of activated carbon at 35°C for various initial catechol concentration in the solution. The R^2 values were comparatively lesser that varied between 0.479 to 0.801 for the range of initial concentration from 25 to 100 mg/L of catechol. This indicated that the values of q_e and q_t do not fir properly into the plot of ln($q_e - q_t$) vs. t. This further revealed that the process of adsorption of catechol on the surface of activated carbon did not follow the first-order reaction.

4.4.2. Pseudo-second-order kinetic model

The pseudo-second-order equation [34] based on equilibrium adsorption is expressed in terms of Eq. (4) as shown below:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

where k^2 (g/mg h) is the rate constant of pseudo-second-order adsorption.

A straight line was obtained when the linear plot of t/q_t versus t was drawn having $1/q_e$ as the slope and $1/k^2q^2_e$ as the intercept. This assisted in evaluation of the behavior over the wide spectrum of adsorption process. The linear plot of t/q_t versus t, showed an appreciable correlation existing between the experimental data and the calculated values of q_e (Table 3). Additionally, the values of correlation coefficient for the second-order kinetic model nearly attained unity at all the catechol concentrations. This suggested the applicability of the second-order kinetic model to explain the mechanism of adsorption of catechol onto the surface of prepared activated carbon from water hyacinth.

4.5. Adsorption isotherm

The equilibrium curves should be adequately studied to optimize the adsorption process. In the present study equilibrium data for adsorptive removal of catechol were fitted into Langmuir, Freundlich, Temkin isotherms model. The linearized form of the equations these adsorption isotherms were used. Langmuir isotherm assumes that the monolayer adsorption onto a surface harbours a finite number of adsorption sites which allows no transmigration of adsorbate across the plane of surface [35]. The linear equation of Langmuir isotherm equation is shown below:

$$\frac{C_e}{q_e} = \frac{1}{Q_o K_L} + \frac{C_e}{Q_o} \tag{7}$$

where C_e (mg/L) is the equilibrium concentration of the catechol, q_e (mg/g) is the amount of catechol adsorbed for each unit weight of adsorbent, Q_o and K_L are Langmuir constants which explains the adsorption power and rate of adsorption, respectively. The plot between C_e/q_e versus C_e furnished a straight line having slope of $1/Q_o$ and intercept $1/Q_oK_L$. The parameters of Langmuir isotherm are summarized in Table 4.

Freundlich model is frequently used to describe the adsorption on a heterogeneous surfaces or in other words surfaces containing binding regions of wide-ranging affinities. It is based on the assumption that the binding sites

Table 4
Parameters of Langmuir, Freundlich and Temkin isotherm models

Langmuir Isotherm					
28°C			35°C		
Q_o (mg/g)	K_L (1/mg)	R^2	Q_o (mg/g)	K_L (1/mg)	R^2
0.042	29.24	0.997	0.073	28.37	0.0957
Freundlich isotherm					
28°C			35°C		
n	KF (mg/g) (L/mg)$^{1/n}$	R^2	n	KF (mg/g) (L/mg)$^{1/n}$	R^2
3.13	1.69	0.905	1.729	1.500	0.948
Temkin isotherm					
28°C			35°C		
A (L/g)	B (mg/L)	R^2	A (L/g)	B (mg/L)	R^2
6.118	4.240	0.974	4.957	2.934	0.957

Table 3
Pseudo first-order and pseudo second-order kinetic parameters for the adsorption of catechol onto the CWH at 35°C

C_0 (mg/L)	q_e exp (mg/g)	Pseudo-first-order model			Pseudo-second-order model		
		k_1 (h^{-1})	q_e (cal) mg/g	R^2	k_2 (g/mg h)	q_e (cal) mg/g	R^2
25	22.49	0.82	11.33	0.768	0.40	20.75	0.997
50	44.66	0.77	13.77	0.479	1.51	40.66	0.999
75	69.46	0.60	17.26	0.626	0.0.5	65.23	0.999
100	86.32	1.32	31.79	0.801	0.17	85.42	0.999

with high strength affinity are occupied first and thereafter the binding strength steadily declines with the increasing extent of site occupation [36]. The logarithmic form of Eq. (8) of Freundlich isotherm is shown below:

$$\log q_e = \log K_F + \left(\frac{1}{n}\right)\log C_e \tag{8}$$

where K_F is the Freundlich constant with n indicating the degree of success in the adsorption process and K_F (mg/g (L/mg)1/n) is defined as the adsorption ability of the adsorbent. K_F is termed as the adsorption or distribution coefficient which represents the quantity of catechol adsorbed onto the surface of activated carbon per unit equilibrium concentration. The slope of 1/n varies between 0 and 1 that exhibit the extent of adsorption rate or surface heterogeneity which turns to more heterogeneous as the value approaches to zero [37]. The value of 1/n being less than one signifies the occurrence of a normal Langmuir isotherm whereas the values above one implies the cooperative adsorption. The plot between log q_e versus log C_e showed a straight line having slope of 1/n and intercept of log K_F. The values of n and K_F at different temperatures are listed in Table 4.

Temkin isotherm [38] contains a factor that predominantly considers the interactions between the adsorbent-adsorbate. This isotherm considers that the process involving the heat of adsorption of all the molecules present in a specific layer would deplete linearly with coverage owing to the interactions between the adsorbent and adsorbate. Such kind of adsorption is well characterized by even distribution of binding energies. Temkin isotherm is expressed in terms of Eq. (9) as shown below:

$$q_e = \left(\frac{RT}{b_T}\right)\ln\left(AC_e\right) \tag{9}$$

where $RT/b_T = B$ (J/mol) is referred as the Temkin constant which is related to heat of sorption. A (L/g) is defined as the equilibrium binding constant related with the maximum binding energy. R is defined as the universal gas constant having the value 8.314 J/mol K and T (K) is termed as the absolute solution temperature. The values of n and K_F at different temperatures are tabulated as shown in Table 4.

4.6. Scanning electron microscope (SEM) analysis

SEM is an important tool for analyzing the detailed surface morphology of an adsorbent. SEM was thoroughly employed for the investigation of surface morphology of prepared CWH samples used before and after adsorption of catechol. Before treatment, the native CWH surface illustrated the presence of rough, uneven and heterogeneous structure with porous structure. The rough surface facilitates in increasing the availability of surface area to carry out the process of adsorption. However, after treatment the porous textural structure did not appear on the surface of catechol loaded CWH surface (Fig. 7). This furnished the appearance of smooth texture of CWH surface after treatment.

4.7. Fourier Transform Infrared (FTIR) analysis

The spectral analysis revealed the nature of interaction and adsorption behavior of CWH. Fourier Transform Infrared (FTIR) spectroscopy detected the alterations in the functional groups existing on the surface of CWH before and after catechol adsorption. The upper spectrum represents the infrared spectrum of CWH before adsorption is presented in Fig. 8a whereas Fig. 8b shows the infrared spectrum of CWH after adsorption. As illustrated in the Fig. 8, the spectra revealed the adsorption behaviour of CWH and the type of interaction that occurred between the adsorbent and the catechol

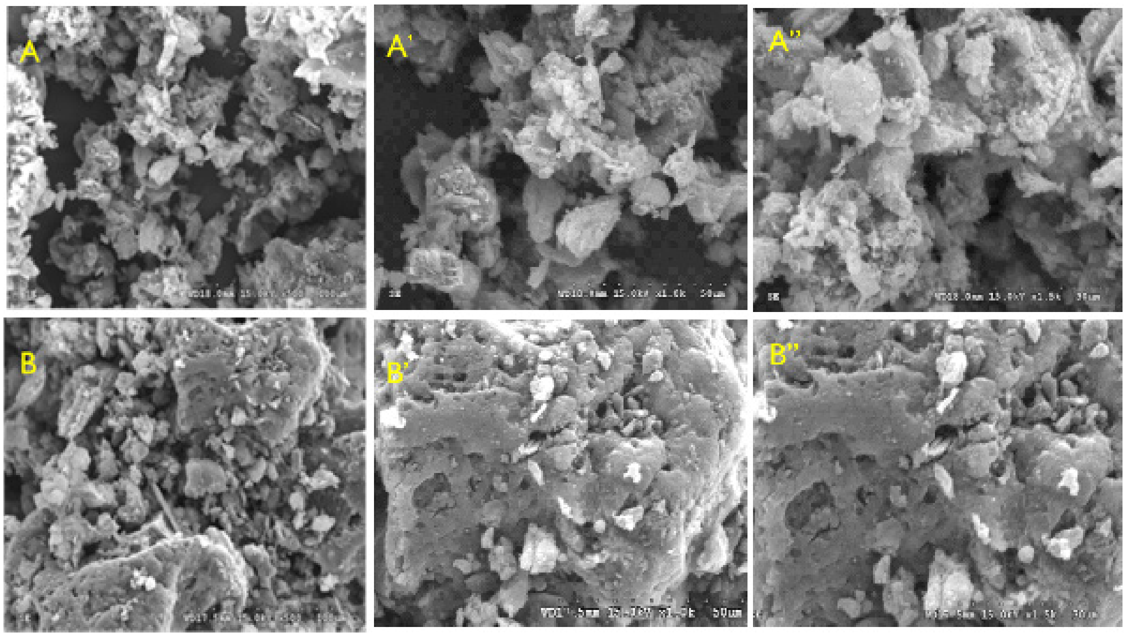

Fig . 7. Scanning electron micrographs of the (A,A',A'') untreated and (B,B',B'') treated adsorbent.

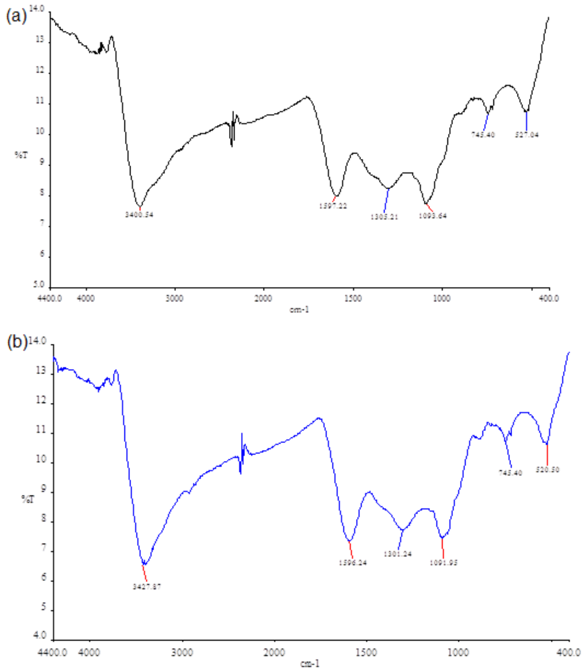

Fig. 8. FTIR spectra of (a) CWH before treatment (b) CWH after treatment.

which is being adsorbed onto the CWH surface. Significant changes in the frequency of the functional groups present on the surface of CWH occurred after catechol adsorption which results in the shifting of peaks in the IR spectrum. Fig 8(a) indicated the occurrence of broad band at 3427 cm^{-1} which corresponds to the stretch vibration of hydrogen-bonded hydroxyl groups. A prominent peak at 1596 cm^{-1} signified the stretching of aromatic ring vibration [39].

5. Conclusion

The present investigation explored the utilization of undesirable weed (Water hyacinth) for the preparation of a potential and viable cost-competent adsorbent to remove of catechol from its aqueous solution. The removal process of catechol was modelled by using response surface methodology (RSM). The maximum removal of 82% catechol at the initial concentration of 100 mg/L were reached under the optimized parameters of pH 4 at 35°C at the weight of CWH 1.5 g which can be harnessed for adsorption mediated wastewater treatment. Langmuir isotherm model was satisfactorily fitted to the equilibrium model. The detailed kinetic evaluation of the data revealed that the adsorption followed pseudo-second-order model. The successful application of water hyacinth to mitigate catechol related pollution also efficiently solves the issue related to the disposal and spread of this unwanted weed. Furthermore, use of Water hyacinth for preparing the activated carbon as potential adsorbents pave the way towards minimizing the expenses of commercial adsorbents attributed to the plenty and ease in the availability of raw materials.

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