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Research Article

Preparation and Characterization of Activated Carbon from Tamarind Seed Coats and its Application for Removal of Organic Pollutants

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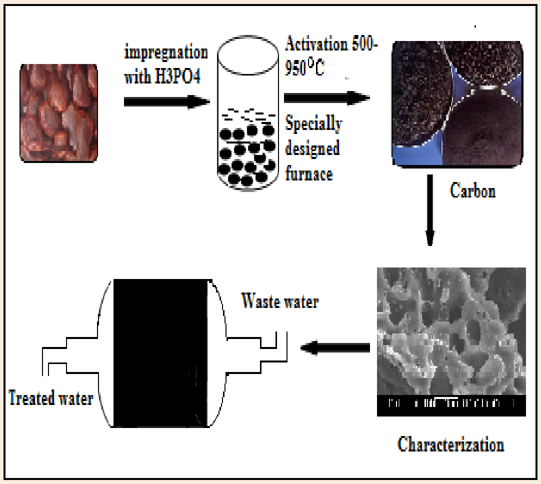
Abstract

In the present study, activated carbon was prepared from tamarind seed shells by chemical activation using orthophosphoric acid as activating agent. The tamarind seed shells were impregnated with orthophosphoric acid in suitable ratio. This impregnated mass was carbonized in a modified muffle furnace at 500-950^0 C. Various process parameters such as ratio of impregnation, temperature of carbonization, time period of carbonization were optimized. The prepared activated carbon was characterized for proximate & ultimate analysis, iodine number, N_2-BET surface area, pore volume, scanning electron microscopy (SEM) and FT-IR spectroscopy. It has been observed from the results that the produced activated carbon has very high iodine number: 2010 mg/g, N_2-BET surface area: 2447 m2/g and pore volume: 1.4003cm3/g. The SEM of activated carbon shows lot of cracks, crevices and different size pores. FT-IR spectra show the presence of various functional groups with predominant presence of phenolic -OH. Phenol adsorption and kinetic studies were carried out to evaluate the adsorption capacity of produced activated carbon in comparison with commercially available Filtrasorb 400(F-400) activated carbon. It has been observed that the produced activated carbon has better adsorption capacity than commercially available F-400 activated carbon.



Keywords: Tamarind seed shells, phenol adsorption and kinetic, chemical activation carbonization

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Introduction

India is the major producer of Tamarind (Botanical name: Tamarindus indica L.) on a large scale. Tamarind is important adjunct/condiments used as sour ingredient in an Indian cookery. India produces about 0.25 million tones of tamarind per annum. The tree produces brown pod like fruits which contain pulp and hard coated seeds. A mature tree may annually produce 150-225 kg of fruits, of which the pulp may constitute 30-55%, the shells and fiber 11-30% and seeds 33-40%. Thus a large quantity of tamarind seed is available as agriculture waste which becomes a serious problem not only in storage but also for disposal. Tamarind seed can be considered as a potential source material for preparation of activated carbon. There are several reports on the preparation of activated carbon from agriculture waste which include number of nutshells such as oil palm shell [1,3], almond shell [2,4,5], coconut shell [6-8], pistachio shell [9], hazelnut shell [5], and other byproducts such as olive stones [10], date stone [11], coffee residue [12], apricot stone [13], peach and cherry stone [2,4], grape seeds [4] and rubber wood sawdust [14].

Activated carbon is a non-graphitic carbonaceous material with high surface area, pore volume and widely used as an adsorbent in chemical and food industry. The principal objective of this study is to prepare a value added activated carbon from tamarind seed shell an agriculture waste material by chemical activation using orthophosphoric acid. This activation is carried out in a single stage carbonization and examines the influence of preparation conditions and optimization of process parameters and to clarify the suitable parameters where optimizations work effectively to increase the surface area of activated carbon. The sample was characterized to analyze its structural and adsorption capacity in comparison with commercially available Filtrasorb F-400 activated carbon.

Experimental

Materials and Method

Tamarind seeds were collected from agriculture industry as a waste material. It is broken to separate out seed shells from seeds. Orthophosphoric acid (H_3PO_4) with a purity of 99.9% (Merck, India) was used as activating agent. Iodine resublimed, Potassium Iodide, Phenol was procured from local market in the purest form.

Method for Preparation of Activated Carbon

Tamarind seed shells were washed with distilled water to remove dust and other unwanted materials. These washed shells were dried in a moisture oven at 108 ± 2^0 C for 24 hours. Dried seed shells were impregnated with orthophosphoric acid in a suitable ratio and keep it as such for 24 hours. Impregnated sample was carbonized in a modified muffle furnace at 600^0 -950^0 C for 2-6 hours. After carbonization, the sample was washed first with 5N HCl and then with distilled water to remove any acid present in the sample. The pH of the washed water was checked with a portable pH meter. The product was dried at 108 ± 2^0 C in a moisture oven and kept in desiccators.

Method for Adsorption Isotherm and Kinetics study

To evaluate adsorption equilibrium data for phenol, experiments were carried out in batch system. 100ml of the phenol solution of known concentration were placed in 300 ml BOD bottles and accurately weighing 0.1 gm of prepared carbon was added into each bottles. The BOD bottles were put into the shaker and stirred for 72 hours. After equilibrium reached adsorbate concentration Ce was determined by UV/visible spectrophotometer.

The specific amount of phenol adsorbed was calculated from the following equation;

$$Qe = (C0 - Ce) \times V/W \qquad \text{----------------} \ (1)$$

Where Qe is the adsorption amount (mol/g) in the solid at equilibrium, C0 & Ce are initial equilibrium concentration of phenol (mol/L) respectively; V is volume (L) of aqueous solution of phenol and W is weight (g) of activated carbon.

In case of kinetics study a cylindrical vessel of 5L capacity fitted with 8 baffles was used. 1gm of accurately weight prepared activated carbon was introduced into 2L of phenol solution of known concentration with constant stirring. The adsorbate was taken out from the vessel at regular time intervals and concentration was determined by using UV/visible spectrophotometer.

Result and Discussion

Thermo gravimetric analysis of raw Material

Thermo gravimeric analysis of raw material was carried out in TGA601 Leco USA make in N_2-atmosphere. The temperature range was selected from room temperature to 900^0 C with rate of heating 5^0 C. TGA analysis of tamarind seed coat indicate weight loss from 50^0C to 250^0C due to removal of moisture and after 255^0C continuous weight loss is observed in **Figure 1**. It is inferred from the data that there is no secondary devolatization stage for these raw materials.

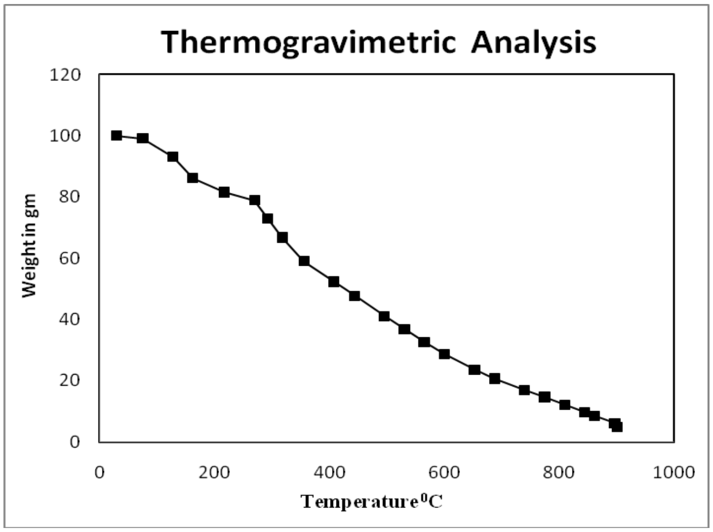

Figure 1 TGA of raw tamarind seed shell

Characterization of activated carbon

Proximate and ultimate analysis

Proximate and ultimate analysis of raw material and prepared activated carbon (TSCAC) are reported in the **Table 1**. The proximate data of the raw material indicates a high volatile matter; 48.7% and moisture content; 17.6%. The DMMF Basis analysis of raw material shows %carbon; 60.0 and %hydrogen; 4.3 The proximate and ultimate data indicate that tamarind seed shells are very suitable raw material for preparation of activated carbon. The proximate and ultimate analysis of the TSCAC show very low ash content: 1.5% and high carbon: 90.11%.The low ash content of TSCAC make it very useful particular in medicinal industry.

Surface area and Pore volume

The surface area and pore volume of TSCAC was carried out by *Micromeritics N_2-BET surface area analyzer* (USA make) at JNARDDC Nagpur. The results, **Table 3** show that TSCAC has very high surface area and pore volume, 2447 m^2/g and 1.4003 cm^3/g, respectively.

Iodine number

To determine the micro pores structure of carbon iodine number was determined as per *ASTM D4607-94(1999).* The iodine number data, **Table 2**, shows high micro pores surface.

Table 1 Proximate and Ultimate analysis of raw, tamarind seed shell, TSCAC and F-400 activated carbons

Activated carbon	Moisture %	Ash %	Volatile Matter %	Fixed carbon%	Carbon %	Hydrogen %
Raw material	17.6	1.3	48.74	32.4	56.05	6.27
TSCAC	12.8	1.5	12.2	73.5	90.11	2.10
F-400	1.9	6.1	2.7	89.3	96.04	0.29

Table 2 Characteristics of activated carbon

Activated Carbon	Iodine number mg/g	N2-BET surface area m^2/g	Pore Volume cm^3/g
TSCAC	2010	2447	1.4007
F-400	1193	998	0.825

Scanning Electron Microscopy (SEM) of TSCAC

The physical surface morphology was examined using a JEOL Scanning Electron Microscope (JSM-6380 Model). A thin layer was mounted on the Al Specimen holder by a double-sided tape. It was coated with Au/Pd, with a thickness of about 30nm. The SEM of activated carbon was recorded at 500xand 300x magnifications. It could be observed from **Figure 2** that the surface is full of pores of various shape and sizes, cracks and crevices. It indicates that the precursor material as well as the method of preparation plays an important role in formation of pores. During activation phosphoric acid acts as a stabilizer, H_3PO_4 fills up the cavities of the cellulose structure and then due to high temperature during carbonization H_3PO_4 evaporates out of those cavities forming active pores on activated carbon.

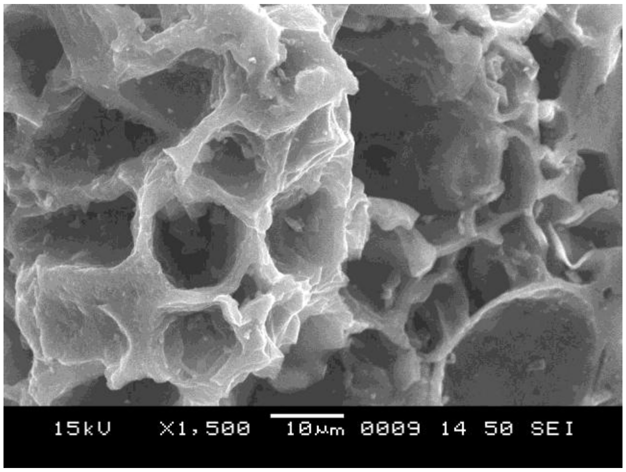

Figure 2(a) SEM Micrograph of TSCAC

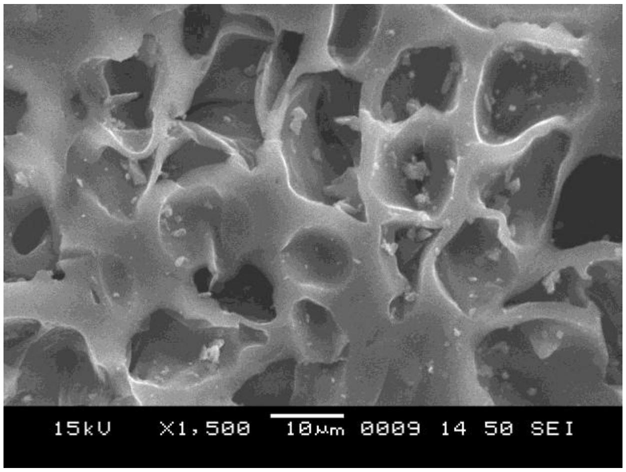

Figure 2(b) SEM Micrograph of TSCAC

FT-IR analysis of TSCAC

To resolve the functional groups and its wave numbers, FT-IR of prepared carbon is carried out using Fourier transform infrared spectrometer (FT-IR) (Perkin Elmer, PE-RXI) in the range of 450-4000cm^{-1}. In this analysis, finely grounded sorbent was encapsulated with KBr in the ratio 1:20 in order to prepare the translucent sample disks. The FT-IR spectra in **Figure 3** shows that the predominant presence of free-OH stretch vibration was found at 3733 cm^{-1} and N-H stretching vibrations due to primary and secondary amine was found at 3443 cm^{-1}. The C-H stretch vibration around 2945-2871 cm^{-1} observed due to methylene group. The C=O stretch vibration due to saturated acyclic compounds at1889 cm^{-1}.The peaks corresponds to the vibration of C=O in the quinine configuration around 1634-1566 cm^{-1}. The C-H stretch vibration due to alkanes was found at 1488 cm^{-1}. The C-O stretch vibration at 1256 cm^{-1} due to phenol, COO^-. The spectra below 1000 cm^{-1} are noisy spectrum.

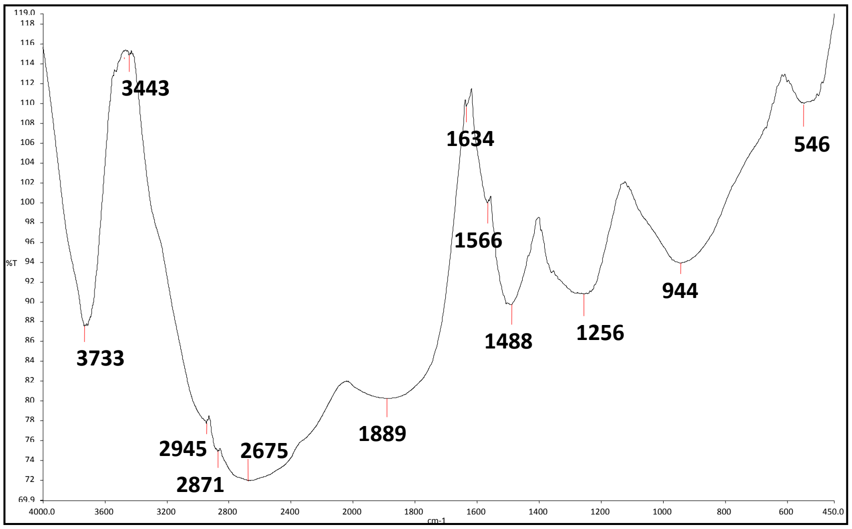

Figure 3 FTIR Spectrum of TSCAC

Adsorption Isotherm

In order to study to study the dominant adsorption mechanism and to compute various adsorption parameters two adsorption models namely Langmuir, Freundlich and BET were used. Since the concentration of phenol in present study is very low hence the BET equation behaves similar to Langmuir equation in the present study. BET model therefore was not used in the present study.

The Langmuir adsorption equation can be represented in linear form as follows;

$$1/Q_e = (1/Q_0) + (1/Q_0 b) \times 1/C_e \qquad \text{---------------} \; (2)$$

The plots of Qe (amount of adsorbate on the adsorbent, mol/ g) versus the equilibrium concentration of adsorbate in solution C_e (mol/L) in **Figure 4**. Where Q_0 is the maximum amount of the phenol adsorbed per unit weight of adsorbent to form a complete monolayer on the surface, Qe and Ce are adsorption capacity of activated carbon at equilibrium concentration Ce and b is the Langmuir adsorption constant. Langmuir parameters Q_0 and b were calculated for the slope and intercept of the linear plots of 1/Qe vs. 1/Ce (**Figure 5**)

The linear form of Freundlich Adsorption model is as follows:

$$\text{Log}\,(Qe) = \text{Log}K_f + 1/n\ \text{Log}\,(Ce) \qquad \text{----------------} \; (3)$$

Where, Kf and 1/n are Freundlich constants, related to adsorption capacity and adsorption intensity respectively. The value of Kf and 1/n are obtained from the slope and intercept of the linear Freundlich plot of Log Qe vs. Log Ce (**Figure 6**).

The BET adsorption equation can represented as:

$$C_e/Q_e\,(C_s-C_e) = 1/Q_0 z + (z-1/Q_0 z)*C_e/C_s \qquad \text{---------------} \; (4)$$

Where, C_e, Q_e, Q_0, have same meaning as in Langmuir model, C_s is the saturated concentration of the adsorbate and z is BET constant. BET parameters Q_0 and z were calculated from the graph plotted between C_e vs C_e/Q_e (C_s-C_e) **Figure 7**.

The plot of Qe versus Ce, **Figure 4** fairly indicates typical type I favorable isotherm as referred in most of the literature. From the Langmuir, Freundlich adsorption parameters, it has been observed that the Langmuir model was best fitted to the experimental data. The Q^o value for TSCAC is found more than the Q^o value of commercial activated carbon Filtrasorb-400. Hence the adsorption capacity of prepared activated carbon is more than the commercial activated carbon F-400.

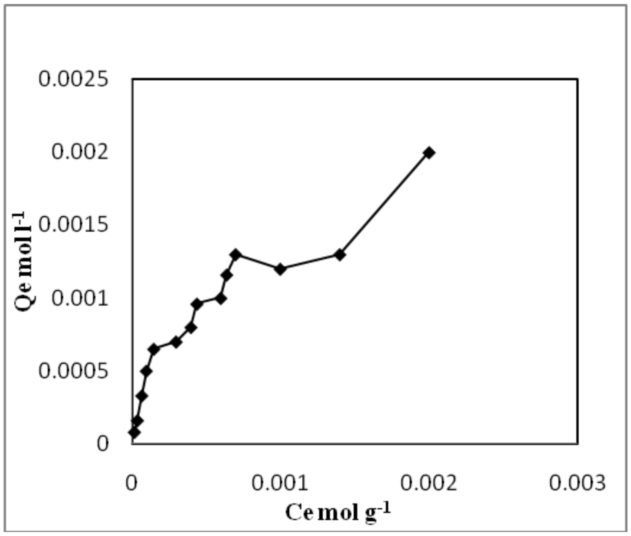

Figure 4 General graph of TSCAC

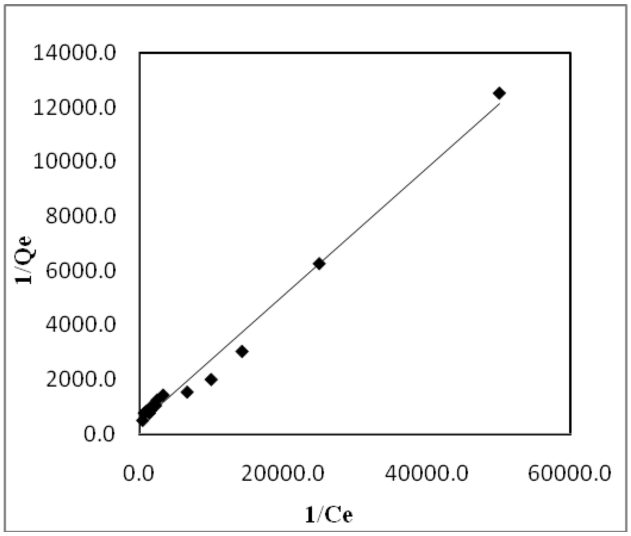

Figure 5 Langmuir Adsorption of TSCAC

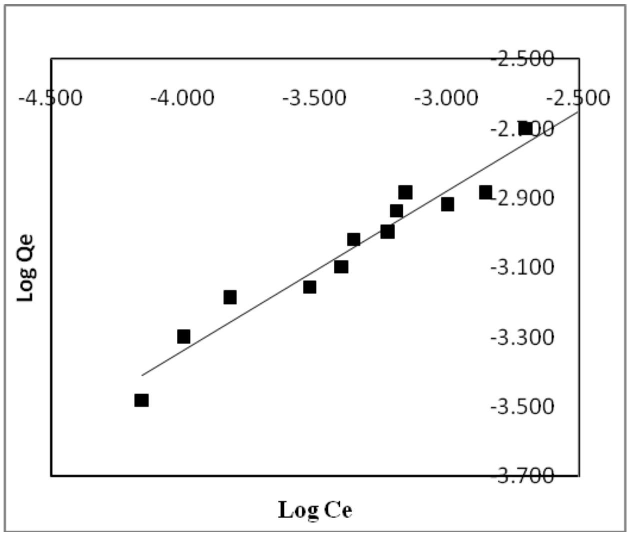

Figure 6 Freundlich Adsorption of TSCAC

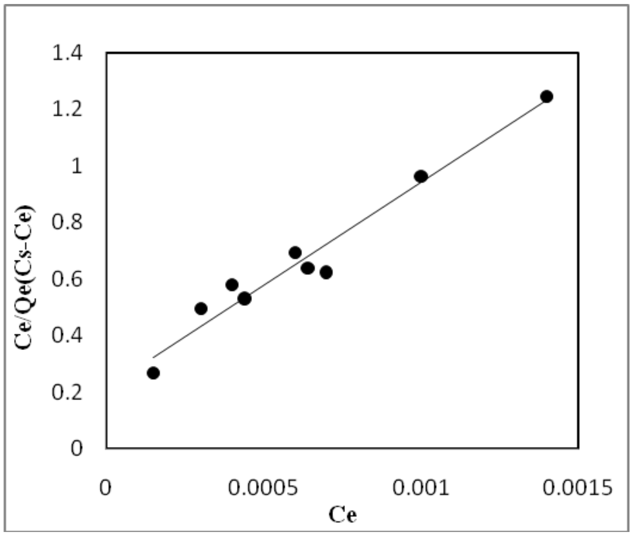

Figure 7 BET Adsorption graph of TSCAC

Kinetic study

A simplified interpretation of the kinetic data based on Langmuir theory was used and the rate was expressed as a function of a directly measurable system variable, the fluid phase adsorbate concentration. Following rate equation based on Langmuir theory was used to analyze the kinetic data;

$$\ln [(C_t-C_e)/(C_t+{}_a)] = -kC_e t + \ln[(C_0-C_e)/(C_0+a)] \qquad \text{----------------- (5)}$$

Where, $a= (C_0/kC_e)$

The rate of adsorption in kinetics of TSCAC is more at initial time intervals shown in **Figure 8**. The adsorption and desorption rate constants were evaluated by plotting ln $[(C_t-C_e)/ (C_t+a)]$ against, t (**Figure 9**). The adsorption and desorption constants (**Table 3**) indicate that the desorption is very fast in case of TSCAC system while adsorption rate was found more in commercially activated carbon F-400.

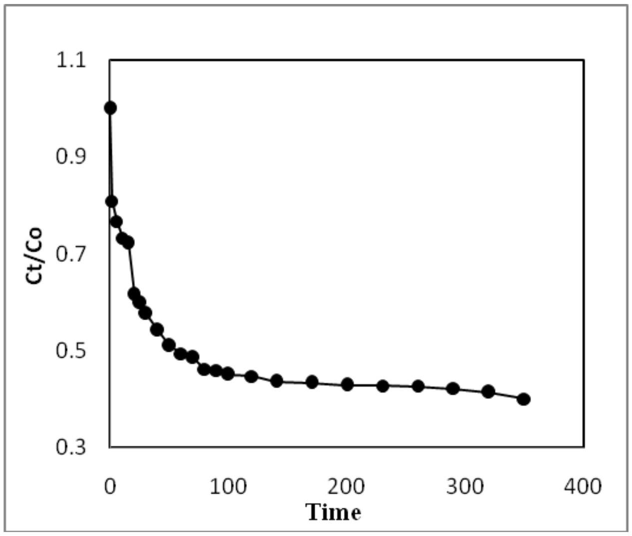

Figure 8 Kinetics graph of TSCAC

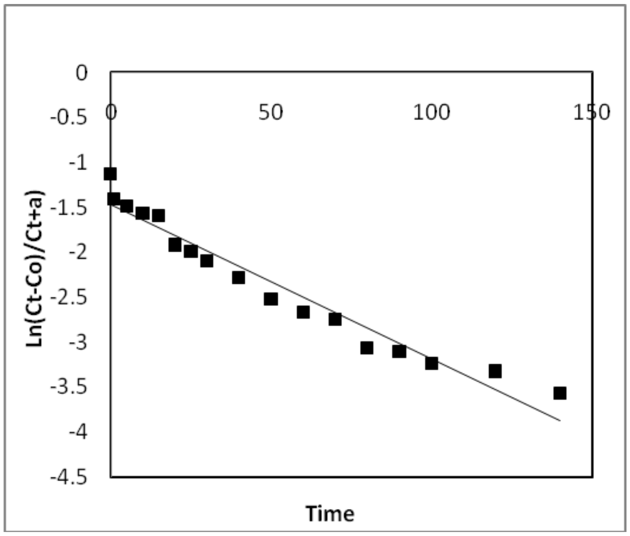

Figure 9 Langmuir Kinetics graph of TSCAC

Table 3 Adsorption isotherm and Kinetic data

Adsorbent	Langmuir constants		Freundlich constants		BET constants		Langmuir kinetic constants	
Activated carbon	Q^o (mol/g)	b	K_f	1/n	Q^o	z	Ka	Kd
F-400	0.0018	13910.5	0.0102	0.250	0.0026	6720.2	0.028	0.00015
TSCAC	0.0026	1614.4	0.0314	0.458	0.0013	3398.6	0.017	0.00091

Conclusions

From the present study, it can be concluded that:

1. Raw material, method of activation, temperature of carbonization, rate of carbonization and ratio of impregnation play important role in preparing a high surface area activated carbon.
2. In chemical activation low temperature gives higher yield as well as high surface area and pore volume.
3. Presence of micro pores in comparison of meso and macropores is high in chemical activation method.
4. Surface group phenolic –OH is dominant in comparison of other surface groups.
5. Activated carbon with very high surface area, pore volume and phenol adsorption capacity could be prepared by chemical activation method.

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