

Adsorption of phenol from aqueous solutions using activated carbons prepared from *Tectona grandis* sawdust by $ZnCl_2$ activation

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Abstract

Activated carbons prepared from *Tectona grandis* sawdust, a timber industry waste, have been examined for the removal of phenol from aqueous solutions. The activated carbon was prepared by zinc chloride activation under four different activation atmospheres, to develop carbons with well-developed porosity. Experiments were carried out at different chemical ratios (activating agent/precursor). Effects of carbonization temperature and time are the important variables, which had significant effect on the pore structure of carbon. Developed activated carbon was characterized by SEM analysis. Pore volume and surface area were estimated by Hg porosimetry and BET surface area analyses. The carbons showed surface area and micropore volumes of around 585 m²/g and 0.442 cm³/g, respectively. The activated carbon developed showed substantial capability to adsorb phenol from aqueous solutions. The kinetic data were fitted to the models of Lagergren, pseudo-second-order and intraparticle diffusion, and followed closely the pseudo-second-order chemisorption model. The Freundlich and Langmuir isotherm models were well fitted. The solution pH markedly affected the sorption process. The maximum uptake of phenol was found to be 2.82 mg/g at pH 3.5.

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Keywords: Wastewater treatment; Activated carbon; *Tectona grandis* sawdust; Surface area; Chemical activation; Phenol removal

1. Introduction

Adsorption is one of the most effective processes of advanced wastewater treatment, which reduces trace hazardous organic and inorganic wastes left in effluents after the conventional treatment. It is also used to remove toxic inorganic and organic compounds from contaminated ground water. However, in water treatment the most widely used method is adsorption onto the surface of activated carbon [1]. The relative advantages of adsorption over other conventional advanced treatment methods are: (1) it can remove both organic as well as inorganic constituents even at very low concentrations, (2) it is relatively easy and safe to operate, (3) both batch and continuous equipment can be used, (4) no sludge formation, and (5) the adsorbent can be regenerated and used again. Moreover the process is economical because it requires low capital cost and there are abundant low-cost materials available which can be used as adsorbents.

Activated carbon has been the water industry's standard adsorbent for the reclamation of municipal and industrial wastewater for potable use for almost three decades [2]. Activated carbons have the advantage of exhibiting a high adsorption capacity for organic pollutants due to their high specific surface area, adequate pore size distribution, and relatively high mechanical strength [3,4]. Despite its prolific use in the water and waste industries, activated carbon remains an expensive material. In view of the high cost and tedious procedures for the preparation and regeneration of activated carbons, there is a continuing search for low-cost potential adsorbents.

In practice, coal and waste biomasses of lignocellulosic materials are two main sources for the production of commercial activated carbons. Waste biomass, which includes forest as well as agricultural byproducts have emerged as a better choice. Though these raw wastes can be used as adsorbents without further treatment, activation could enhance their adsorption capacity. The production of activated carbons from such wastes converts unwanted, surplus waste, of which billions of kilograms are produced annually, to useful valuable adsorbents. There are a quite large number of studies regarding the preparation of activated carbons from agricultural wastes [5,6], nuts [7,8], nutshells

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Nomenclature

b	Langmuir constant (l/g)
C_e	equilibrium phenol concentration (mg/l)
C_0	initial phenol concentration (mg/l)
$1/n$	sorption intensity (dimensionless)
<i>Chemical</i>	
ratio	activating agent ($ZnCl_2$)/precursor (g/g)
CR	chemical recovery (g/g)
k	measure of adsorbent capacity (l/g)
K_{ad}	equilibrium rate constant of pseudo-first-order adsorption (min^{-1})
K_L	Langmuir constant (mg/g)
q_e	amount of phenol adsorbed at equilibrium (mg/g)
T	temperature ($^{\circ}\text{C}$)
t	time (min)
V	volume of the solution (l)
W	weight of the adsorbent (g)
W_c	weight of chemical used (g)
W_{pf}	weight of product after washing (g)
W_{pi}	weight of product before washing (g)

[9,10], fruit stones [11], bagasse [12], coirpith [13], oil palm waste [14] and agricultural residues from sugarcane [15], rice [16] and peanut [17,18], sawdust [19] and canes from some easy-growing wood species [20].

Basically, there are two different processes for the preparation of activated carbon: physical activation and chemical activation. In comparison with physical activation, there are two important advantages of chemical activation. One is the lower temperature in which the process is accomplished. The other is that the global yield of the chemical activation tends to be greater since burn-off char is not required. Among the numerous dehydrating agents, zinc chloride in particular is the widely used chemical agent in the preparation of activated carbon. Knowledge of different variables during the activation process is very important in developing the porosity of carbon sought for a given application. Chemical activation by $ZnCl_2$ improves the pore development in the carbon structure and because of the effect of chemicals the yields of carbon are usually high [8,9].

Phenolic compounds are considered to be hazardous wastes, which are released into the aquatic environment by industries such as coke ovens in steel plants, petroleum refineries, petrochemical, phenolic resin, and pharmaceutical, chemical, and dye industries, etc. [4,21,22]. The discharge of phenolic waste into waterways may adversely affect human health as well as that of flora and fauna. Ingestion of a small amount of phenol (TLV of 5 ppm_v) by human beings may cause nausea, vomiting, paralysis, coma, greenish or smoky colored urine, and even death from respiratory failure or cardiac arrests. Phenols also impart undesirable taste to water even at extremely low concentration (USEPA recommends a maximum allowable limit of 0.001 ppm). Fatal poisoning may also occur by adsorption of phenol by skin, if a large area of it is exposed. It is therefore

necessary to remove phenol completely from wastewater (general effluent discharge standard of phenol is 0.05 ppm), before being discharged into waterways.

In this work we report the results obtained on the preparation of activated carbons from *Tectona grandis* sawdust with zinc chloride activation and their ability to remove phenol from wastewater. Different preparation variables on the characteristics of activated products were studied to find the optimum conditions for making activated carbons with a high surface area and well-developed porosity. The activated carbons thus produced were used for the removal of phenol from dilute aqueous solutions. Kinetic models were used to identify the possible mechanisms of such adsorption process. The Langmuir and Freundlich models were used to analyze the adsorption equilibrium.

2. Experimental technique

2.1. Preparation of activated carbon

T. grandis sawdust collected from nearby locality was first washed with distilled water to remove the water-soluble impurities and surface adhered particles and then dried at 60 $^{\circ}\text{C}$ to get rid of the moisture and other volatile impurities. Then the precursor was grounded in the ball mill and sieved to particle size range of 150–200 μm . The proximate analysis of the precursor yielded, moisture 8.1%, volatile matter 37%, fixed carbon 53% and ash 1.9%.

Chemical activation of the powdered precursor was done with $ZnCl_2$. Ten grams of dried precursor was well mixed with 100 ml solution that contained 10 g of $ZnCl_2$. The chemical ratio (activating agent/precursor) was 100% in this case. The mixing was performed at 50 $^{\circ}\text{C}$ for 1 h. After mixing, the slurry was subjected to vacuum drying at 100 $^{\circ}\text{C}$ for 24 h.

The resulting chemical loaded samples were placed in a stainless steel tubular reactor and heated (5 $^{\circ}\text{C min}^{-1}$) to the final carbonization temperature under a nitrogen flow rate of 150 $\text{cm}^3 \text{min}^{-1}$ STP. Samples were held at the final temperature (carbonization temperature) for different carbonization times of 1, 2, and 3 h before cooling down under nitrogen. Nitrogen entering in the reactor was first preheated to 250–300 $^{\circ}\text{C}$ in a preheater. The products were washed sequentially with 0.5N HCl, hot water and finally cold distilled water to remove residual organic and mineral matters, then dried at 110 $^{\circ}\text{C}$. In all experiments, heating rate and nitrogen flow were kept constant. The experiments were carried out for different chemical ratio (100–300%) and carbonization temperature (300–600 $^{\circ}\text{C}$).

Weight loss of the carbon samples was calculated on a chemical free basis and chemical recovery (CR) was estimated according to

$$\text{CR} = \frac{W_{pi} - W_{pf}}{W_c} \times 100 \quad (1)$$

where W_{pi} and W_{pf} are the weight of product before and after washing and W_c is the weight of chemical used. Chemical recovery and weight loss are regarded as

Table 1
Physico-chemical characteristics of *Tectona grandis* sawdust activated carbon

Serial number	Control tests	<i>T. grandis</i> sawdust
1	Carbon yield (%)	42
2	Ash content (%)	9.4
3	Moisture content (%)	11.35
4	Bulk density (g/ml)	0.96
5	BET surface area (m ² /g)	585
6	Total pore volume (cm ³ /g)	0.442
7	Iodine number (mg/g)	1036
8	Methylene blue number (mg/g)	362
9	Phenol number (mg)	14.28
10	Matter soluble in water (%)	2.22
11	Matter soluble in acid (%)	2.64

indicators of the process efficiency in the chemical activation process.

Characterizations of the activated carbons were determined by nitrogen adsorption at -196°C with the help of Micromeritics Flowsorb-2300 and Quantachrome Autoscan Mercury Porosimeter. The BET surface area was calculated from N_2 adsorption isotherms by using the Brunauer–Emmett–Teller (BET) equation [23]. The cross-sectional area for the nitrogen molecule was assumed to be 0.162 nm^2 . The Dubinin–Radushkevich (DR) equation [23] was used to calculate the micropore volume from the N_2 adsorption data. The micropore surface area was then determined from the values obtained from the micropore volumes [24]. The amount of N_2 adsorbed at a pressure near unity corresponds to the total amount adsorbed at both micropores and mesopores and consequently, the subtraction of the micropore volume (from the DR equation) from the total amount (determined at $p/p_0=0.98$ in this case) will provide the volume of the mesopore. The average pore diameter can be determined according to the surface area and the total pore volume (the sum of the micropore and the mesopore volumes), if the pores are assumed to be parallel and cylindrical. The various physico-chemical characteristics of the activated carbon prepared from *T. grandis* sawdust is given in Table 1.

2.2. Phenol adsorption procedure

Adsorption kinetics and equilibrium studies were conducted using the bottle-point isotherm technique by placing a known quantity of the adsorbent in glass bottles containing 100 ml of an aqueous solution of phenol with a predetermined concentration. The final adsorbent concentration thereby achieved was 5 g/l, unless otherwise stated. After such solution preparation, each bottle was shaken vigorously in a thermostatic incubator-cum-shaker for specific time intervals till the equilibrium is reached. At the end of the adsorption process, the adsorbent particles were filtered out and the phenol concentration in the supernatant was then analyzed.

The concentrations of phenol were determined following the method [23] based on the spectrophotometric analysis of the color developed as a result of the reaction of phenol with 4-aminoantipyrine. The phenol concentration retained in the

adsorbent phase was calculated according to

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

where C_0 and C_e are the initial and equilibrium concentrations (mg/l), respectively, of phenol in solution; V the volume (l), and W is the weight (g) of the adsorbent. Two replicates per sample were done and the average results are presented.

Adsorption equilibrium isotherms on the selected carbon were determined using sample dosages of 0.4 g/200 ml aqueous solutions of initial concentrations in the range of 10–100 mg/l, at pH 1.0. For these experiments, the bottles were shaken, keeping the temperature (25°C) and agitation speed (120 rpm) constant for a period (of minimum contact time) required to the attain equilibrium, as determined from the kinetic measurements detailed above.

The effect of pH on the equilibrium adsorption of phenol on selected carbon was further investigated over a pH range of 2–8. The pH values were adjusted with dilute sulphuric acid and sodium hydroxide solutions.

3. Results and discussions

The results for the characterization of the prepared activated carbon are discussed in this paper. The tests for characterization include weight loss, chemical recovery, BET surface area, micropore volume and adsorption capacities of the activated carbon towards phenol removal.

3.1. Effect of different variables on the preparation of activated carbons

3.1.1. Carbonization time

The effects of carbonization time on weight loss, chemical recovery, BET surface area and micropore volume of ZnCl_2 activated carbons are shown in Fig. 1. For all these samples the carbonization temperature is 500°C and the chemical to nutshell ratio is 100% (mass basis). As seen in the figure, carbonization time does not have much effect on the weight loss (although the weight loss increases with carbonization time, the increase is slight), whereas BET surface area and pore volume first increases with carbonization time and reaches its maximum at 1 h and thereafter it decreases. This decrease (after 1 h) was possibly due to some of the pores being sealed off as a result of sintering for a prolonged time. Generally, a longer carbonization time is needed to enhance porosity as well as to clear blocked pore entrances before detrimental effects set in at prolonged times. From an initial high surface area and pore volume, it deteriorated with increasing carbonization time. It can be seen from Fig. 1 that the chemical recovery values decreases with the carbonization time. This might be due to the evaporation of ZnCl_2 , from the precursor at longer carbonization time. Therefore, it can be concluded that in chemical activation with ZnCl_2 the impregnation method with a shorter carbonization time (1 h in this case) produces activated carbons with a well-developed pore structure.

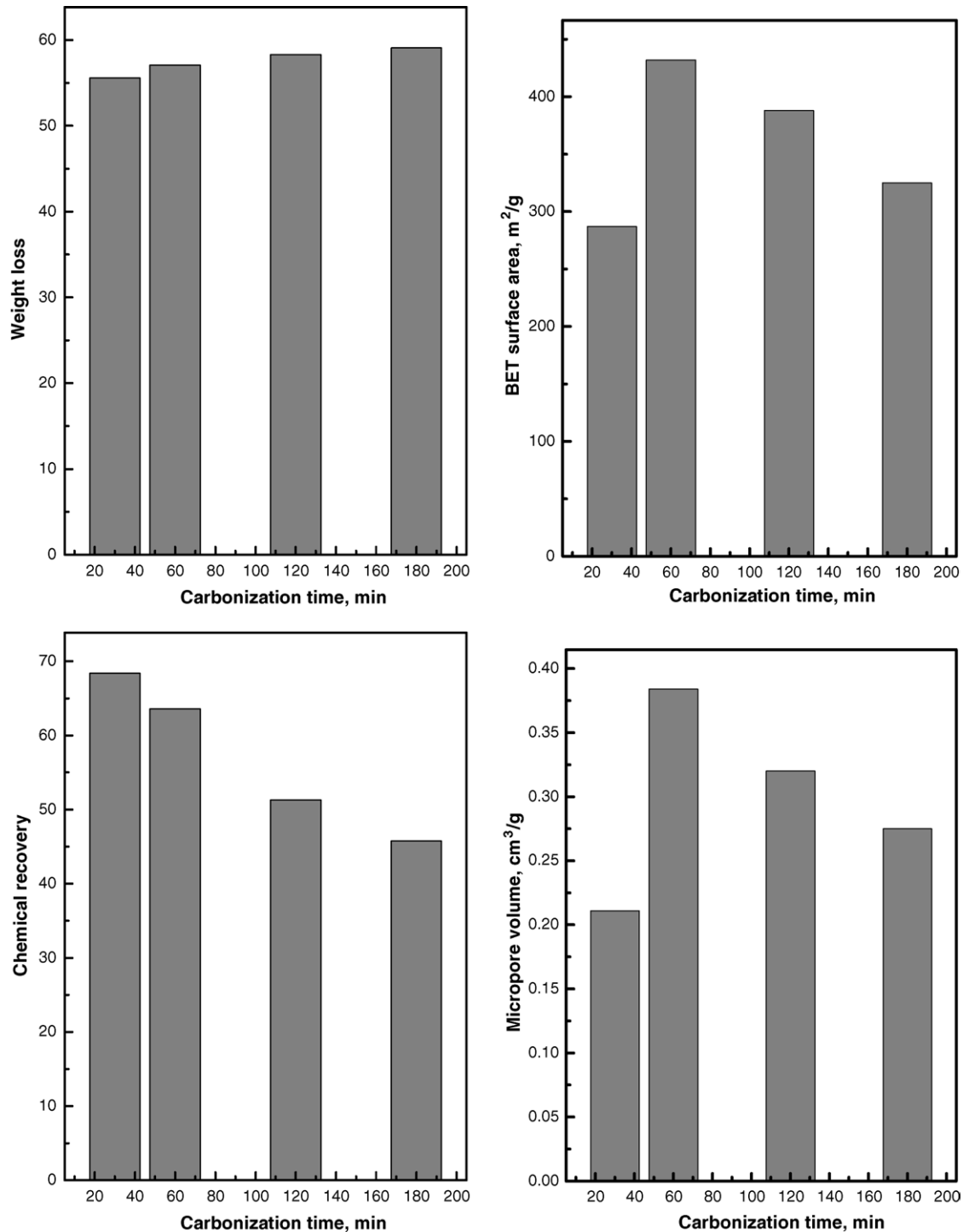


Fig. 1. Effect of carbonization time on weight loss, chemical recovery, BET surface area and pore volume of activated carbons prepared from *Tectona grandis* sawdust by ZnCl_2 activation.

3.1.2. Carbonization temperature

The effects of carbonization temperature on weight loss, chemical recovery, BET surface area and micropore volume of ZnCl_2 activated carbons are shown in Fig. 2 for a carbonization time of 60 min and a chemical ratio of 100% (mass basis). Our preliminary studies revealed that this time and chemical ratio were optimum. As can be seen in the figure, that the carbonization temperature does not have much effect on the

weight loss. Overall weight loss was found to increase with increasing temperature, resulting in decreased yield of char with the rise in temperature. This weight loss was essentially due the volatilization of the *T. grandis* fibres upon heating and as expected, the quantity of volatiles evolved increased with increasing temperature. The final yields of the char resulting from carbonization at different temperatures were ranging between 38% and 42% of the original weight of the predried

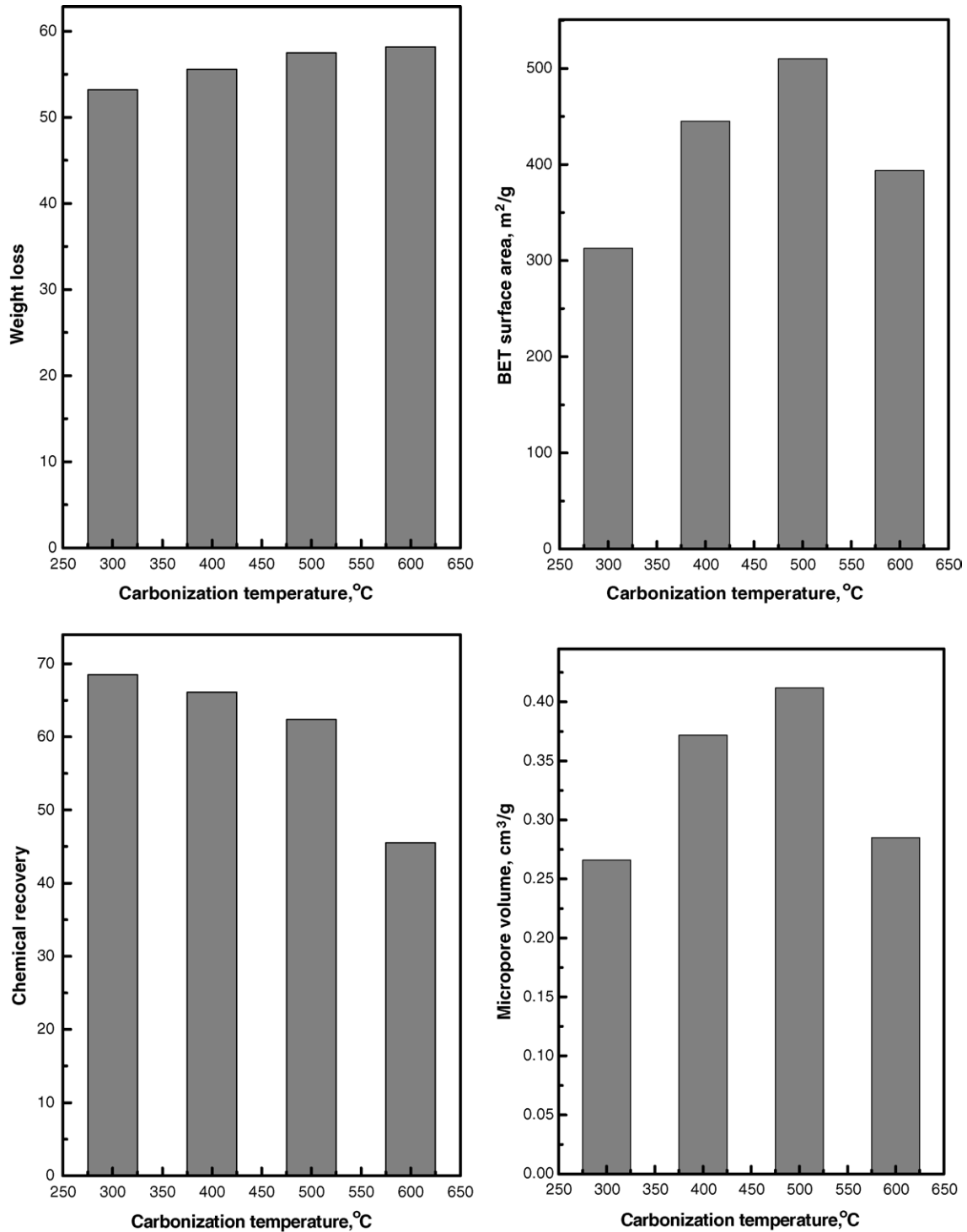


Fig. 2. Effect of carbonization temperature on weight loss, chemical recovery, BET surface area and pore volume of activated carbons prepared from *T. grandis* sawdust by $ZnCl_2$ activation.

extracted fibre. The chemical recovery values decreases with the carbonization temperature which may be due to the evaporation of $ZnCl_2$ from the precursor at higher carbonization temperature.

The effect of carbonization temperature on BET surface area and micropore volume is shown in Fig. 2. When the carbonization temperature was 300 °C, pyrolysis reactions had just

commenced, thereby creating very small BET surface area as well as pore volume. This phenomenon was due to the inadequate of heat energy produced at this low carbonization temperature and the release of volatiles was insignificant for the pore development. As the temperature was further increased to 400 °C and subsequently to 500 °C, more volatile matters were progressively released during carbonization, thereby

resulting in the development of some new pores, and hence the BET surface area increased progressively. The decrease in surface area with further increase in temperature to 600 °C might be due to the sintering effect at high temperature, followed by shrinkage of the char, and realignment of the carbon structure which resulted in reduced pore areas as well as volume.

3.1.3. Chemical ratio

The effects of chemical ratio (ZnCl_2 to nutshell ratio) on weight loss, chemical recovery, BET surface area and micropore volume of activated carbons are shown in Fig. 3. For all these samples the carbonization temperature of 500 °C and the carbonization time of 60 min. Our previous experiments revealed that this temperature and time were optimum. It can be seen

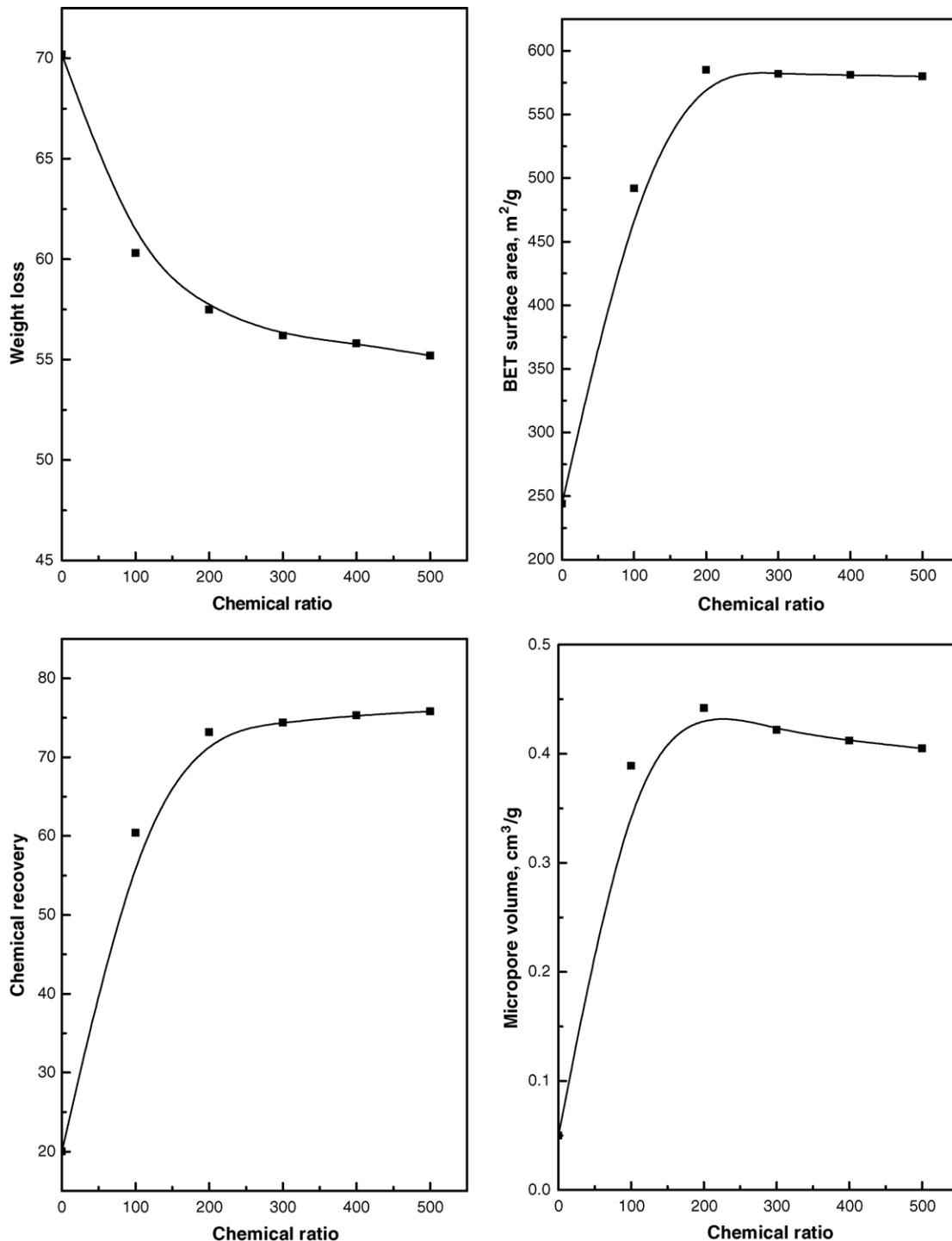


Fig. 3. Effect of chemical ratio on weight loss, chemical recovery, BET surface area and pore volume of activated carbons prepared from *T. grandis* sawdust by ZnCl_2 activation.

in the figure that the addition of chemical agents to the precursor decreases the weight loss of the carbon products. The reduction of weight loss is most likely due to the effect of the chemical agent in which it promotes the Scholl condensation (polymerization) reactions. These reactions, which occur among the aromatic hydrocarbons and tar-forming compounds, result in the formation of large molecules (viz. polycyclic aromatics) in the structure of the activated carbon and increase the carbon yield. The effect of chemical ratio on chemical recovery is shown in Fig. 3. A portion of chemicals added to the carbon precursor can be recovered during the washing stage of the activated products after carbonization. It is obvious that with increasing the chemical ratio, the recovery should be increased as well.

The effects of chemical ratio on BET surface area and micropore volume is shown in Fig. 3. It shows that surface area as well as the pore volume increases with the increase in chemical ratio. The two distinct regions of pore evolution can be observed. In the first region (chemical ratio <150%), the surface area and the micropore volume increase at a high rate, while in the second region (chemical ratio >150%), in addition to pore opening, some portion of the chemicals are responsible for the widening of the micropores, resulting in slower rate of increase in porosity. The destructive effect of high ZnCl₂ ratio on the micropore structure of active carbon can be observed in this region.

3.1.4. SEM analysis of the activated carbons

Scanning electron microscopy (SEM) technique was employed to observe the surface physical morphology of the nutshell derived activated carbon. Fig. 4 shows the SEM photographs of the *T. grandis* sawdust before and after the carbonization at the optimum operating condition with 1000× magnification. Pores of different size and different shape could be observed. It can be seen from the micrographs that the external surface of the chemically activated carbon is full of cavities. The reason for the formation of the cavities on the ZnCl₂-activated carbon is not clear. According to the micrograph, it seems that the cavities resulted from the evaporation of ZnCl₂ during carbonization, leaving the space previously occupied by the ZnCl₂. The carbonization temperature for chemical activation was too low to cause the agglomeration of the char structure. Since the carbonization temperature for physical activation is high (900 °C), caking and agglomeration occurred on the char

structure and thus resulted in the formation of chars with an intact external surface. It can also be seen that some salt particles are scattered on the surface of the activated carbon, probably due to the presence of remaining zinc chloride or other metal compounds on the activated carbon. Some particles were even trapped into the pores and could possibly block the entry of pores to some extent. The above findings were verified with the results obtained by Hg porosimetry of activated carbon. Clearly, it demonstrates that the adsorptive capacity of the products could be further increased on improving the washing procedure.

3.2. Phenol removal

3.2.1. Kinetics of phenol adsorption process

The relationship between contact time and phenol removal by activated carbon obtained by ZnCl₂ activation of *T. grandis* sawdust for four different initial concentrations is presented in Fig. 5 for an adsorbent dosage of 5 g/l and at natural pH of the solution. It can be seen from the figure that an increase in initial phenol concentration results in a decrease in the percentage phenol removal but results in an increase in the actual phenol adsorbed. It can be concluded that the rate of phenol binding with activated carbon is high at initial stages, which gradually decreases and becomes almost constant after a period of 300 min. This observation is in support of the findings reported by several authors [10,22].

Numerous kinetic models have been proposed to elucidate the mechanism by which pollutants may be adsorbed. The mechanism of adsorption depends on the physical and/or chemical characteristics of the adsorbent as well as on the mass transport process. In order to investigate the mechanism of phenol adsorption, three kinetic models are selected in this study. These mechanisms are described as follows.

3.2.1.1. Lagergren model. Lagergren proposed a pseudo-first-order kinetic model [6,10,12,22]. The integral form of the model is

$$\log(q_e - q) = \log q_e - \frac{K_{ad}}{2.303} t \quad (3)$$

where q is the amount of phenol sorbed (mg/g) at time t (min), q_e the amount of phenol sorbed at equilibrium (mg/g) and K_{ad} is the equilibrium rate constant of pseudo-first-order adsorption

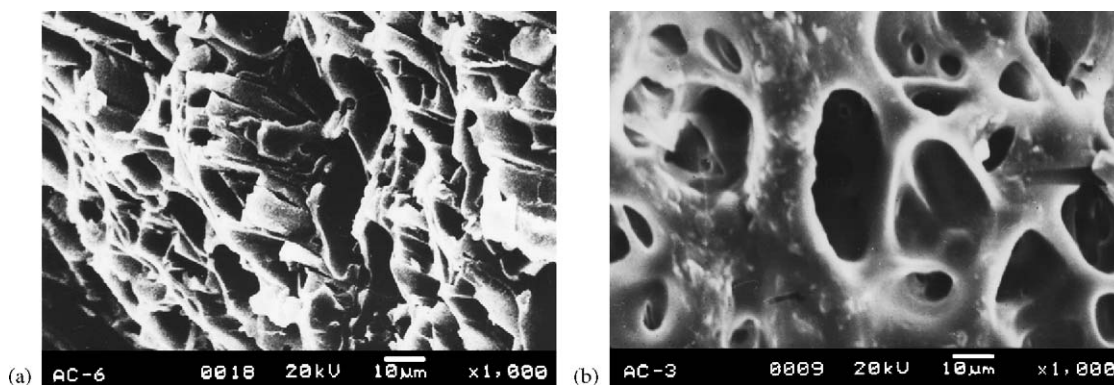


Fig. 4. SEM micrographs of the *T. grandis* sawdust (a) before and (b) after carbonization (at 500 °C, 60 min, 200% chemical ratio).

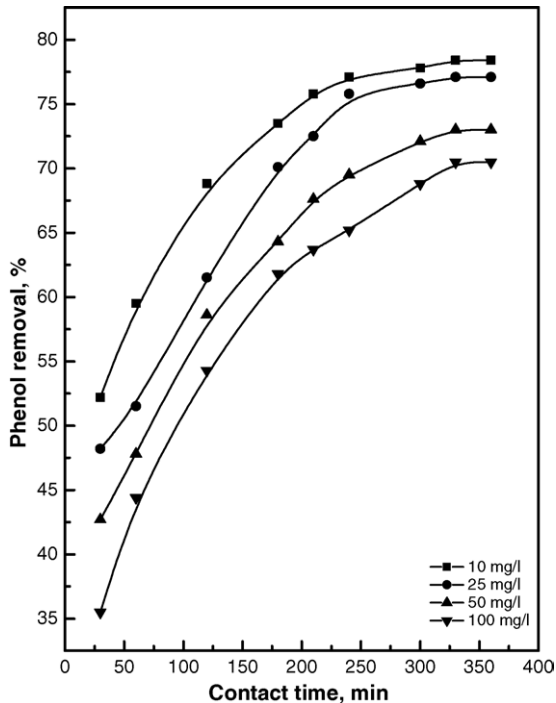


Fig. 5. Effect of contact time on percent removal of phenol (adsorbent dose = 5 gm/l).

(min^{-1}). This model was successfully applied to describe the kinetics of many adsorption systems.

3.2.1.2. Pseudo-second-order model. The adsorption kinetics may also be described by a Pseudo-second-order reaction. The linearized-integral form of the model [6,10,12,22] is

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where K_2 is the pseudo-second-order rate constant of adsorption.

3.2.1.3. Diffusion model. The intraparticle diffusion model is based on the theory proposed by Weber and Morris [6,10,12,22]. According to this theory

$$q = k_d \sqrt{t} \quad (5)$$

where k_d is the rate constant of intraparticle diffusion ($\text{mg/g min}^{-1/2}$).

The applicability of the above three models can be examined by each linear plot of $\log(q_e - q)$ versus t , (t/q) versus t , and q versus $t^{1/2}$, respectively and are presented in Figs. 6–8. In order to quantify the applicability of each model, the correlation coefficient (R^2) was calculated from these plots. The linearity of these plots indicates the applicability of the three models. However, the analyses of the correlation coefficients (R^2) showed that the experimental data ($R^2 > 0.998$) fit the pseudo-second-order model (an indication of a chemisorption mechanism) better the experimental data than the pseudo-first-order model (R^2 ranging between 0.963 and 0.986). The intraparticle diffusion was also involved in the adsorption of phenol by activated carbons (Fig. 8). The linear portion of the plot for a wide range of contact

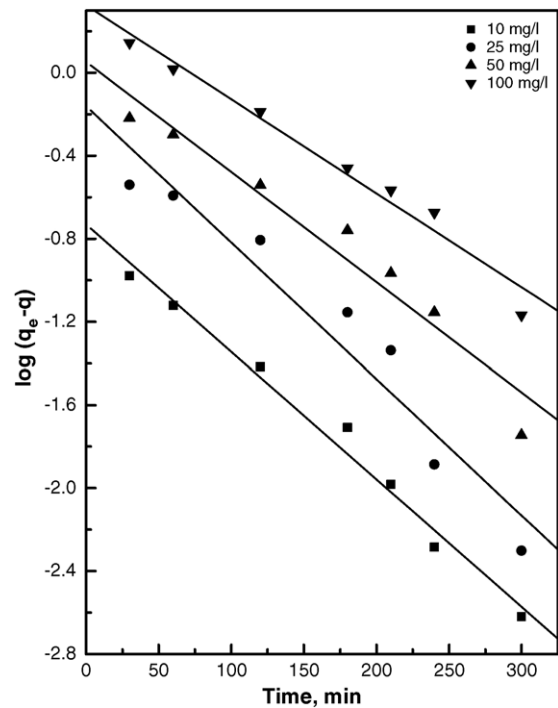


Fig. 6. Kinetics of phenol removal according to the Lagergren model.

time between adsorbent and adsorbate does not pass through the origin. This deviation from the origin or near saturation may be perhaps due to the difference in the rate of mass transfer in the initial and final stages of adsorption [8,25]. Further, such deviation from origin indicates that the pore diffusion is not the only rate controlling step [8]. It may be seen from Fig. 8 it may be seen that there are two distinct regions—the initial pore diffusion

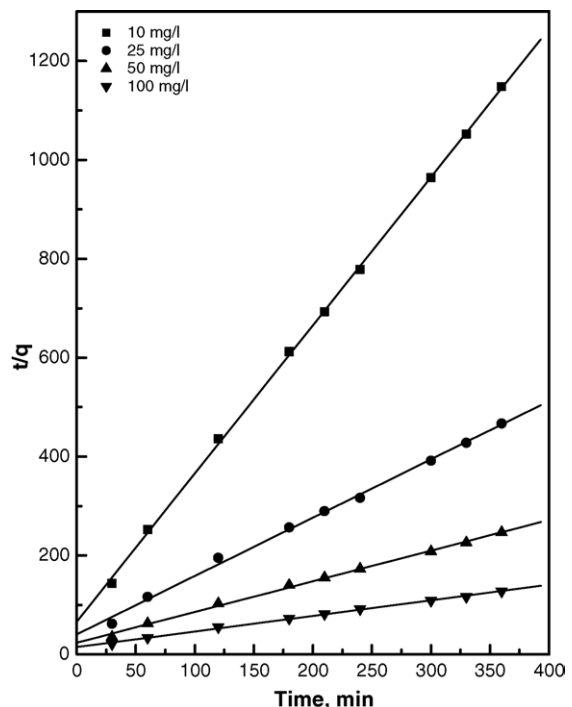


Fig. 7. Kinetics of phenol removal according to pseudo-second-order model.

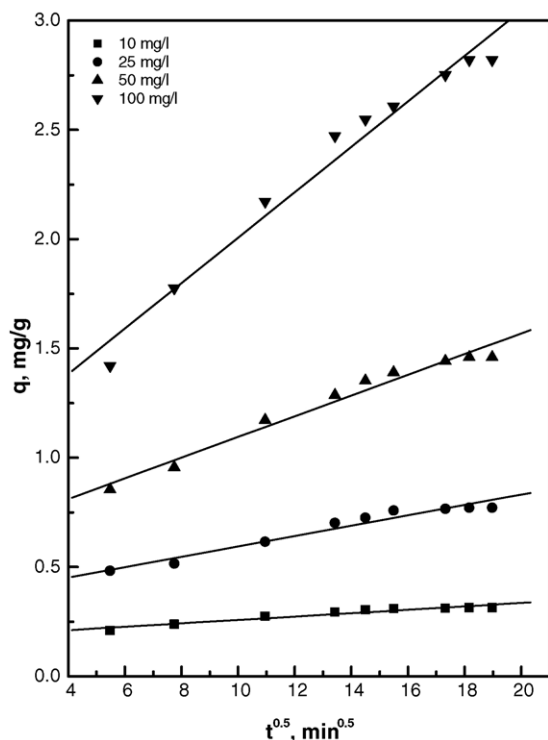


Fig. 8. Kinetics of phenol removal according to the intraparticle diffusion model.

due to external mass transfer effects followed by the intraparticle diffusion [8,26].

3.2.2. Adsorption isotherms

Several models have been used in the literature to describe the experimental data of adsorption isotherms. The Langmuir and Freundlich models are the most frequently employed models. In the present work both models were used.

The phenol sorption isotherm followed the linearized Langmuir model as shown in Fig. 9. The Langmuir equation relates solid phase adsorbate concentration (q_e), the uptake, to the equilibrium liquid concentration (C_e) as follows:

$$q_e = \left(\frac{K_L b C_e}{1 + b C_e} \right) \quad (6)$$

where K_L and b are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption, respectively. It can be seen from figure that the isotherm data fit the Langmuir equation well ($R^2 = 0.9998$). The values of K_L and b were determined from the figure and were found to be 13.45 mg/g and 0.00132 l/mg, respectively. These values are in well agreement with the values reported by several authors [10,22].

The phenol adsorption isotherm followed the linearized Freundlich model as shown in Fig. 10. The relation between the phenol uptake capacity ' q_e ' (mg/g) of adsorbent and the residual phenol concentration ' C_e ' (mg/l) at equilibrium is given by

$$\ln q_e = \ln k + \frac{1}{n} \ln C_e \quad (7)$$

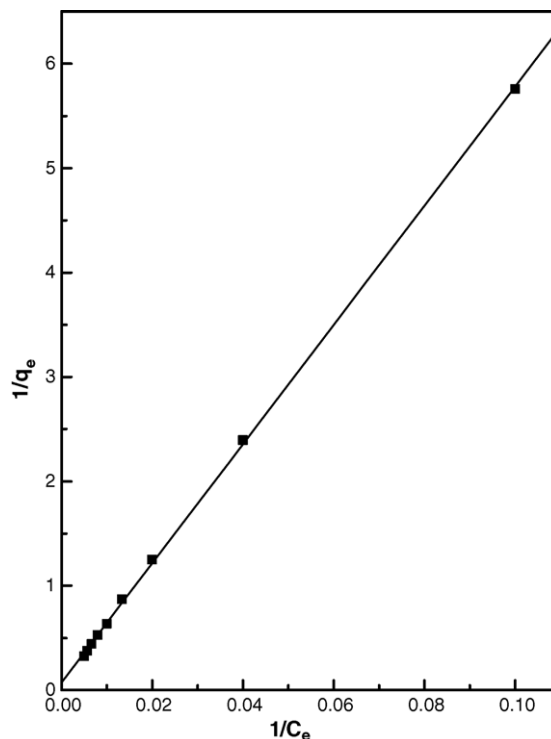


Fig. 9. Langmuir isotherm model: adsorbent dose = 5 gm/l, temperature = 25 °C.

where the intercept $\ln k$ is a measure of adsorbent capacity and the slope $1/n$ is the sorption intensity. The isotherm data fit the Freundlich model well ($R^2 = 0.9998$). The values of the constants k and $1/n$ were calculated to be 0.0191 and 0.954. Since the value of $1/n$ is less than 1, it indicates a favorable adsorption [10,22].

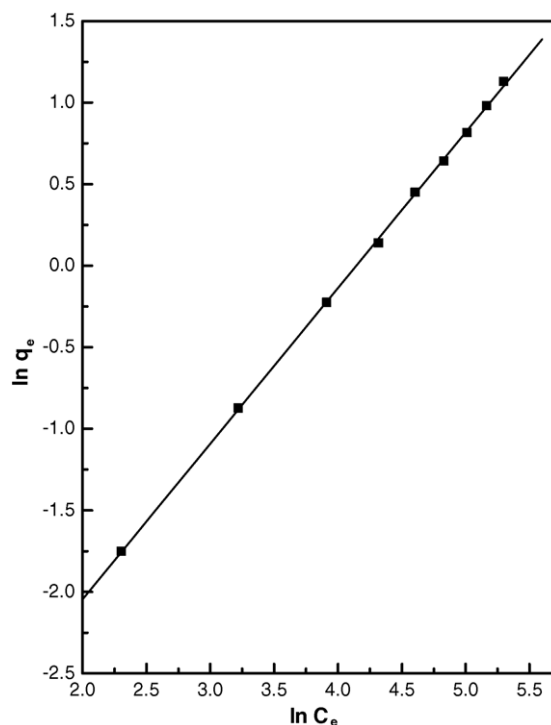


Fig. 10. Freundlich isotherm model: adsorbent dose = 5 gm/l, temperature = 25 °C.

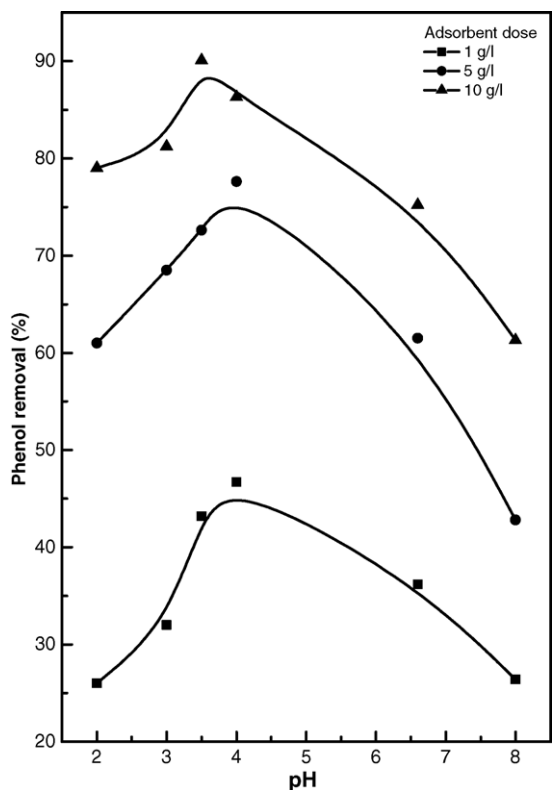


Fig. 11. Effect of pH on phenol removal.

3.2.3. Effect of pH on removal of phenol

The adsorption of phenol by activated carbons obtained by ZnCl_2 activation was studied at various values of pH. The experiments were performed for an initial concentration of 100 ppm and for different adsorbent doses (1, 5 and 10 gm/l) and the results are shown in Fig. 11. It is clear from this figure that the percentage adsorption of phenol increases with the increase in pH from 2.0 to 3.5 and decreases thereafter. It is important that the maximum adsorption at all the concentrations takes place at pH 3.5.

This behavior can be explained considering the nature of the adsorbent at different pH in phenol adsorption. The surface of the activated carbon contains a large number of functional groups. The pH dependence of phenol adsorption can largely be related to the type and ionic state of these functional groups and also on the phenol chemistry in solution. Adsorption of phenol up to pH 3.5 suggests that the positively charged $\text{C}_6\text{H}_5\text{OH}_2^+$ ions (formed by $\text{C}_6\text{H}_5\text{OH}$ in acidic media) bind through electrostatic attraction to negatively charged functional groups on the surface of activated carbon because at this pH more functional groups carrying negative charge would be exposed. But on raising the pH, as indicated in the figure, the rate of removal is considerably reduced. But on raising the pH above 3.5 the concentrations of $\text{C}_6\text{H}_5\text{OH}_2^+$ and $\text{C}_6\text{H}_5\text{O}^-$ both are to be considered. Experimental results revealed that $\text{C}_6\text{H}_5\text{O}^-$ is relatively important at pH >3.5 and these negatively charged ions are no longer attracted by the activated carbon on its surface resulting in the reduction of phenol removal. Hence, it can be concluded that above pH 3.5, other mechanism like physical adsorption on the surface

of adsorbent could have taken an important role in the adsorption of phenol and exchange mechanism might have influenced markedly [10,22].

4. Conclusions

This study has demonstrated that high surface area activated carbons can be prepared from the chemical activation of *T. grandis* sawdust with ZnCl_2 as activating agent. For the carbonization of the ZnCl_2 treated sample, the release of moisture and ZnCl_2 represents most of the evolution, indicating that ZnCl_2 plays an important role in retarding tar escape during carbonization. The washing process following carbonization with ZnCl_2 has a significant influence on the surface properties of resulting char. It was found that acid washing is a necessary step for the preparation of high-porosity carbons.

Study of various parameters during chemical activation revealed that the most important variable is the ratio of chemical agent to the nut precursor. The other important operating variables with a direct effect on the porosity development are temperature and carbonization time. Under the experimental conditions investigated, the best conditions for the production of high surface area activated carbon from *T. grandis* sawdust by chemical activation are: chemical ratio (activating agent/precursor) of 200%, carbonization time of 1 h and carbonization temperature of 500 °C. At this optimal condition, the BET surface area and micropore volume obtained were 585 m²/g and 0.442 cm³/g, respectively.

The batch adsorption tests indicate that the *T. grandis* sawdust derived activated carbon had a good adsorption capacity for phenol from aqueous solutions. The kinetics of phenol adsorption followed nicely the pseudo-second-order rate expression. The Langmuir and Freundlich models also fit the isotherm data well. Solution pH has great effect on the uptake of phenol. The data thus obtained may be helpful for designing and establishing a continuous treatment plant for water and wastewaters enriched in phenol.

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