

Production and characterization of activated carbon derived from brewer's yeast

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Abstract—Activated carbon (AC) was produced from brewer's yeast with K_2CO_3 activation. The effects of K_2CO_3 /yeast ratio and activation temperature on the yield and adsorption properties of the AC were investigated. The results indicate that the optimum conditions were as follows: ratio of K_2CO_3 /yeast=2 and activation temperature 800 °C. The AC produced under the optimum conditions has BET surface area of 1,603 m²/g, pore volume of 1.43 cm³/g and average pore diameter of 3.5 nm. Adsorption of phenol onto the AC was determined by batch test at solution pH of 7. The effects of contact time and initial phenol concentration were investigated. The adsorption process was found to follow pseudo-second-order kinetics. The rate of phenol adsorption onto the AC produced was rapid with the adsorption equilibrium reached within 5 min. The experimental data fitted well with the Langmuir isotherm model. The maximum phenol uptake by the AC was estimated to be 513.5 mg/g.

Key words: Activated Carbon, Brewer's Yeast, Adsorption, K_2CO_3

INTRODUCTION

Activated carbon is widely used in decontamination of air and wastewater [1]. Its effectiveness in removing pollutants has been found to be superior to many other absorbents. Its capacity is mainly due to its structural characteristics and its porous texture, which give it a large surface area [2]. The presence of various functional groups on the activated carbon surface contributes to their unique and specific preferential uptake of different molecular species [3]. The surface functional groups can be classified into two major groups: acidic groups consisting mainly of hydroxyl, carboxylic and carbonyl, and basic groups such as pyrone and chromene. These functional groups play a vital role by inducing formation of chemical bonding between adsorbate and adsorbent, especially in the adsorption of organic compounds.

However, the widespread use of activated carbon is restricted due to its high cost [4]. Thus, lower cost activated carbons have to be found as an alternative for expensive coal-based activated carbon. It has been shown that any cheap material with high carbon content and low level of inorganic compounds can be used as raw material for the production of activated carbon. In recent years, there has been growing interest in the production of activated carbons from wastes, such as used newspaper [5,6], used tires [7,8], sludge [9] and agricultural by-products [10-17]. The processing and transformation of agricultural by-products and residual wastes into activated carbon with good adsorption properties would alleviate the problems of their disposal and management while providing a useful low cost end product.

Brewer's yeast, a by-product of the brewing industry, is being produced in large amount due to increasing beer production. It is

generally sold as inexpensive animal feed after inactivation by heat, and is considered as an industrial organic waste that causes a great deal of concern [17]. Yeast is carbonaceous and rich in organic material; it is potentially suitable for the production of activated carbon. Moreover, the surface of brewer's yeast has many functional groups, such as sulfonate, carboxyl and amine groups which are potentially beneficial for the formation of functional groups on the surface of prepared activated carbon.

The production of activated carbon involves two major steps: carbonization and activation. Carbonization is a thermal process in an inert atmosphere to convert raw material into solid char, leaving other liquids and gaseous as by products. Whereas, activation serves to enhance the char's porosity and to clean out tar-clogged pores, thus increasing the surface area of the activated carbon. Activation can be done either physically or chemically or a combination of both. In physical activation, the raw material is first carbonized and the carbonized material is subsequently activated by steam or carbon dioxide or their mixtures. Carbonization temperature may range from 400 °C to 850 °C, reaching 1,000 °C sometimes, and activation temperature may range from 600 °C to 900 °C. In chemical activation, the raw material is impregnated with an activation agent and the impregnated material is heat-treated under inert atmosphere. The carbonization and activation steps are carried out simultaneously in the chemical activation process, with the activating agents also serving as dehydrating agents and oxidants. Physiochemical activation occurs mainly at high temperature ranging from 600 °C to 850 °C in the presence of a dehydrating agent (e.g., potassium hydroxide, zinc chloride or phosphoric acid) and oxidizing agent such as carbon dioxide/steam providing further gasification effect [3,9].

In this study, activated carbons have been produced using brewer's yeast as a precursor by chemical activation with K_2CO_3 , which was estimated to be a kind of effective activation agent by Adinata. Effects of K_2CO_3 /yeast ratio and activation temperature on the yield

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and adsorption capacity of the activated carbons were evaluated using phenol as adsorbate. Surface area, pore volume and pore size distribution of the activated carbon prepared under the optimum condition were determined by the BET method, and the phenol adsorption performances were determined by batch test.

MATERIALS AND METHODS

1. Materials

The brewer's yeast was collected from King Longquan Beer Company in Hubei Province of China. The brewing yeast was washed thoroughly with water to remove any impurities, dried at 60 °C for 24 h and then ground into powder. Fine analytical grade K₂CO₃ (Shanghai chemical reagent, China) was used as the activation agent.

2. Ash Content Determination

Prior to ash content determination, the brewer's yeast was dried at 105 °C for 24 h in a drying oven and cooled in a desiccator. The dried brewer's yeast was weighed in a crucible and heated in a muffle furnace at 650 °C for 4 h. The crucible was then cooled to room temperature in a desiccator and weighed. The residue weight was calculated and reported as percentage of ash by Eq. (1):

$$\text{Ash content (\%)} = \frac{m}{m_0} \times 100 \quad (1)$$

where m_0 and m are respectively the weights of the yeast before and after heating.

3. Elemental Analysis of Brewer's Yeast

Elemental analysis was performed using Elemental Analyzer (PE24002II, USA) to investigate the presence elements of carbon, hydrogen, nitrogen and sulfur.

4. Thermal Analysis

The thermal stability of the brewer's yeast was evaluated by thermogravimetric analysis (TGA, DSCQ100, TA Company, USA). The TGA measurements were carried out under nitrogen atmosphere at a heating rate of 10 °C/min from 20 °C to 800 °C.

5. Production of Activated Carbon

The brewer's yeast powder was mixed with K₂CO₃ at specific weight ratio. The mixture was then placed in a sealed ceramic crucible and kept in a muffle furnace. The temperature was ramped from room temperature to a certain temperature and retained for several hours at that temperature in the muffle furnace. After the heat treatment, the carbon was cooled to room temperature, then boiled in 0.1 mol/L HCl solution for 20 min and washed with deionized water to remove K₂O. The resulting carbon was dried at 120 °C overnight and then ground into fine powder for further analysis and characterization. The yields of activated carbon were calculated by Eq. (2):

$$X(\%) = \frac{m}{m_0} \times 100 \quad (2)$$

where X is activated carbon yield (%), m the activated carbon mass (g) and m_0 is the raw sample mass (g).

To optimize the production conditions, the following parameters, (i) weight ratio of K₂CO₃ to raw material (0.5, 1, 2, 4, 6 and 10) and (ii) activation temperature (600 °C, 700 °C, 800 °C and 900 °C), were varied, and phenol adsorption was carried out to select the best parameters.

6. Textural Characterization of Produced Activated Carbon

The textural characterization of the activated carbon was based on the corresponding N₂ equilibrium adsorption-desorption isotherms determined at 77 K using a Quantachrome Autosorb-1. Prior to the experiment, the sample was out-gassed at 200 °C for 6 h. The surface area was obtained using BET model for adsorption data in a relative pressure ranging from 0.05 to 0.30. The total pore volume was calculated from the amount of N₂ vapor adsorbed at a relative pressure of 0.99. The pore size distribution was evaluated from the desorption branches of the isotherms using the Barrett-Joyner-Halenda (BJH) method.

7. Analysis of Phenol

The concentration of phenol in the aqueous solution was determined using a spectrophotometer (UV-2450, Shimadzu, Japan) at wavelength 270 nm. Prior to the analysis, a calibration curve which is linear and reproducible over the phenol concentration range of 0-50 mg/l was obtained.

8. Adsorption of Phenol

To estimate the applicability of produced activated carbon as an adsorbent for wastewater treatment, phenol was used as the adsorbate in this study. Solutions with different initial concentrations of phenol aqueous solution ranging from 50 to 5,000 mg/l were prepared. To carry out the adsorption experiments, a constant mass of adsorbent (0.15 g) was weighed into a 50-milliliter high-density polyethylene plastic bottle and 30 ml of phenol solution was added. The bottles were sealed and shaken at 160 rpm at a temperature of 25 °C in a shaker. The pH of the solution was adjusted using either 0.1 mol/L HCl or 0.1 mol/L NaOH during the adsorption experiments. After specific time of contact, samples of 2 ml were taken out and separated by centrifugation at 3,000 rpm for 10 min. The solution concentration in the supernatant was determined after an appropriate dilution. The uptake (q_e , mg/g) was calculated from the mass balance by using Eq. (3):

$$q_e = \frac{V_i C_i - V_f C_f}{M} \quad (3)$$

where V_i and V_f are the initial and final (initial plus added acid or alkali solution) volumes (l), respectively, C_i and C_f are the initial and final concentrations (mg/l), respectively, and M is the mass of adsorbent used (g).

RESULTS AND DISCUSSION

1. Brewer's Yeast Characterization

The brewer's yeast composition was determined to evaluate its characters as a precursor of activated carbon. The carbon, hydrogen, nitrogen and sulfur contents in the brewer's yeast were determined by an elemental analyzer and found to be 42.3%, 7.4%, 0.6% and 0.08% (w/w), respectively. The ash content was 9% by weight. So, the brewer's yeast is a suitable precursor for the preparation of activated carbon because of its high carbon content and low ash content.

The brewer's yeast sample was subjected to thermogravimetric analysis (TGA) and the result is shown in Fig. 1. There are three weight loss stages at the heating rate of 10 °C/min. From the start of the experiment until ~155 °C, the weight loss of ~5.4% was due to the losses of moisture and the physically bound water. The second

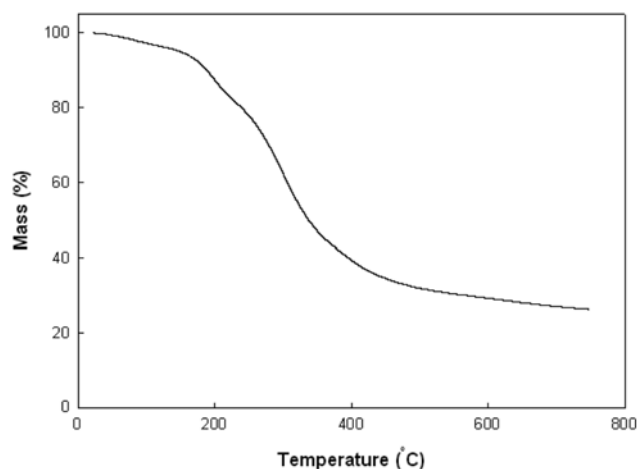


Fig. 1. Thermogram analysis (TGA) curve of brewing yeast.

stage of 155–450 °C corresponding to primary carbonization is the major weight loss of ~65.3% due to the removal of volatile matter. The last broad weight loss stage occurring at above 450 °C was due to structural degradation. The weight loss was small above 650 °C, indicating that complete pyrolysis occurred approximately at 650 °C.

2. Effects of K_2CO_3 /Yeast Ratios on Adsorption Capacity and Yield of Activated Carbons

Effects of K_2CO_3 /yeast ratios on phenol adsorption and the yield of activated carbons were evaluated at activation temperature of 800 °C and activation time of 2 hours. The ratios of K_2CO_3 /yeast were varied from 0.5 to 10, and the phenol adsorption experiments were done with 1,000 mg/L phenol solution at 25 °C and pH 7.

The results revealed that the yields of activated carbons varied within 21.3–22.4% when the ratios of K_2CO_3 /yeast increased from 0.5 to 10, showing that the ratio of K_2CO_3 /yeast did not obviously affect the yield of activated carbon. The effect of K_2CO_3 /yeast ratio on the adsorption capacities of the produced activated carbons is shown in Fig. 2. It is seen that the amount of phenol adsorbed increased from 32.0 mg/g to 298.7 mg/g with increasing ratio of K_2CO_3 /yeast from 0.5 to 2, and then decreased to 58.3 mg/g with further

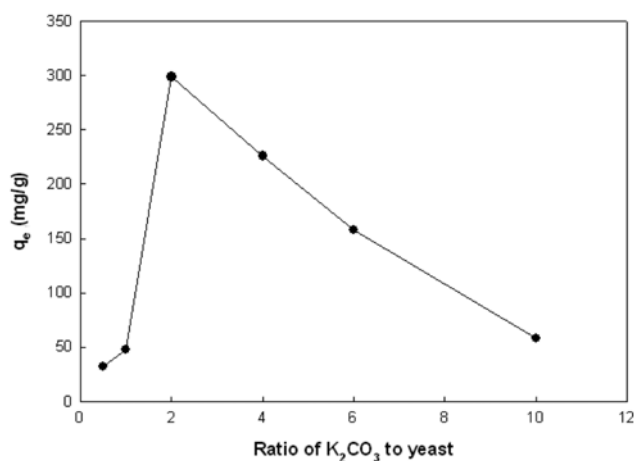


Fig. 2. Effect of K_2CO_3 /yeast ratio on adsorption capacities of activated carbons.

Table 1. The effect of activation temperature on the yield and adsorption amount of the activated carbons

Temperature (°C)	600	700	800	900
Yield (%)	24.6	21.4	21.3	20.8
q (mg/g)	70.4	77.7	298.7	145.7

increase in K_2CO_3 /yeast ratio to 10. The activated carbon with the best adsorption capacity was obtained at the K_2CO_3 /yeast ratio of 2.

The adsorption capacity of the activated carbon is mainly due to its structural characteristics and porous texture, which give it a large surface area. In this study, the formation of pores was due to the evolution of CO_2 from the decomposition of K_2CO_3 . With increasing K_2CO_3 /yeast ratio, more CO_2 was evolved. When this ratio was lower than 2, fewer pores were formed, leading to lower adsorption capacity of the resulting carbon. With the initial increased K_2CO_3 /yeast ratio, the activation reaction was enhanced and a large number of pores were formed. When the ratio of K_2CO_3 /yeast reached 2, the carbons on the active sites reacted completely and the maximum adsorption capacity was reached. When the ratio of K_2CO_3 /yeast was larger than 2, the pores would be widened and burnt off, so that the adsorption capacity of activated carbon decreased.

3. Activation Temperature

The temperature of activation is another vital parameter affecting the physical characteristics of the activated carbon. The yield and phenol adsorption capacities obtained by varying the activation temperature for the production of activated carbon are listed in Table 1. The activation time was 2 hours and the ratio of K_2CO_3 /yeast was 2.

From Table 1, it was observed that the yield of carbon decreased with increase in activation temperature. This is expected because at a higher temperature more volatiles were released resulting in lower yield. The phenol adsorbed by the activated carbons increased from about 70.4 mg/g to 298.7 mg/g with increased activation temperature from 600 °C to 800 °C with the highest adsorption capacities obtained at 800 °C. A further increase in activation temperature to 900 °C resulted in a decrease of the amount adsorbed to 145.7 mg/g. This is because at this high activation temperature, the surface area of the carbons decreased due to the widening and collapse of the pore.

4. Characterizations of the Activated Carbon Produced under Optimum Conditions

Different methods can be employed to determine the surface area and pore size distribution of porous solids. Despite the limitations of the BET model for surface area assessment, nitrogen adsorption is still commonly used for surface area determination as it can give an accurate assessment of surface area for different types of adsorption isotherms in the absence of significant micropore filling and similar structure of the completed monolayer on different surfaces. The N_2 adsorption-desorption isotherm and pore size distribution for the sample prepared under the optimum condition are shown in Fig. 3 and Fig. 4. The hysteresis loop in the isotherm indicates the presence of mesopores [4]. Table 2 summarizes the surface area and pore volume of the activated carbon.

The total BET surface area of prepared activated carbon was found to be 1,603 m^2/g , with total pore volume of 1.43 cm^3/g and average pore diameter of 3.5 nm. In comparison, the surface areas of acti-

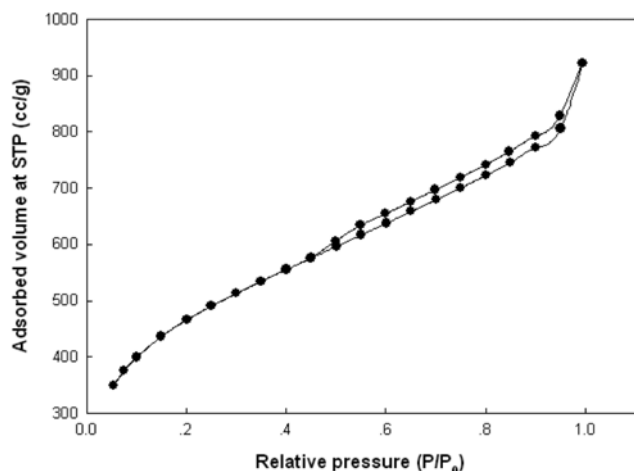


Fig. 3. Adsorption-desorption isotherms of N₂ at 77 K on prepared AC.

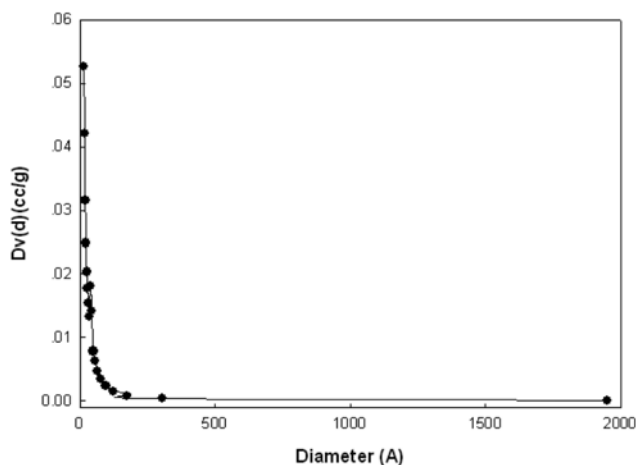


Fig. 4. The pore size distribution of prepared activated carbon.

Table 2. BET surface area, total pore volume and average pore diameter of AC

AC	
Surface area (m ² /g)	1063
Total pore volume (cm ³ /g)	1.43
Average pore diameter (nm)	3.5

vated carbons derived from other biomaterials are: 200-1,300 m²/g from sugar beet pulp activated with carbon dioxide [18]; 697-2,123 m²/g from bamboo activated with phosphoric acid [4]; 248-1,170 m²/g from palm shell activated with potassium carbonate [15]; 200-700 m²/g from rice bran activated with sulfuric acid [19] and others [3,20,21]. It can be concluded that the surface area and pore volume of activated carbon prepared were reasonable and comparable to other activated carbon prepared from other materials.

5. Adsorption Test

5-1. Kinetics of Phenol Adsorption

The kinetic experiments of phenol adsorption onto the activated carbon were carried out in aqueous phenol solution at pH 7 with initial concentrations of 400 mg/l, 1,000 mg/l and 2,500 mg/l. To de-

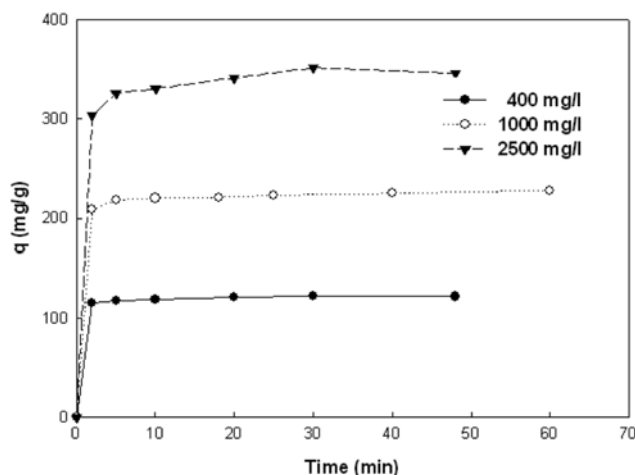


Fig. 5. The variation of adsorption capacity with adsorption time at different initial phenol concentrations at 25°C and pH 7.

termine the equilibration time the adsorption, the amount adsorbed at various time intervals was assessed until no further adsorption was detected. Fig. 5 shows the adsorbed amount versus adsorption time at various initial phenol concentrations. It is observed that the contact time required for equilibrium for phenol solutions with initial concentrations of 400 to 2,500 mg/l was about 5 min. Further, the amount of phenol adsorbed on the activated carbon increased sharply with time initially, after which a constant value was obtained with no further phenol removal from solution. At this point, the phenol that desorbs from the activated carbon is in a state of dynamic equilibrium with the phenol being adsorbed onto the activated carbon. The amount of phenol adsorbed at the equilibrium is the maximum adsorption capacity of the adsorbent under those operating conditions. The adsorption capacity at equilibrium increased from 121.6 to 345.9 mg/l with an increase in the initial phenol concentrations from 400 to 2,500 mg/l. The result indicates that the rate of phenol adsorption onto the prepared activated carbon is rapid with short contact time, which is important for practical wastewater treatment applications.

Two simplified kinetic models were adopted to examine the mechanism of the adsorption process. The adsorption data was first analyzed by using the pseudo-first-order equation of Lagergren and Svenska. The pseudo first-order model assumes that the rate of change of solute uptake with time is directly proportional to the difference in amount at saturation and amount of solute adsorbed. This pseudo first-order model can be written as Eq. (4):

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (4)$$

where q_e and q_t are the amounts of solute adsorbed on the adsorbents at equilibrium and at time t , respectively, and k_1 is the first-order adsorption rate constant.

Values of k_1 were calculated from the slopes of the plot of $\log(q_e - q_t)$ versus t (Fig. 6) for different initial concentrations of phenol. The parameters of pseudo first-order model are summarized in Table 3. The R^2 values obtained were relatively small and the calculated q_e values obtained from the linear plots did not agree with the experimental q_e value.

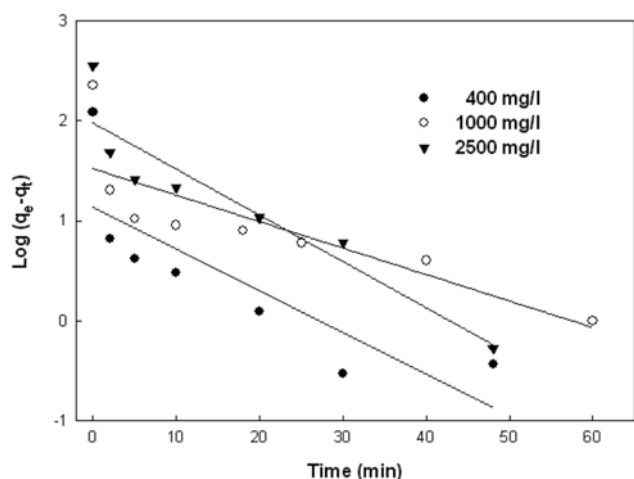


Fig. 6. Pseudo-first-order kinetics model plots of adsorption phenol onto activated carbon at 25 °C and pH 7.

The pseudo-second-order model was then used for the analysis of adsorption kinetics. The pseudo-second-order model is based on the assumption that the rate-limiting step may be chemical adsorption, which may or may not involve valence forces through sharing or exchange of electrons between adsorbent and adsorbate. It is assumed that the adsorption capacity is proportional to the number of active sites on the adsorbent; then the kinetic rate law can be written as Eq. (5):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where k_2 is the rate constant of the pseudo second-order adsorption. The initial adsorption rate, h , at $t \rightarrow 0$ is defined as Eq. (6):

$$h = k_2 q_e^2 \quad (6)$$

The linear plots of t/q_t versus t are shown in Fig. 7. The parameters of the pseudo-second-order model are summarized in Table 3. The values of R^2 are greater than 0.999 for all phenol concentration. Good agreement between the experimental and the calculated q_e values was obtained indicating the applicability of this model for the adsorption process of phenol onto the produced activated carbon. This suggests that chemical reaction was the rate-controlling step [18]. The k_2 value decreased with increasing initial phenol concentration. Similar behavior has been reported in previous works [22,23].

The phenol adsorption kinetics onto the prepared activated carbon was verified at different initial concentrations. The validity of each model was determined by the sum of squared errors (SSE, %) given by Eq. (7):

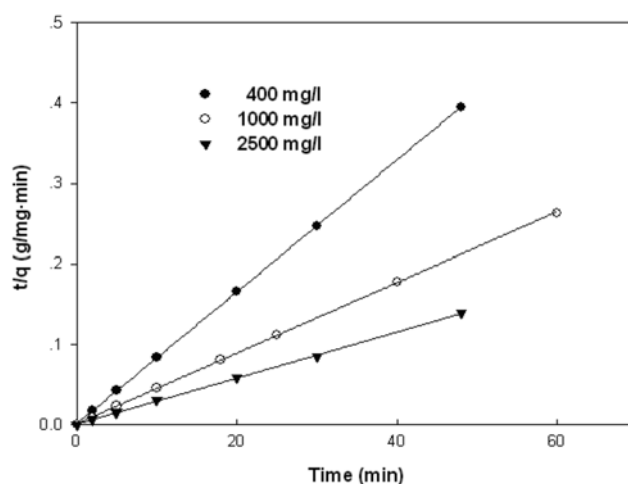


Fig. 7. Pseudo-second-order kinetics model plots of adsorption phenol onto activated carbon at 25 °C and pH 7.

$$SSE = \sqrt{\frac{\sum (q_{e,exp} - q_{e,cal})^2}{N}} \quad (7)$$

where N is the number of data points.

A lower SSE value indicates better fit. Table 3 lists the values of SSE obtained for the two kinetic models studied. It was found that the pseudo-second-order kinetics model yielded the lower SSE value. This agrees with the R^2 values obtained earlier and proves that the adsorption of phenol onto the brewer's yeast derived activated carbon could be well described by the pseudo-second-order kinetics, which is based on the equilibrium chemical adsorption. This behavior was observed over the whole range of concentrations studied, confirming chemisorption as the rate-controlling step.

5-2. Adsorption Isotherm of Phenol

Equilibrium relationships between adsorbent and adsorbate are usually described by adsorption isotherms, which describe the distribution of molecules between the liquid and solid phases at equilibrium state and the interactions between solute and the adsorbent. The fitting of the adsorption data to various isotherms is important for finding a suitable model to be used for process design.

Langmuir and Freundlich adsorption isotherms were used to fit the experimental data in this study. The Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of uniform adsorption sites without migration of adsorbed molecules on the surface. The linear form of the Langmuir isotherm model is given as Eq. (8):

$$\frac{C_e}{q_e} = \frac{1}{q_m \times b} + \frac{1}{q_m} C_e \quad (8)$$

Table 3. Kinetic parameters for phenol adsorption by produced activated carbon

Initial phenol concentration (mg/l)	$q_{e,exp}$ (mg/l)	Pseudo first-order model				Pseudo second-order model			
		$q_{e,cal}$ (mg/g)	k_1 (1/min)	R^2	SSE (%)	$q_{e,cal}$ (mg/g)	k_2 (g/(mg·min))	R^2	SSE (%)
400	121.7	13.5	0.0957	0.6781	108.2	121.9	0.0636	1.0000	0.2
1000	228.0	33.0	0.0608	0.6807	195.0	227.8	0.0152	0.9999	0.2
2500	346.0	94.7	0.1062	0.8781	251.3	348.9	0.0107	0.9998	2.9

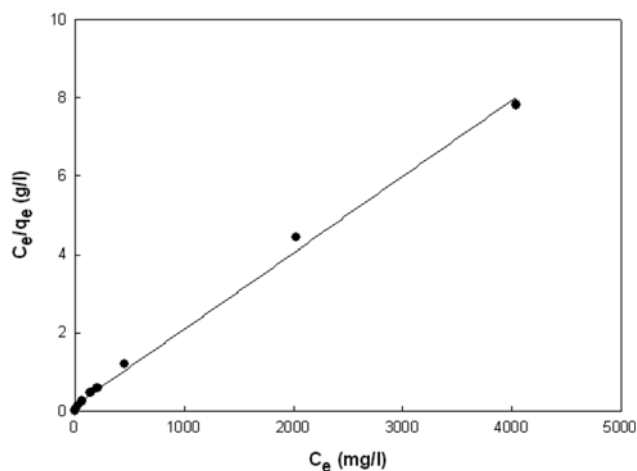


Fig. 8. Langmuir adsorption isotherm of phenol onto activated at 25 °C and pH 7.

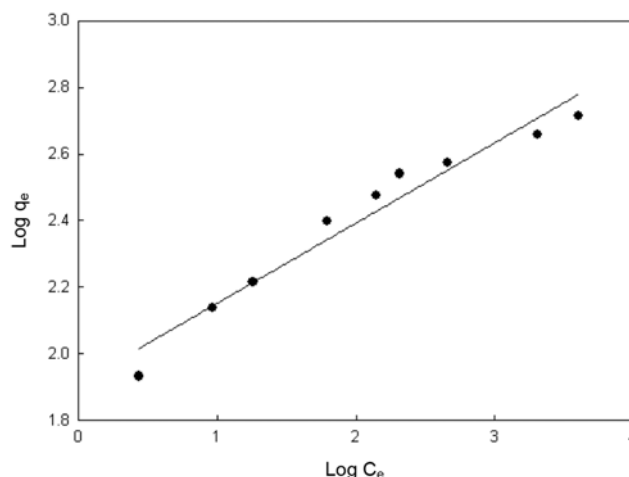


Fig. 9. Freundlich adsorption isotherm of phenol onto activated carbon at 25 °C and pH 7.

Table 4. Estimated parameters of the Langmuir and Freundlich models

Langmuir	
q_m (mg/g)	513.5
b (1/mg)	0.014
r^2	0.996
Freundlich	
K_F	81.30
n	4.15
r^2	0.954

where q_e is the amount of phenol adsorbed per unit mass of adsorbent, C_e is the equilibrium concentration of the phenol in solution, q_m is the adsorption capacity and b is a constant related to the free energy of adsorption. When C_e/q_e is plotted against C_e , a straight line with slope of $1/b$ is obtained, as shown in Fig. 8. The R^2 value of 0.996 indicates that the adsorption of phenol onto the produced activated carbon was well fitted to the Langmuir isotherm model. The q_m and constants b were calculated from Eq. (8) and their values are listed in Table 4.

The Freundlich isotherm is commonly used to fit the experimental data. This model assumes heterogeneous surface energies. The well-known logarithmic form of the Freundlich isotherm is given as Eq. (9):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (9)$$

where q_e is the amount of phenol adsorbed per unit mass of adsorbent (mg/g), C_e is the equilibrium phenol concentration, K_F and $1/n$ are empirical constants depending on several environmental factors. K_F can be defined as the adsorption or distribution coefficient representing the quantity of adsorbed molecule for a unit equilibrium concentration. The slope of $1/n$, ranging between 0 and 1, is a measure of adsorption intensity or surface heterogeneity, as the surface heterogeneity increases this slope approaches zero [24]. A value for $1/n$ below one indicates a normal Langmuir isotherm while

$1/n$ above one is indicative of cooperative adsorption [25]. The plot of $\log q_e$ versus $\log C_e$ gives a straight line, as shown in Fig. 9. The slope of the line, $1/n$, has a value of 0.226, indicating normal Langmuir adsorption. Freundlich constants K_F and n were also calculated and listed in Table 4.

From Table 4, the Langmuir isotherm model yielded a better fit with higher R^2 value compared to the Freundlich model, indicating the homogeneous nature of the activated carbon derived from brewer's yeast. The result also demonstrated the formation of monolayer coverage of phenol molecule on the surface of the produced activated carbon. Maximum phenol uptake by the activated carbon, which was estimated to be 513.5 mg/g, was higher than that of activated carbon produced from oil-palm shells (q_m =166 mg/g) [26] and coconut shell (205.8 mg/g) [3].

CONCLUSION

Activated carbons have been produced from brewer's yeast by employing K_2CO_3 as an activating agent. The effects of K_2CO_3 /yeast ratio and activation temperature on the yield and adsorption properties of activated carbon were investigated and optimum conditions about these were obtained: ratio of K_2CO_3 /yeast 2 and activated temperature 800 °C.

The activated carbon produced at the optimum conditions had a total BET surface area of 1,603 m²/g, total pore volume of 1.43 cm³/g and average pore diameter of 3.5 nm. It was superior to those activated carbons prepared from other materials. Phenol was found to adsorb strongly onto the surface of produced activated carbon. The rate of phenol adsorption onto produced activated carbon is rapid with short contact time. The kinetics of the adsorption process was found to follow the pseudo-second-order kinetic model. Langmuir and Freundlich isotherm models were used to fit the experimental data with Langmuir isotherm model having a better fit. The maximum phenol uptake by the prepared activated carbon was estimated to be 513.5 mg/g. The adsorption property of the brewer's yeast derived activated carbon was compared to other activated carbon reported in earlier literatures. These results indicate that brewer's yeast is a promising precursor for the preparation of activated carbon.

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