



ELSEVIER

Journal of Hazardous Materials B85 (2001) 301–315

**Journal of
Hazardous
Materials**

www.elsevier.com/locate/jhazmat

Production of granular activated carbon from waste walnut shell and its adsorption characteristics for Cu^{2+} ion

Jin-Wha Kim^a, Myoung-Hoi Sohn^a, Dong-Su Kim^{a,*},
Seung-Man Sohn^b, Young-Shik Kwon^c

^a Department of Environmental Science and Engineering, Ewha Womans University, Seoul, South Korea

^b Advanced Materials Research Institute, LG Chemical Ltd., Daejeon, South Korea

^c Suwon Science College, Department of Environmental Engineering, Kyounggido, South Korea

Received 2 January 2001; received in revised form 15 April 2001; accepted 23 April 2001

Abstract

Production of granular activated carbon by chemical activation has been attempted employing walnut shells as the raw material. The thermal characteristics of walnut shell were investigated by TG/DTA and the adsorption capacity of the produced activated carbon was evaluated using the titration method. As the activation temperature increased, the iodine value increased. However, a temperature higher than 400°C resulted in a thermal degradation, which was substantiated by scanning electron microscopy (SEM) analysis, and the adsorption capacity decreased. Activation longer than 1 h at 375°C resulted in the destruction of the microporous structure of activated carbon. The iodine value increased with the increase in the concentration of ZnCl_2 solution. However, excessive ZnCl_2 in the solution decreased the iodine value. The extent of activation by ZnCl_2 was compared with that by CaCl_2 activation. Enhanced activation was achieved when walnut shell was activated by ZnCl_2 . Applicability of the activated carbon as adsorbent was examined for synthetic copper wastewater. Adsorption of copper ion followed the Freundlich model. Thermodynamic aspects of adsorption have been discussed based on experimental results. The adsorption capacity of the produced activated carbon met the conditions for commercialization and was found to be superior to that made from coconut shell. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Activated carbon; Walnut shell; Chemical activation; Adsorption; Cu^{2+} ion

* Corresponding author. Fax: +82-2-3277-3275.

E-mail address: dongsu@mm.ewha.ac.kr (D.-S. Kim).

1. Introduction

Activated carbon is one of the most widely employed adsorbents. It is mainly composed of carbonaceous material with various microporous structures. Its industrial usage can be found in the treatment process for flue gas and volatile solvents, etc. [1]. In the treatment of wastewater, it is used for purification, decolorization, and the removal of toxic organics and heavy metal ions [2]. Recently, its usage has been broadened to advanced wastewater treatment. As a result, the demand for activated carbon is increasing.

Physicochemical characteristics of activated carbon depend on the kind of raw material used and activation conditions [3]. Activated carbon is classified into one of three types, such as powder, granular, and fibrous according to its size and shape, and each type has its specific application. Raw materials for activated carbon are chosen depending on their purity, price, potential extent of activation, and stability of supply. Presently, the materials being used to produce carbon are usually coal, wood, petroleum residue, sawdust, coconut shell, pulp sludge, and pitches resulting from the pyrolysis of fossil fuel [4,5].

The production process of activated carbon is mainly divided into three steps, dehydration, carbonization, and activation. Dehydration is a drying process for removal of moisture from raw material and during carbonization organics contained in raw material are changed into primary carbon, which is a mixture of amorphous and crystallized carbon, tar, and ash. Activation, which is the main step in the process, is generally carried out in two ways, gas activation and chemical activation. Gas activation is a physical process in which raw material passes through carbonization at a low temperature and is activated usually by CO₂, water steam, and air. The most widely used type of gas activating process is the one utilizing steam as the activating gas under high temperature and long treatment conditions. The disadvantage of the gas activation process lies in low yield and lack of homogeneity of the product.

In contrast, chemical activation utilizes chemicals, such as ZnCl₂, H₃PO₄, H₂SO₄, KOH, and CaCl₂, that have dehydration and oxidation characteristics [6–11]. Carbonization and activation are usually carried out simultaneously in the chemical activation process.

To obtain activated carbon with increased specific surface area, the product undergoing activation needs to be washed with hydrochloric acid and rinsed with hot water to remove inorganic matter from the surface. The chemical activation process is known to be effective for the production of activated carbon used for water/wastewater treatment. There have been several studies regarding change in adsorbent capacity and specific surface area based on the kind of chemicals and activating conditions, these studies used coconut shell, fly ash, and petroleum residue as raw materials [12,13].

In this study, waste walnut shell was utilized as the raw material for the production of granular activated carbon by chemical activation and its adsorption capacity for heavy metal ions was evaluated. The activating agent used was zinc chloride and conditioning variables examined were temperature, time, agent concentration, and weight ratio of raw material and agent solution. The change in the microstructure of the raw material and produced activated carbon was examined by scanning electron microscopy (SEM). Adsorption time and temperature were considered as variables for the adsorption experiment and isotherm and some thermodynamic parameters have been estimated from experimental results.

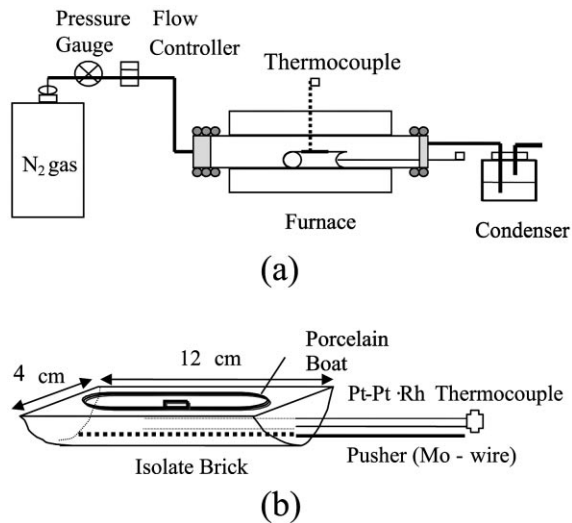


Fig. 1. Schematic of the experimental apparatus for activation (a), and sample boat (b).

2. Materials and methods

2.1. Materials and apparatus

Black walnut shells were crushed and ground using a stainless blade and the resulting product sieved to the size of 14–60 mesh (1410–250 μm). This was used as the raw material. The prepared walnut shell was stored in a desiccator and the storage period was intended not to exceed a few days before experiment to maintain its freshness. Apparatus used for activation consisted of three parts, gas inlet, furnace, and gas condenser. The entire schematic is shown in Fig. 1(a). A tube furnace whose size was $\text{\O} 60 \text{ mm} \times 1200 \text{ mm}$ (Chang Shin Scientific Co., 2 kW) was used and, to maintain inert atmosphere, highly pure N₂ gas (>99.999%) was charged to the furnace at the flow rate of 150 ml/min during the activation process. A porcelain boat was used as a sample holder and was located at the center of tube using molybdenum wire (Fig. 1(b)).

2.1.1. Activation

Chemical analysis of the walnut shell was conducted using elemental analyzer (CE Instrument, Carlo Erba EA 1108). The analytical results for C, H, N and S are shown in Table 1.

Table 1
Chemical composition of walnut shell

Element	C	H	N	S
Wt. (%)	46.64 \pm 0.01	6.05 \pm 0.02	0.73 \pm 0.03	0.03 \pm 0.01

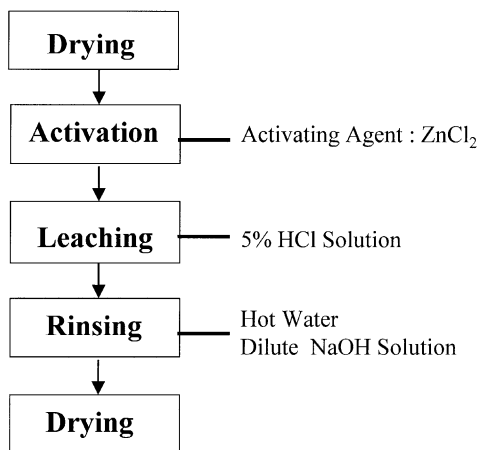


Fig. 2. Flow diagram for activation process.

It can be seen that the shell is mainly composed of carbon. Its thermal characteristics were examined by TG/DTA (TA Instrument, SDT 2960).

The general procedure of the activation process for this study is described below and is schematically outlined in Fig. 2.

1. A mixture of walnut shell and ZnCl_2 (Aldrich Co.) solution with the desired concentration was put in a sample boat and heated in the furnace at a controlled temperature.
2. Thermally treated product was boiled in 5% HCl solution to leach out the activating agent; it was rinsed with hot distilled water several times. Then, it was rinsed again with dilute NaOH solution for neutralization.
3. Final product was stored in a desiccator filled with N_2 gas to prevent oxidation.

Activation experiments were performed under various conditions to obtain the optimal condition for activation. The activation temperature was varied from 250 to 550°C and activation time was controlled as 0.5, 1, 2, 3, 4 h. The concentration of activating agent was 1, 3, 5, and 7 M. The weight ratio of raw material and ZnCl_2 solution was varied as 1:1, 1:3, 1:5, and 1:7. In the derived optimal conditions, an activation experiment was carried out using CaCl_2 as the activating agent to compare the activating ability with ZnCl_2 .

2.2. Characterization of activated carbon

The Iodine value for produced activated carbon was measured by titration [14] to evaluate its adsorption capacity and SEM (JEOL, JSM-5400) was employed for the observation of surface microporous structure.

2.3. Adsorption test

To estimate the applicability of produced activated carbon as an adsorbent for wastewater treatment, the adsorption test was performed using copper ion as the adsorbate. For the

preparation of synthetic copper wastewater, 1.1403 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Fisher Co.) was dissolved in 1 l of thrice distilled water ($>18 \text{ M}\Omega$) to make 300 mg/l solution. This solution was diluted to 50, 100, and 200 mg/l for adsorption experiments with different initial copper ion concentrations. Known amounts of activated carbon were placed in a 250 ml conical flask and 100 ml of wastewater was added. After shaking using a mechanical shaker (Vision Science Co., K.M.S. 8480S) which was equipped with a temperature controller, the activated carbon was separated from solution by filtration using Whatman no. 5 filter paper. The concentration of copper ion remaining in solution was measured by Atomic Absorption Spectrophotometry (Perkin-Elmer, AANALYST 100) after diluting the filtrate to an adequate concentration.

3. Results and discussion

3.1. Activation

3.1.1. Thermal characteristics of walnut shell

The thermal behavior of the walnut shell, which was used as the raw material for the production of activated carbon, was evaluated as a function of the temperature in air and Ar gas environment (Fig. 3(a) and (b)). As can be seen from TG curves, the weight of walnut shell decreases gradually with temperature up to 430°C but no more reduction of weight is observed above this temperature in air. In Ar gas, the weight decreases rapidly until temperature reaches 340°C and its reduction proceeds slowly at higher temperatures. The initial weight loss in temperatures below 200°C comes from the evaporation of moisture originally contained in walnut shell. Weight loss occurring above this temperature is considered to be due to vaporization of volatile organic compounds, which results in the carbonization of walnut shell. The DTA curves imply that the thermal decomposition of walnut shell is exothermic.

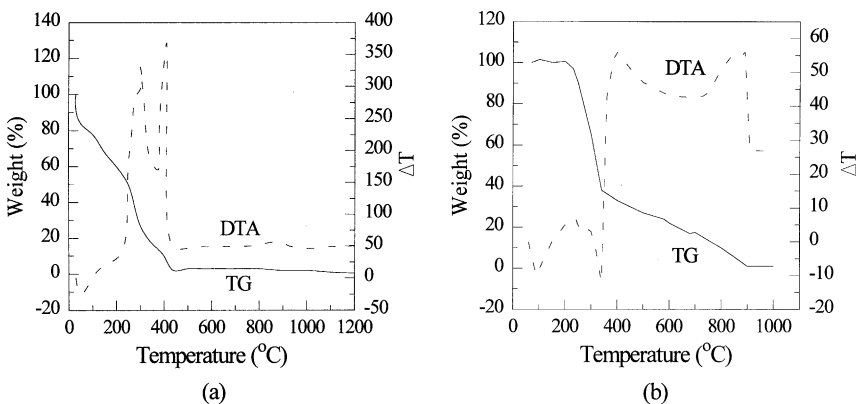


Fig. 3. TG/DTA curve for walnut shell in the air (a), and Ar gas environment (b).

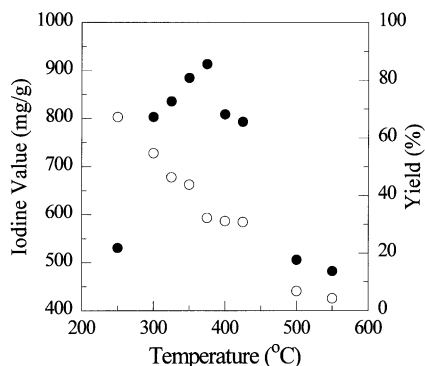


Fig. 4. Effect of activation temperature on the iodine value (●) and yield (○) of activated carbon (activation time, 1 h; weight ratio of walnut shell and 1 M ZnCl₂ solution = 1:3).

3.1.2. Activation temperature

The changes in iodine value and yield for activated carbon produced from walnut shell have been investigated as a function of activation temperature using 1 h of activation time and 1:3 weight ratio of walnut shell and 1 M ZnCl₂ solution (Fig. 4). The iodine value is the amount of iodine adsorbed on a unit weight of adsorbent. It can be estimated by following equation

$$I = \frac{\{(10 \times f' - K \times f) \times 12.69 \times 5\}}{S} \quad (1)$$

where I is iodine adsorption amount (mg/g), K the titration volume of 0.1 M sodium thiosulfate solution (ml), f' and f are concentration factors of iodine and 0.1 M sodium thiosulfate solution, respectively, 12.69 is content of iodine in 1 ml of 0.1 M sodium thiosulfate solution (mg), and S the dry weight of adsorbent (g).

The yield for activated carbon was defined as the weight percentage of product compared with that of raw material.

Zinc chloride used as the activating agent lowers the carbonization temperature and brings about dehydration and oxidation of walnut shell in the course of thermal treatment, resulting in the development of microporous structure of activated carbon [15]. Well developed micropores can provide the adsorbent with a high specific surface area and adsorbability. It is shown in Fig. 4 that iodine value increases gradually with activation temperature; however, it decreases above 400°C. This result is presumably due to the thermal degradation of the formed activated carbon in this temperature range, which hinders its adsorption capacity so that iodine value is decreased. In general, carbonization and activation temperature are known to be very influential on the micropore structures of activated carbon, which determines the adsorption capacity [16]. Thus, it can be concluded that appropriate activation temperature for the production of activated carbon using walnut shell as the raw material is approximately 375°C.

At low temperatures, activation is not sufficiently accomplished and elements, such as H, O, N, and S remain in large amounts along with C after thermal treatment. Thus, as

the activation temperature becomes higher, the yield of product is expected to decrease. This result is usually dependent on the kind of raw material. Fig. 4 shows the variation of yield decreasing with activation temperature. The yield is observed to be ca. 65% at 250°C. It is reduced to 32% at 375°C, where the iodine value reaches at its maximum. It is <10% above 500°C since the activated carbon itself is oxidized to ashes at this temperature.

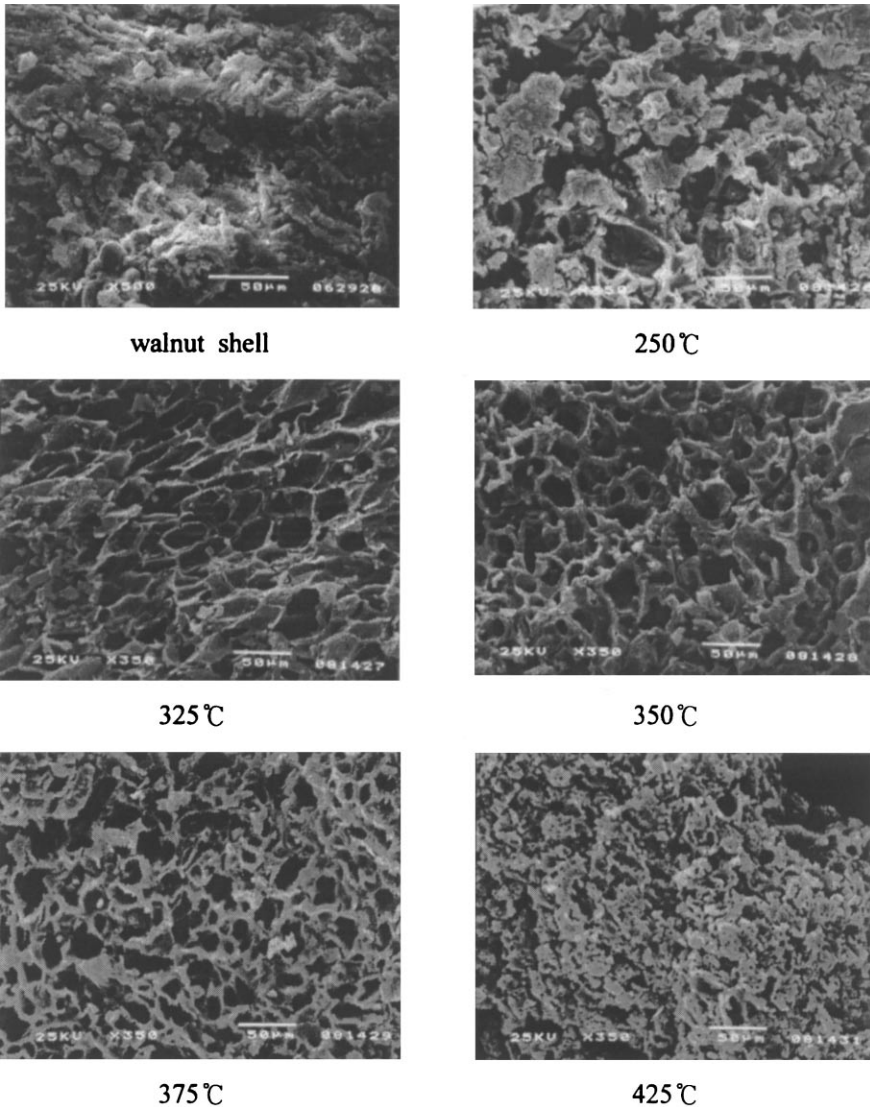


Fig. 5. SEM morphology of walnut shell and activated carbon at different temperatures.

The size distribution of micropores of activated carbon is understood to be one of the critical factors determining its applicability [17]. It is governed by the method of activation and the shape of micropores is determined by raw materials [18]. The microstructures of walnut shell and activated carbon at different temperatures have been observed by SEM in the same activation condition as in Fig. 4 (Fig. 5). There are almost no micropores for the walnut shell in a raw state and as activation progresses micropores are generated and developed. It can be seen that at 375°C well developed uniform micropores are generally distribute. At 425°C, the structure of activated carbon collapses, which results in the extinction of micropores. This result is considered to be due to the thermal degradation of activated carbon occurring at this temperature and will induce a reduction of specific surface area and adsorption capacity of activated carbon. This has been verified by experimental results regarding the iodine value.

3.1.3. Activation time

The effect of activation time on the iodine value and yield of activated carbon is shown in Fig. 6. The activation was conducted at 375°C using 3 M ZnCl₂ solution. The iodine value was measured as 1100 and 1297 mg/g after 30 min and at 1 h of activation time, respectively. When activation is carried out for a longer time, the iodine value decreases gradually and the equilibrium value is 740 mg/g at 4 h. It has been recognized that, in general, adsorption capacity rises with activation time [19]. The decrease in iodine value when activation time is longer than 1 h may come from excessive activation of walnut shell. That is, under extended activation, the microporous structure of the produced activated carbon deteriorates and turns into macropores. The yield of product decreases rapidly in the time range of increase in iodine value. This result is possibly due to the volatilization of organic materials from walnut shell, which results in the formation of activated carbon. The extent of decrease in product yield is observed to be reduced when excessive activation occurs.

3.1.4. Concentration and amount of activating agent solution

For the purpose of examining the influence of the concentration of activating agent on the adsorption capacity of activated carbon, the variation of iodine value with ZnCl₂

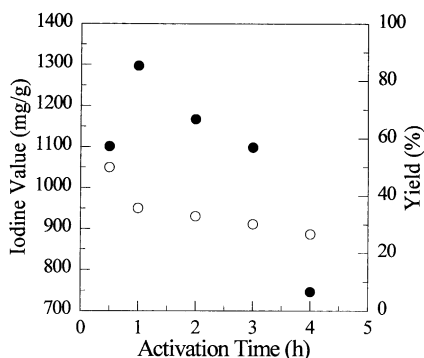


Fig. 6. Variation in the iodine value (●) and yield (○) of activated carbon according to the activation time (activation temperature, 375°C; weight ratio of walnut shell and 3 M ZnCl₂ solution = 1:3).

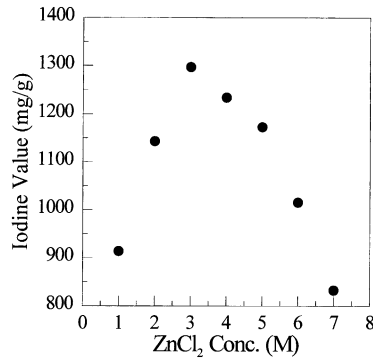


Fig. 7. Effect of the concentration of activating agent on the iodine value of activated carbon (activation time, 1 h; activation temperature, 375°C, weight ratio of walnut shell and ZnCl₂ solution = 1:3).

concentration has been investigated at 1 h activation time and 375°C, which were previously observed to be the optimal activation conditions. Fig. 7 shows that the iodine value is 913 mg/g at 1 M ZnCl₂ solution and reaches its highest at 3 M solute concentration. SEM micrographs of activated carbon at these concentrations are shown in Fig. 8 and it can be noted that micropores are more well-developed at 3 M. In the case of higher concentrations than 3 M, it decreases with concentration and becomes 832 mg/g at 7 M, which is lower than that at 1 M.

ZnCl₂ is known to be a strong dehydrator which subtracts hydrogen and oxygen from raw material in inert atmosphere during activation process and develops carbonaceous microporous structure [20]. The decrease in iodine value at the higher concentration of ZnCl₂ may be caused by the deterioration of the microporous structure of activated carbon due to excessive dehydration.

Fig. 9 shows the effect of the weight ratio of ZnCl₂ solution and walnut shell properties on the iodine value. As seen in this figure, iodine value increases gradually as the weight ratio is raised and becomes almost constant beyond the ratio of 5. The total volume occupied

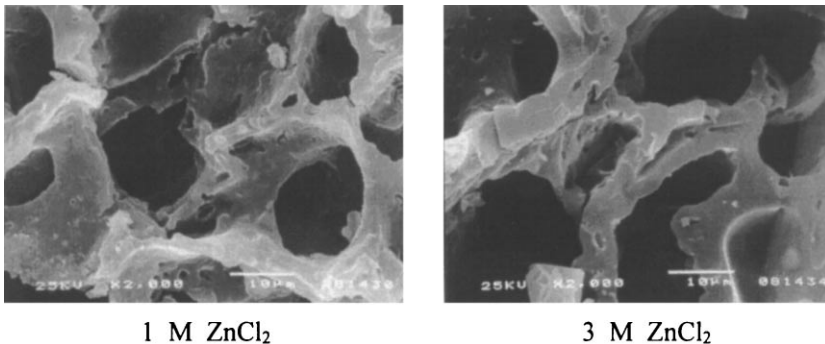


Fig. 8. SEM morphology of activated carbon for 1 M and 3 M ZnCl₂ concentration.

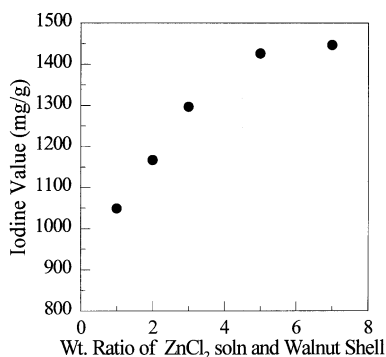


Fig. 9. Variation in the iodine value of activated carbon according to the weight ratio of 3 M ZnCl₂ solution and walnut shell (activation time, 1 h; activation temperature, 375°C).

by micropores is increased with the amount of activating agent solution and no further significant development of micropores is considered to occur when the weight ratio reaches 5. In practice, an increase in the weight ratio implies the increase in the amount of ZnCl₂. However, the iodine value here has been observed to increase in the range of ZnCl₂ amount where iodine value decreases thereafter in Fig. 7. At present, the reason for this behavior is not clear, but the increased amount of water used for making the activating agent solution may function as the prohibitor for the erosion of microporous structure.

3.1.5. Comparison of activating agents

In chemical activation the kind of activating agent used is expected to significantly affect the extent of activation. In the present study, activation by CaCl₂ has been evaluated and compared to activation by ZnCl₂. Fig. 10 represents the change of iodine value with the mixing ratio of the weight of 3 M ZnCl₂ and 3 M CaCl₂ solutions while maintaining

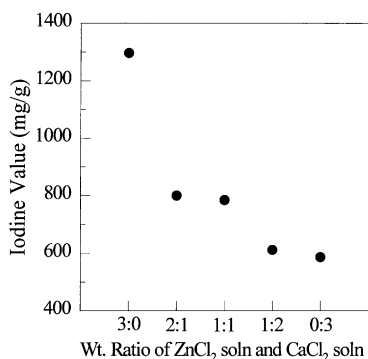


Fig. 10. Change of the iodine value of activated carbon depending on the weight ratio of 3 M ZnCl₂ solution and 3 M CaCl₂ solution (activation time, 1 h; activation temperature, 375°C; weight ratio of walnut shell and total activating agent solution = 1:3).

the weight ratio of raw material and total activating agent solution as 1:3. The experimental data show that as the concentration of CaCl_2 in the activating solution increases, the iodine value of activated carbon decreases, implying that activation is promoted when employing ZnCl_2 as the activating agent. However, CaCl_2 is cheaper than ZnCl_2 so that both degree of activation and economics should be considered in a practical activation process.

The iodine values of walnut shell, after carbonization without an activating agent, and activated carbon obtained after chemical activation were measured and compared with that of commercial activated carbon made from coconut shell. The iodine value of the product after carbonization, which is ca. 360 mg/g is nearly same as that of raw material. However, the iodine value increases significantly when activated by ZnCl_2 so that the function of activating agent is regarded to be essential in an activation process. The adsorption capacity of the produced activated carbon was superior to that of the commercial activated carbon made from coconut shell.

3.2. Adsorption

3.2.1. Adsorption time

To evaluate the adsorption characteristics of the produced activated carbon for heavy metal ions, the change of adsorption rate with time for copper ion with different initial solution concentrations has been investigated (Fig. 11). For an initial concentration of 300 mg/l the adsorption rate rises rapidly at an initial stage of adsorption reaching about 63% after 30 min. No appreciable increase in adsorption rate was observed beyond this time and equilibrium adsorption was essentially reached within 60 min. Similar adsorption behavior was shown for the entire range of initial concentration of Cu^{2+} . However, the increase in the adsorption rate at the initial stage decreased as the initial concentration was decreased. This result is presumably due to the decreased diffusivity of adsorbate across the liquid film formed on the adsorbent as the initial concentration of copper ion is reduced. Also, the result showed that although the equilibrium adsorption rate was raised with initial concentration the degree of increase was not proportional to the initial concentration, i.e. a two-fold increase in the

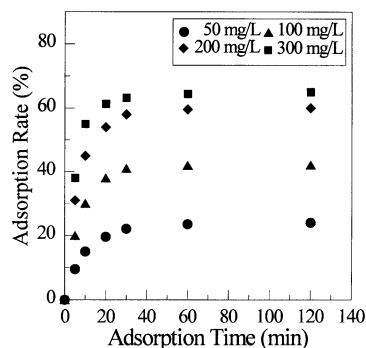


Fig. 11. Variation in the adsorption rate of Cu^{2+} according to the adsorption time for different initial concentrations of adsorbate (adsorption temperature, 30°C, amount of adsorbent, 0.3 g/l).

initial concentration of Cu^{2+} does not lead to doubled equilibrium adsorption. The reason for this can be found in the definite surface area of substrate on which competitive adsorption of copper ions occur.

The variation of Cu^{2+} adsorption rate before reaching equilibrium described in Fig. 11 can be discussed using a general equation for n th-order reaction kinetics [21]

$$k = -\frac{dC}{(C^n)dt} \quad (2)$$

when Eq. (2) is applied to the adsorption reaction, k and C indicate the rate constant and the concentration of adsorbate remaining in solution at time t . After integrating both sides of the Eq. (2) with the time interval from 0 to t , and applying t to the initial stage of adsorption (0–10 min), it was revealed that the adsorption of Cu^{2+} was a first-order reaction. Fig. 12 shows the plots of $\log(C/C_0)$ versus adsorption time for different initial concentrations of Cu^{2+} . Rate constants derived from the slopes of linear plots were 0.016, 0.036, 0.060, and 0.080 min^{-1} , respectively for initial adsorbate concentrations of 50, 100, 200, and 300 mg/l.

The verification of the adsorption mechanism of Cu^{2+} on the activated carbon has been attempted by considering sorption isotherms. As a result, the experimental data were found to obey the Freundlich Model [22]. The general form of Freundlich isotherm is expressed as follows:

$$\frac{X}{M} = kC_e^{1/n} \quad (3)$$

where X/M is amount of adsorbate adsorbed per unit weight of adsorbent (mg/g), k the adsorption capacity (l/g), C_e the equilibrium concentration of adsorbate remaining in solution (mg/l), and n the adsorption intensity.

By taking the logarithm on both sides of Eq. (3), $\log(X/M)$ can be expressed as a linear function of $\log C_e$. Fig. 13 shows that the equilibrium adsorptions of Cu^{2+} for different initial concentrations are linearly well arranged with r^2 of 0.99, therefore, the regression line can be taken as the linearized Freundlich isotherm.

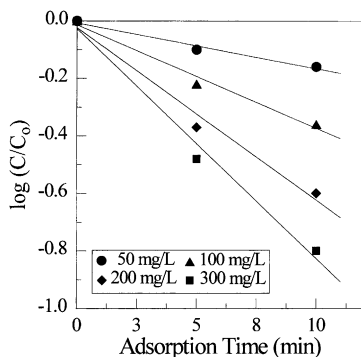


Fig. 12. Plots of $\log(C/C_0)$ vs. adsorption time for different initial concentrations of adsorbate.

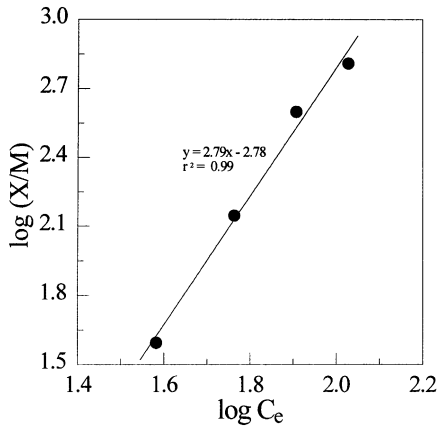


Fig. 13. Linearized Freundlich isotherm for adsorption of Cu²⁺.

3.2.2. Adsorption temperature

Fig. 14 represents the variation of equilibrium adsorption of Cu²⁺ according to temperature and it can be seen that about 48% of adsorption rate was attained at 20°C. The rate decreases gradually with temperature implying that the adsorption of Cu²⁺ on activated carbon is exothermic. The influence of temperature on equilibrium adsorption can be examined thermodynamically by using van't Hoff equation [23]

$$\log K_2 - \log K_1 = - \left(\frac{\Delta H^0}{R} \right) (T_2^{-1} - T_1^{-1}) \tag{4}$$

where K_1 and K_2 are equilibrium constants at T_1 and T_2 , respectively, T is the absolute temperature (K), ΔH^0 the standard enthalpy at equilibrium (kJ/mol), and R the gas constant (8.314×10^{-3} kJ/mol K).

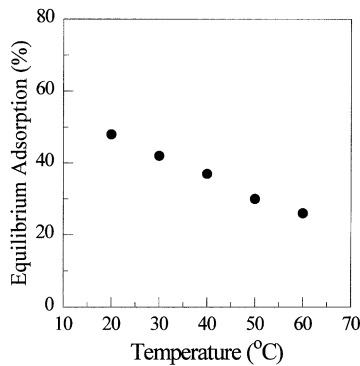


Fig. 14. Effect of temperature on the equilibrium adsorption of Cu²⁺ (initial concentration of adsorbate, 100 mg/l).

Table 2

Equilibrium constant and thermodynamic parameters for the adsorption of copper ion on activated carbon

Temperature (°C)	<i>K</i>	ΔG^0 (kJ/mol)	ΔS^0 (kJ/mol K)	ΔH^0 (kJ/mol)
20	0.9231	1.9568×10^{-4}	-6.7767×10^{-5}	
30	0.7241	8.1632×10^{-4}	-6.7579×10^{-5}	
40	0.5873	1.3902×10^{-3}	-6.7253×10^{-5}	-0.0197
50	0.4186	2.2838×10^{-3}	-6.7938×10^{-5}	
60	0.3514	2.9064×10^{-3}	-6.7767×10^{-5}	

Eq. (4) explains the relationship between equilibrium constant and temperature under the assumption that ΔH^0 is constant in the temperature range concerned. Since, the value of ΔH^0 known to be nearly constant in a wide range of temperature for most physicochemical reactions [24], the ΔH^0 for the adsorption of Cu^{2+} can be considered to be constant in the temperature range considered for the present study. Defining the adsorption equilibrium constant as the amount ratio of adsorbate adsorbed onto the substrate compared to that remaining in solution at equilibrium state, it is possible to calculate ΔH^0 for adsorption by Eq. (4) based upon experimental results. Also, thermodynamic parameters for adsorption, such as ΔG^0 and ΔS^0 can be obtained from the calculated ΔH^0 and the following relations

$$\Delta G^0 = -RT \log K \quad (5)$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (6)$$

The estimated thermodynamic parameters and equilibrium constants at each temperature are summarized in Table 2. The negative value of ΔH^0 thermodynamically substantiates that the adsorption of Cu^{2+} on the produced activated carbon to be exothermic. Even though the values are small, ΔG^0 is calculated to be positive for the entire temperature range. This result probably means that the adsorption of Cu^{2+} is not a thermodynamically spontaneous phenomenon, that is, copper ions adsorb on activated carbon mainly due to the physical process of diffusion. ΔS^0 are estimated to be very small in the experimental conditions, therefore, the entropic change occurring from adsorption is thought to be negligible.

4. Conclusions

Employment of the waste walnut shell as a raw material for the production of activated carbon is a useful recycling process. Furthermore, the superior adsorption capacity of the produced activated carbon suggests the process is potentially commercializable. Chemical activation of walnut shell by ZnCl_2 was evaluated as a function of activation temperature, activation time, and amount and kind of activating agent, etc. In addition, the thermodynamic estimation of the adsorption test results has supported the interpretation of the adsorption characteristics for the produced activated carbon in relation to its adsorbent applicability for wastewater treatment. Considering the large amount of ligneous wastes including walnut shell, their utilization as a source of material for activated carbon is expected to provoke a significant economical benefit.

Acknowledgements

This work was supported financially by Ministry of Education (BK 21) of Korean Government. The authors acknowledge the SEM analysis by Mr. Sung-Yong Park at Chang Sung Corporation.

References

- [1] U. Yasumitsu, K. Satoshi, S. Yoshihiro, Characteristics of activated carbon prepared from acetic acid lignin, in: *Proceeding of the Fourth Asian Textile Conference*, 24–26 June 1997, pp. 36–41.
- [2] O.L. Walker, *Chemistry and Physics of Carbon*, Marcel Dekker, New York, 1993.
- [3] D. Robert, Nosa O. Egiebor, Activated carbon production from synthetic crude coke, *Fuel Process. Technol.* 46 (1996) 157–169.
- [4] H. Wolfgang, K. Erhard, On the suitability of agricultural by-products for the manufacture of granular activated carbon, *Fuel* 74 (12) (1995) 1786–1791.
- [5] R.K. Nasrin, M. Campbell, G. Sandi, J. Golas, Production of micro- and meso-porous activated carbon from paper mill sludge, I. Effect of zinc chloride activation, *Carbon* 38 (14) (2000) 1905–1915.
- [6] M. Molina-Sabio, F. Rodriguez-Reinoso, F. Caturla, M.J. Selles, Porosity in granular carbons activated with phosphoric acid, *Carbon* 33 (8) (1995) 1105–1113.
- [7] T.H. El-Nabarawy, M.R. Mostafa, A.M. Youssef, Activated carbons tailored to remove different pollutants from gas stream and from solution, *Adsorpt. Sci. Technol.* 15 (1) (1997) 61–68.
- [8] E. Gonzalez-Serano, T. Cordero, J. Rodriguez-Mirasol, J.J. Rodriguez, Development of porosity upon chemical activation of Kraft lignin with $ZnCl_2$, *Ind. Eng. Chem. Res.* 36 (1997) 1723–1732.
- [9] H. Benaddi, T.J. Bandoz, J. Jagiello, J.A. Schwarz, J.N. Rouzaud, D. Legras, F. Béguin, Surface functionality and porosity of activated carbons obtained from chemical activation of wood, *Carbon* 38 (5) (2000) 669–674.
- [10] T. Hsisheng, W. Sheng-Chi, Preparation of porous carbons from phenol-formaldehyde resins with chemical and physical activation, *Carbon* 38 (6) (2000) 817–824.
- [11] H. Jun'ichi, A. Kazehaya, K. Muroyama, A.P. Watkinson, Preparation of activated carbon from lignin by chemical activation, *Carbon* 38 (13) (2000) 1876–1878.
- [12] A. Ahmadpour, D.D. Do, The preparation of active carbons from coal by chemical and physical activation, *Carbon* 34 (4) (1996) 471–479.
- [13] A. Ahmadpour, D.D. Do, The preparation of activated carbon from macadamia nutshell by chemical activation, *Carbon* 35 (12) (1997) 1723–1732.
- [14] Association of Korea Industrial Standard, Test methods for activated carbon, KS M 1210, 1993, pp. 1–7.
- [15] B. Laine, A. Calaft, Factors affecting the preparation of activated carbons from coconut shell catalyzed by potassium, *Carbon* 29 (1991) 949–953.
- [16] H. Zhonghua, E.F. Vansant, A new composite adsorbent produced by chemical activation of elutrilite with zinc chloride, *J. Colloid Interface Sci.* 176 (2) (1995) 422–431.
- [17] S. Blacher, B. Sahouli, B. Heinrichs, P. Lodewyckx, R. Pirard, J.P. Pirard, Micropore size distributions of activated carbons, *Langmuir* 16 (16) (2000) 6754–6756.
- [18] L. Krisztina, B. Attila, G.N. Lajos, C. Israel, Porous carbon from polymer waste materials, *Colloids Surf. A: Physicochem. Eng. Aspects* 151 (1999) 311–320.
- [19] N. Mameri, F. Aiouèche, D. Belhocine, H. Grib, H. Lounici, D.L. Piron, Y. Yahiat, Preparation of activated carbon from olive mill solid residue, *J. Chem. Technol. Biotech.* 75 (7) (2000) 625–631.
- [20] R.C. Bansal, J. B. Donnet, F. Stoeckli, *Activated Carbon*, Marcel Dekker, New York, 1988.
- [21] V.L. Snoeyink, D. Jenkins, *Water Chemistry*, Wiley, New York, 1980.
- [22] I.M. Richard, *Principles of Adsorption and Reaction on Solid Surfaces*, Wiley, New York, 1996.
- [23] V.L. Snoeyink, D. Jenkins, *Principles of Adsorption and Reaction on Solid Surfaces*, Wiley, New York, 1996.
- [24] P.W. Atkins, *Physical Chemistry*, 4th Edition, Freeman, New York, 1990.